Insights into measurements of water-soluble ions in PM$_{2.5}$ and their gaseous precursors in Beijing

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**Abstract**

To better understand the characteristics and transformation mechanisms of secondary inorganic aerosols, hourly mass concentrations of water-soluble inorganic ions (WSIs) in PM$_{2.5}$ and their gaseous precursors were measured online from 2016 to 2018 at an urban site in Beijing. Seasonal and diurnal variations in water-soluble ions and gaseous precursors were discussed and their gas-particle conversion and partitioning were also examined, some related parameters were characterized. The (TNH$_3$)$_{\text{Rich}}$ was also defined to describe the variations of the excess NH$_3$ in different seasons. In addition, a sensitivity test was carried out by using ISORROPIA II to outline the driving factors of gas-particle partitioning. In Beijing, the relative contribution of nitrate to PM$_{2.5}$ has increased markedly in recent years, especially under polluted conditions. In the four seasons, only a small portion of NO$_2$ in the atmosphere was converted into total nitrate (TNO$_3$), and more than 80% of TNO$_3$ occurred in the form of nitrate due to the abundant ammonia. The concentration of total ammonia (TNH$_3$) was much higher than that required to neutralize acid gases, and most of the TNH$_3$ occurred as gaseous NH$_3$. The nitrous acid (HONO) concentration was highly correlated with NH$_3$ concentration and had increased significantly in Beijing compared with previous studies. The total chloride (TCl) was the highest in winter, and $i$(Cl$^-$) was more sensitive to variations in the ambient temperature (T) and relative humidity (RH) than $i$(NO$_3^-$).

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**Introduction**

Atmospheric particulate matter, as an essential component of the atmospheric environment, has a significant impact on visibility reduction, acid deposition, air quality, global climate change, and human health (Anderson et al., 2003; Nel, 2005; Wang et al., 2015b; Tang et al., 2017). Fine particles (PM$_{2.5}$) are of particular importance because they frequently dominate the total particulate matter mass concentrations and have longer lifetimes and more toxicity than coarse particles. An important portion of PM$_{2.5}$ is formed in the atmosphere through chemical transformations of gaseous precursors such as nitrogen oxides (NOx), sulfur dioxide (SO$_2$), and ammonia (NH$_3$). The pollution characteristics and formation mechanisms of water-soluble inorganic ions (WSIs) in PM$_{2.5}$, and their effects on the environment have attracted great attention (Hu et al., 2008; Ianniello et al., 2011; Seinfeld and Pandis, 2016; Wang et al., 2020). The North China Plain (NCP) is well known as an area with severe aerosol pollution. The WSIs are major chemical components and greatly contribute to the regional haze (Zhao et al., 2013; Chen et al., 2015; Wang et al., 2015a).

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Studies have shown that sulfate gas-particle conversion in aerosols mainly follows two pathways: homogeneous gas-phase reactions of SO$_2$ with OH and heterogeneous liquid-phase reactions of SO$_2$ in clouds and fog or on the aerosol droplet surface (Zhuang et al., 1999; Yao et al., 2003; Wang et al., 2005; Guo et al., 2010). Sulfuric acid (H$_2$SO$_4$) as the prominent product of the above two reactions, is more likely to be present in the particle phase because of its low saturated vapor pressure. The heterogeneous liquid-phase reaction of SO$_2$ is generally regarded as the dominant mechanism for sulfate formation in the North China Plain (NCP) (Li et al., 2011; Wang et al., 2012; Zhang et al., 2018b).

The formation mechanism of nitrate is more complicated than that of sulfate, which starts with NOx and proceeds via HNO$_3$ and mainly includes homogeneous gas-phase reactions of NO$_2$ with OH or O$_3$ and heterogeneous N$_2$O$_5$ hydrolysis (Khneder, 2002; Pathak et al., 2009; Seinfeld and Pandis, 2016). Many studies have shown that N$_2$O$_5$ hydrolysis is an important nitrate source in the NCP (Chen et al., 2018; Wang et al., 2017a; Li et al., 2018). The main sources of HCl are biomass burning (Andreae et al., 1996), coal combustion, waste incineration (McCulloch et al., 1999), and the reaction of HNO$_3$ and sea salt (NaCl) (Elderling et al., 1991).

Gaseous ammonia (NH$_3$) is the most abundant alkaline gas in the atmosphere, which mainly comes from agricultural fertilizer application and animal husbandry (Ianniello et al., 2010). As the sole NH$_4^+$ precursor, atmospheric gaseous ammonia (NH$_3$) is abundant in the NCP and neutralizes H$_2$SO$_4$, HNO$_3$, and HCl to form (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$, and NH$_4$Cl (Wei et al., 2015; Meng et al., 2018), respectively, and has an important influence on the acidity of aerosols (Ding et al., 2019b).

Nitrous acid (HONO) is an important nitrogen trace gas in the atmosphere, and its photolysis product is the main source of hydroxyl radicals (OH) which determines the atmospheric oxidative capacity and plays vital role in tropospheric chemistry such as ozone and secondary aerosol formation (Ravishankara, 1997; Aliche et al., 2002; Kleffmann et al., 2005; Hofzumahaus et al., 2009; Cheng et al., 2016). It has been reported that the photolysis reaction of HONO can contribute up to 60% of the hydroxyl radicals in the atmosphere in the daytime (Aliche et al., 2003; Lu et al., 2012; Michoud et al., 2012; Spataro et al., 2013; Hou et al., 2016). HONO sources were generally grouped into direct emissions, homogeneous gas-phase reactions, heterogeneous reactions, surface photolysis, and biological processes (Su et al., 2011; Spataro et al., 2014). The heterogeneous reaction of NO$_2$ was considered to be a dominant source of HONO, especially during nighttime (Kleffmann et al., 1999; Finlayson-Pitts et al., 2005). Studies of Xu et al. (2019b) and Kuang et al. (2020) showed that the NH$_3$-promoted NO$_2$ hydrolysis could explain the missing daytime HONO source. In the NCP, some HONO measurements had been carried out in previous studies (Hendrick et al., 2014; Tong et al., 2016; Wang et al., 2017b; Zhang et al., 2019).

In fact, there is another important mechanism in the transformation of aerosols and their gaseous precursors: gas-particle partitioning. Gas-particle partitioning and conversion are completely different, but they occur simultaneously. The gas-particle partitioning is a thermodynamic process and reflects the phase state changes in pollutants, which are mainly influenced by the concentrations of secondary ions and their gaseous precursors and meteorological conditions. For instance, the equilibrium relationships between NH$_3$ and NH$_4^+$, HCl and Cl$^-$, or HNO$_3$ and NO$_3^-$ are closely related to the gaseous precursor concentrations (NH$_3$, HCl, or HNO$_3$), aerosol chemical compositions, temperature, and relative humidity (RH) (Mozurkewich, 1993; Seinfeld and Pandis, 2016). These factors largely determine the partitioning of semivolatile compounds (NH$_4$NO$_3$ and NH$_4$Cl) into gaseous or aerosol states (Fridlin et al., 2000). Understanding the atmospheric gas-particle partitioning can help us to better formulate aerosol control strategies (Guo et al., 2018; Ding et al., 2019b).

Many studies have placed special emphasis on the spatial-temporal characteristics, formation mechanism, and source apportionment of WSIs in aerosols in Beijing (He et al., 2001; Yao et al., 2002; Sun et al., 2005; Ianniello et al., 2011; Duan et al., 2012; Zhao et al., 2013, 2017). Many previous studies on WSIs were carried out using filter-based methods followed by laboratory analyses, which usually had a long sampling time spanning hours to days. An aerosol mass spectrometer (AMS) can provide the concentrations of sulfate, nitrate, ammonium, and organic matter at a high time resolution, but they cannot provide data on other water-soluble components and their gaseous precursors (Zhang et al., 2015; Sun et al., 2015). Only a few in-situ studies have been reported for the simultaneous observation of WSIs and relevant gases (SO$_2$, HNO$_3$, NH$_3$, HCl, and HONO) relying on hourly resolution methods in Beijing (Zhang et al., 2018b). Moreover, in recent years, with the efforts in emission reduction, PM$_{2.5}$ has been greatly reduced in the NCP. In particular, the concentrations of SO$_4^{2-}$ and SO$_2$ have dramatically decreased due to the reduction of coal consumption. The annual average concentration of PM$_{2.5}$ in Beijing decreased from 89.5 $\mu$g/m$^3$ in 2013 to 42.0 $\mu$g/m$^3$ in 2019. Meanwhile, the concentrations of main gaseous precursors have also changed a lot. Therefore, significant changes are likely to take place in source contribution, chemical composition, and secondary formation process of PM$_{2.5}$.

Based on hourly data of WSIs and their gaseous precursors obtained by in-situ measurement, this study provides variation characteristics of the water-soluble ions in PM$_{2.5}$ and their gaseous precursors in the typical seasons and under the different pollution conditions in Beijing. The parameters reflecting gas-particle conversion and partitioning of the main secondary ions were also calculated to describe the oxidation and thermodynamic processes. Moreover, a sensitivity test was carried out by using the thermodynamic model to discuss the driving factors of gas-particle partitioning. The results in this study are helpful to understand the current pollution situation and acquire more details of secondary formation mechanism, and will be a useful reference for formulating future emission-control policies.

1. **Date and methods**

1.1. **Observation site**

The measurements were performed at the observation site of the Institute of Urban Meteorological in the Haidian District, which is located in the northwest urban area of Beijing, out-
side the Third Ring Road (29°56′N, 116°17′E). The site is located next to a high-density residential area and experiences no significant industrial emissions from the surrounding neighborhood. Therefore, the observation data represent the air quality levels of typical Beijing urban areas.

1.2. Instruments and measurements

An online MARGA instrument (IS, Metrohm Analytical B.V.) with a PM$_2.5$ inlet was used to measure the mass concentrations of WSIs (SO$_2^{2−}$, NO$_3^{−}$, NH$_4^{+}$, K$^+$, Cl$^−$, Na$^+$, Ca$^{2+}$, and Mg$^{2+}$) in the aerosol phase and the corresponding inorganic gases (SO$_2$, NH$_3$, HNO$_3$, HONO, and HCl) in the gas phase at a time resolution of one hour. Briefly, the online MARGA instrument consists of a sample box, a detector box, and a flow control box. The sample box includes one wet rotating denuder (WRD) for absorbing gas and one steam jet aerosol collector (SJAC) for aerosol collection. The ambient airflow into the sample box was controlled by an air pump at a rate of 1 m$^3$/h. When air enters the sample box, the gases are absorbed by diffusion into a liquid film in the WRD, and the aerosols in the air are collected with the SJAC. Then, the hourly mass concentrations of WSIs and gases are determined by an automatic ion chromatography (IC) system in the detector box. The MARGA was calibrated using internal standard solution (LiBr), and the detecting limits for SO$_2^{2−}$, NO$_3^{−}$, NH$_4^{+}$, K$^+$, Cl$^−$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, SO$_2$, NH$_3$, HNO$_3$, HONO, and HCl were 0.04, 0.05, 0.05, 0.09, 0.01, 0.05, 0.09, 0.06, 0.03, 0.05,0.05, 0.02,0.01 µg/m$^3$, respectively. This device had been used in many studies before (Wen et al., 2015; Zhang et al., 2018b; Liu et al., 2017; van Beelen et al., 2014; Huang et al., 2013; Leng et al., 2014a,b; Schobesberger et al., 2015). More details about the performance of MARGA and the comparison with other methods can be found in some studies (Runsey et al., 2014; Chen et al., 2017).

In this study, we conducted four campaigns for each typical season in Beijing from 2016 to 2018, namely, spring observations from 2016–04 to 2016–05, summer observations from 2017–07 to 2017–08, autumn observations from 2017–10 to 2017–11, and winter observations from 2017–12 to 2018–02. In addition, the PM$_{2.5}$ concentration was also synchronously recorded by a dichotomous ambient particulate monitor (Thermo TEOM 1405-DF). The hourly NO$_2$ concentrations and meteorological parameters (ambient temperature (T), RH, wind speed (WS), and wind direction (WD)) were obtained from the nearest environmental protection monitoring station (the Guanyuan station) and the Haidian meteorological station (no. 54,399), respectively.

1.3. Methods

To better understand the temporal variations in aerosols and gaseous precursors, the following variables were studied: TNO$_2$ (total nitrate (gas and aerosols) expressed as equivalent HNO$_3$), TNH$_3$ (total ammonium (gas and aerosols) expressed as equivalent NH$_3$), and TCI (total chloride (gas and aerosols) expressed as equivalent HCl). To evaluate the degree of the gas-particle secondary transformation reactions from SO$_2$ and NO$_2$ into SO$_2^{2−}$ and TNO$_2$, the sulfur oxidation ratio (SOR) (SO$_2^{2−}$/SO$_2^{2−}$+SO$_2$), mol/mol) and nitrogen oxidation ratio (NOR) (TNO$_2$/TNO$_2$+NO$_3$) mol/mol were also calculated in this study, where the SOR and NOR are defined as oxidation ratios. Moreover, the gas-particle partitioning coefficients, which include ε(NH$_4^{+}$) (NH$_4^{+}$/TNH$_3$, mol/mol), ε(NO$_3^{−}$) (NO$_3^{−}$/ TNO$_2$, mol/mol)), and ε(Cl$^{−}$) (Cl$^{−}$/TCI, mol/mol), are evaluated to better understand the phase partitioning of these semivolatile species. High ε(NH$_4^{+}$), ε(NO$_3^{−}$) and ε(Cl$^{−}$) values indicate that the above semivolatile compounds are more likely to occur as aerosol phases.

2. Results and discussion

2.1. General characteristics of the WSIs and gaseous pollutants

Summary statistics for PM$_{2.5}$, major water-soluble ions, and gaseous pollutants, as well as meteorological parameters during the whole observation period in the urban area of Beijing, are listed in Table 1. The time series of these data are shown in Figs. 1–4. The average PM$_{2.5}$ concentrations were 55.05, 40.94, 50.39, and 35.01 µg/m$^3$ during the spring, summer, autumn, and winter measurement periods, respectively. The PM$_{2.5}$ was unexpectedly low in winter mainly due to the good atmospheric diffusion conditions during that period (Fig 4). According to the PM$_{2.5}$ mass concentration, the hourly data were divided into two categories: clean (C-type) PM$_{2.5} ≤$ 75 µg/m$^3$ and polluted (P-type) PM$_{2.5} >$ 75 µg/m$^3$ conditions. In this study, the observation data were also divided in day and night, which generally ranged from 6:00 a.m. to 18:00 p.m. and from 18:00 p.m. to 6:00 a.m., respectively.

As shown in Figs. 1–4 and Table 1, the total concentrations of SO$_2^{2−}$ and SO$_2$ were the highest in spring and the lowest in autumn. The higher temperature and RH conditions in summer allow SO$_2$ to be more easily converted into SO$_2^{2−}$. This explained the highest SO$_2^{2−}$ concentration and the lowest SO$_2$ concentration in summer. In winter, the meteorological conditions are not conducive to sulfate gas-particle conversion. Therefore, the SO$_4^{2−}$ concentration was relatively low, only 4.14 µg/m$^3$. The SOR was high in summer (0.82) and autumn (0.73), while the SOR was the lowest in winter, at only 0.24. In our previous study from 2009 to 2010 (Zhao et al., 2013), the annual average SO$_4^{2−}$ in PM$_{2.5}$ was 19.1 µg/m$^3$, indicating a significant decrease have taken place in sulfate in recent years.

The observation periods can be ranked based on the TNO$_2$ concentration, from high to low, as follows: autumn (20.03 µg/m$^3$) > spring (13.84 µg/m$^3$) > summer (10.63 µg/m$^3$) > winter (7.19 µg/m$^3$). Apparently, the NO$_3^{−}$ concentration was also the highest in autumn. More than 80% of TNO$_2$ occurred in the form of NO$_3^{−}$. In autumn, the average NO$_3^{−}$ concentration reached 52.09 µg/m$^3$ under polluted conditions, which was almost 5.4 times as high as that under clean conditions. Compared with sulfate, the NOR was much lower in all seasons, and the NOR in winter was the lowest, at only 0.07.

In this study, the average NO$_3^{−}$ concentration was higher than the SO$_2^{2−}$ concentration in all seasons, and the mass fractions of NO$_3^{−}$ in PM$_{2.5}$ were 23.22%, 23.94%, 37.94%, and 19.28%, respectively. The growth rate of nitrate under polluted conditions was significantly higher than that of sulfate. A de-
<table>
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<th>Winter</th>
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<td>1.97</td>
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</table>

* C: Clean; P: Polluted.
Fig. 1. – Temporal trends of the major components in PM$_{2.5}$ and gaseous precursors with the meteorological parameters in spring.

Increasing SO$_4^{2-}$ concentration and an increasing NO$_3^-$ relative contribution to the PM$_{2.5}$ mass loading could be inferred from previous studies in Beijing (Sun et al., 2010, 2012; Zhao et al., 2013; Zhang et al., 2016a, 2016b; Xu et al., 2019). The significant reductions in SO$_2$ had diminished the role of sulfate aerosols and increased the availability of NH$_3$ to form NH$_4$NO$_3$.

The TNH$_3$ concentration in Beijing was the lowest (7.02 μg/m$^3$) in winter and the highest (27.93 μg/m$^3$) in summer. However, the TNH$_3$ concentrations in spring and au-
Fig. 2. – Temporal trends of the major components in PM$_{2.5}$ and gaseous precursors with the meteorological parameters in summer.

Autumn were also high, both higher than 20 $\mu$g/m$^3$. Volatility from soil and animal husbandry activities mainly contributed to the TNH$_3$ concentration in summer (Meng et al., 2017). The dew and guttation droplets were also considered important sources of NH$_3$ (Kuang et al., 2020). Most TNH$_3$ occurred as gaseous NH$_3$, which resulted in the NH$_3$ concentration exhibiting the same seasonal variations as those in TNH$_3$. The NH$_4^+$ concentration also exhibited a considerable season variation, ranging from 3.42 (winter) to 8.21 $\mu$g/m$^3$ (autumn). Some previous studies focusing on the concentration level of
Fig. 3. – Temporal trends of the major components in PM$_{2.5}$ and gaseous precursors with the meteorological parameters in autumn.

gaseous NH$_3$ also showed similar seasonal characteristics of the highest value in summer (Ianniello et al., 2010; Meng et al., 2011; Hu et al., 2014; Kuang et al., 2020).

Excess NH$_3$ was one of the reasons for the high NO$_3^-$ concentration in the atmosphere. In this study, (TNH$_3$)$_{\text{Rich}}$ was defined to describe the variations in the excess NH$_3$ in the different seasons in Beijing, which represents the extent to which the TNH$_3$ exceeds the required ammonia, and is defined as:

$$(\text{TNH}_3)_{\text{Rich}} = \frac{\text{TNH}_3}{\text{Required NH}_x}$$ (1)
Fig. 4. – Temporal trends of the major components in PM$_{2.5}$ and gaseous precursors with the meteorological parameters in winter.
Fig. 5. – Characteristics of (TNH\textsubscript{x})\textsubscript{rich} at the different PM\textsubscript{2.5} pollution levels in every season. The top, middle, and bottom horizontal lines of the boxes mark the 75th, 50th, and 25th percentiles of the data range.

\[
\text{TNH}_3 = 17 \times \left( \frac{[\text{NH}_4^+]}{18} + \frac{[\text{NH}_3]}{17} \right) \\
\text{Required NHx} = 17 \times \left( \frac{[\text{SO}_4^{2-}]}{48} + \frac{[\text{NO}_3^-]}{62} + \frac{[\text{Cl}^-]}{35.5} \right) \\
- \frac{[\text{Na}^+]}{23} - \frac{[\text{K}^+]}{39} - \frac{[\text{Ca}^{2+}]}{20} - \frac{[\text{Mg}^{2+}]}{12} 
\]

where, [NH\textsubscript{4}\textsuperscript{+}], [NH\textsubscript{3}], [SO\textsubscript{4}\textsuperscript{2-}], [NO\textsubscript{3}\textsuperscript{-}], [Cl\textsuperscript{-}], [Na\textsuperscript{+}], [K\textsuperscript{+}], [Ca\textsuperscript{2+}], and [Mg\textsuperscript{2+}] are the measured concentrations (\mu g/m\textsuperscript{3}) of those ions. NH\textsubscript{4}NO\textsubscript{3} and NH\textsubscript{4}Cl are unstable chemical species, and TNO\textsubscript{3} and TCI cannot be completely converted into aerosol phases. Therefore, gaseous HNO\textsubscript{3} and HCl were not considered in the above expressions.

Fig. 5 reveals that (TNH\textsubscript{x})\textsubscript{rich} had the lowest median value (2.43) in winter and the highest median value (6.21) in summer, and was much higher than 1.0 in all four seasons, confirming that sufficient TNH\textsubscript{3} was present to neutralize acidic components (H\textsubscript{2}SO\textsubscript{4}, HNO\textsubscript{3}, and HCl) to form ammonium salts in all seasons. In addition, (TNH\textsubscript{x})\textsubscript{rich} was very high under clean conditions compared to that under polluted conditions in all seasons. The reason is that the SO\textsubscript{4}\textsuperscript{2-} and TNO\textsubscript{3} concentrations were relatively low under clean conditions, while the background TNH\textsubscript{3} concentration in Beijing was relatively high. In study of Song et al. (2018) and Ge et al. (2019), the concentration of excess NH\textsubscript{3} was also calculated, similar results were observed, indicating that Beijing fine particles were nearly always under an NHx -rich conditions.

To better understand the potential impact of surrounding pollution sources on the secondary inorganic ions, the wind dependence of the total SNA (sulfate, nitrate, and ammonium) concentration is shown in Fig. 6. Affected by the terrain, the high concentration was mainly distributed in the direction of northeast and southwest, especially the wind from southwest, which often brought high concentration of PM\textsubscript{2.5}. In spring, autumn, and winter, clean air often comes from the northwest and can effectively remove air pollution in Beijing, resulting low concentration of SNA in the northwest direction. The wind dependence of each of these three ions was similar to Fig. 6 (see Fig. 51 in the supplement), except that the nitrate was distributed relatively evenly in each WD.

The seasonal TCI was the highest in winter (1.70 \mu g/m\textsuperscript{3}) and the lowest in summer (0.62 \mu g/m\textsuperscript{3}). Most TCI occurred in the form of particulate Cl\textsuperscript{-}. High Cl\textsuperscript{-} concentrations occurred in winter, with an average concentration of 1.61 \mu g/m\textsuperscript{3}. Especially under polluted conditions, the average Cl\textsuperscript{-} concentration was 5.10 \mu g/m\textsuperscript{3}, almost five times as high as that under clean conditions. Ianniello et al. (2011) found that the average concentration of Cl\textsuperscript{-} was 2.94 \mu g/m\textsuperscript{3} in winter of 2007, which significantly higher than that of 0.79 \mu g/m\textsuperscript{3} in summer. In the study of Zhang et al. (2018b), the average concentration of Cl\textsuperscript{-} was 4.98 \mu g/m\textsuperscript{3} during the periods of February and March in 2015. The high TCI concentration was mainly due to coal combustion for heating in winter (Yao et al., 2002; Biswas et al., 2008; Ianniello et al., 2011).

In our study, the HONO concentrations displayed a pronounced seasonal profile with a maximum in autumn (4.30 \mu g/m\textsuperscript{3}) and a minimum in winter (1.70 \mu g/m\textsuperscript{3}). In all seasons, the HONO concentration under polluted conditions was 1.30–3.64 times higher than that under clean conditions. In particular, the hourly HONO and NH\textsubscript{3} concentrations were highly correlated. The HONO concentration was also highest in autumn (4.76 \mu g/m\textsuperscript{3}) and lowest in winter (2.20 \mu g/m\textsuperscript{3}) in results observed from September 2015 to July 2016 (Wang et al., 2017b). Compared with results obtained in an earlier study from 2008 to 2009 (Hendrick et al., 2014), the HONO concentra-
tion had increased significantly in Beijing. The average HONO concentrations observed in that study were between 0.19 ppb (0.40 μg/m³, spring) and 0.48 ppb (1.01 μg/m³, winter) in four seasons.

The gaseous HNO₃ and HCl shown in Figs. 1–4 were the residual amounts after reaction with ammonia to form aerosols, which is mainly affected by the thermodynamic equilibrium between gas and particles, so there also existed a good correlation between the gaseous HNO₃ and HCl.

2.2. Diurnal variations

The average diurnal variations in the major water-soluble ions in PM₂.₅, gaseous precursors, and gas-particle partitioning and conversion are shown in Fig. 7. It is clear that the SO₄²⁻ concentration increased gradually after sunrise and reached high levels in the afternoon and night in spring, summer, and autumn. In winter, the SO₄²⁻ concentration continued to decrease in the daytime, increased suddenly after 18:00 LST, and reached its highest level around midnight. In all four seasons, the SO₄²⁻ concentration was low in the morning, and the remaining SO₂ after oxidation was also the lowest in the morning, resulting in the SOR reaching its maximum at 06:00–07:00 LST. There was no significant difference in the average SO₄²⁻ concentration between day- and nighttime. Particularly, in autumn and winter, the average SO₄²⁻ during nighttime was higher than that during daytime. It can be inferred that the heterogeneous reaction of SO₂ was also an important mechanism for sulfate formation. The SO₄²⁻ measured in summer and autumn of 2009 showed its high level around noon (Hu et al., 2014). Obviously, the diurnal variation of SO₄²⁻ was quite different with that eight years ago.

In the four seasons, the NOR was low, that is, only a small portion of NO₂ in the atmosphere was converted into TNO₃. The NOR appeared a higher value in the afternoon or night. The ε(NO₃⁻) levels were very high in the four seasons. As mentioned in the previous section, most of the TNO₃ generated
by the oxidation of NO$_3$ occurs in the aerosol phase (NO$_3^-$). The diurnal variation trends of NO$_3^-$ were consistent with those of NH$_4^+$ in each season. This can be explained by the fact that most nitrates are present as NH$_2$NO$_3$ in the atmosphere. In summary, the NO$_3^-$ concentration is the result of the joint influences of gas-particle conversion (homogeneous and heterogeneous reactions) and partitioning. The diurnal variation of NO$_3^-$ in previous study exhibited similar trend with us (Hu et al., 2014).

In all seasons, $\epsilon$(NH$_4^+$) was mainly in the range of 0.2–0.4; that is, most TNH$_3$ is present as gaseous NH$_3$. Therefore, the diurnal variations in TNH$_3$ were similar to those in NH$_3$ in each season. In spring, summer, and autumn, NH$_3$ concentration maxima and minima were observed from 09:00–11:00 and from 15:00–18:00, respectively. The NH$_3$ morning peak might have resulted from human activities, fertilized soils, plant stomata, and entrainment of ammonia from the residual layer (Basu et al., 2010; Ellis et al., 2011; Meng et al., 2018). In a study of Beijing implemented during 2009 and 2010 (Meng et al., 2011), only NH$_3$ in summer showed the similar diurnal trend. Kuang et al. (2020) investigated dew and gut-tation droplets as significant nighttime reservoirs and strong morning sources of NH$_3$. A low temperature is not conducive to NH$_3$ volatilization and NH$_4$NO$_3$ decomposition, so the NH$_3$ and TNH$_3$ concentrations were low in winter. The diurnal NH$_3$ variation in winter was not significant, and the difference in the average concentration between day- and nighttime was small. In all seasons, NH$_4^+$ showed high correlation coefficients with sulfate and nitrate of 0.87 and 0.93, respectively.

The HONO concentration showed significant diurnal variations. After a high value appeared in the morning, the concentration decreased rapidly due to the rapid photolysis and reached its lowest point in the afternoon. High concentrations occurred in spring and summer at 08:00 LST in the morning, and the HONO concentration reached its peak in autumn and winter at approximately 10:00 LST, similar to previous studies in Beijing (Hendrick et al., 2014; Tong et al., 2016; Zhang et al., 2019). According to Figs. 1–4, the hourly HONO and NH$_3$ concentrations were highly correlated (with correlation coefficients of 0.695, 0.612, 0.780, and 0.813 in the spring, summer, autumn, and winter measurement periods, respectively), and the morning HONO peak was also consistent with that of NH$_3$. Xu et al. (2019b) and Kuang et al. (2020) observed that the morning NH$_3$ peak can lead to an explosive growth in HONO under high ambient RH conditions in the NCP. NH$_3$-promoted NO$_2$ hydrolysis is a significant HONO source, which provides direct insights into the missing daytime HONO source in the NCP.

Due to the excess TNH$_3$ in the atmosphere, most TCI occurred in the aerosol phase (Cl$^-$.). The gaseous HCl in the atmosphere was the result of the thermodynamic equilibrium of NH$_4$Cl. There is almost no secondary TCI in the atmosphere, the diurnal variation of Cl$^-$ is largely affected by the emission from primary sources.

### 2.3. Gas-particle partitioning

As mentioned above, the excess TNH$_3$ concentration was observed, which promotes the formation of a large amount of NH$_4$NO$_3$, NH$_4$SO$_4$, and NH$_4$Cl in the atmosphere. As typical unstable components under normal atmospheric conditions, NH$_4$NO$_3$ and NH$_4$Cl are present according to the reversible phase equilibrium with gaseous precursors as follows:

$$\begin{align*}
\text{NH}_4\text{NO}_3 \text{ (s or aq)} & \rightleftharpoons \text{HNO}_3 \text{ (g)} + \text{NH}_3 \text{ (g)} \\
\text{NH}_4\text{Cl} \text{ (s or aq)} & \rightleftharpoons \text{HCl} \text{ (g)} + \text{NH}_3 \text{ (g)}
\end{align*}$$

(4) (5)

Reversible phase changes continue to occur over time, continuously varying with the meteorological conditions. Therefore, the unique atmospheric process associated with partitioning is key to understanding the aerosol pH, visibility degradation, and air quality.

According to Table 1 and Fig. 7, the seasonal and diurnal variations in $\epsilon$(NO$_3^-$), $\epsilon$(NH$_4^+$), and $\epsilon$(Cl$^-$) are examined in this section. The average $\epsilon$(NO$_3^-$) was above 0.8 in each season, which indicated that most TNO$_3$ existed in the aerosol phase. In summer, the diurnal variation in $\epsilon$(NO$_3^-$) showed a downward trend in the daytime and gradually rose after 18:00 until the next morning. However, in winter, $\epsilon$(NO$_3^-$) has a completely opposite trend and exhibits a clear upward trend in the morning and a significant downward trend after 18:00. The $\epsilon$(NH$_4^+$) values were relatively low in each season, which were 0.21 (spring), 0.24 (summer), 0.27 (autumn) and 0.31 (winter). This result indicated that a large proportion of TNH$_3$ occurred as gaseous ammonia, especially in spring and summer. Because the amount of total ammonia exceeded the required amount several times, the diurnal variation in $\epsilon$(NH$_4^+$) was not notable. The $\epsilon$(Cl$^-$) value showed typical seasonal variations, with high values in winter (0.93) and low values in summer (0.65). The diurnal variation in $\epsilon$(Cl$^-$) in the different seasons showed a distinct downward trend in the daytime and a significant rebound in the nighttime, indicating the influences of T and RH on the thermodynamic equilibrium of NH$_4$Cl.

In our previous paper, due to the good agreement between the predicted and measured NH$_3$, NH$_4^+$, NO$_3^-$, and Cl$^-$ values when the RH was higher than 30% by the thermodynamic model of ISORROPIA II, we calculated the PM$_{2.5}$ pH values and examined the sensitivity of $\epsilon$(NH$_4^+$) and $\epsilon$(NO$_3^-$) to TNO$_3$, TNH$_3$, RH, and T (Ding et al., 2019b). We found that the elevated TNH$_3$ level altered the gas-particle partitioning and shifted more TNO$_3$ into the particle phase, leading to an increase in nitrate. However, the $\epsilon$(NO$_3^-$) response to TNH$_3$ control was highly nonlinear, meaning that a decrease in nitrate would occur only when the TNH$_3$ concentration was greatly reduced. The $\epsilon$(Cl$^-$) results were not provided in that paper. Thus, the sensitivity of $\epsilon$(Cl$^-$) to RH, T, and TCI in all seasons are presented in this paper (Fig. 8). In the sensitivity analysis, RH, T, and TCI were selected as the variables. To assess how a variable affects $\epsilon$(Cl$^-$), the real-time measured values of this variable and the average values of other species and parameters were input into ISORROPIA-II. ISORROPIA-II was run in forward and metastable mode in this study. In forward mode, T, RH, and the TNH$_3$, TNO$_3$, TCI, and TSO$_4$ need to be input. While, in reverse mode, equilibrium partitioning is calculated given only the concentrations of aerosol components, RH, and T as input, the concentration of gaseous components is estimated by the model. Consequently, only the forward model can be used to analyze the gas-particle partitioning process.
The performance of the ISORROPIA II in different modes was discussed in our previous studies (Ding et al., 2019a, b).

Gas-particle partitioning can be directly affected by the concentrations of gaseous precursors and meteorological conditions. As shown in Fig. 8 and according to the results of Ding et al., a lower T and higher RH contribute to the conversion of more TNH₃, TNO₃, and TCI to the particle phase. Remarkably, when the RH exceeded 60%, more than 90% of TCI occurred in the particle phase in autumn and winter. In spring and summer, most TCI would be partitioned into the gaseous phase under lower-RH conditions (< 30%). In winter, the low temperatures promoted the occurrence of Cl⁻ in the aerosol phase, and the average ε(Cl⁻) concentration was higher than 0.8, even at a low RH.

For TCl, the ammonia concentration was more excessive, so ε(Cl⁻) is mainly affected by the equilibrium constant for ammonium chloride solutions, which is a function of T and RH. Therefore, ε(Cl⁻) was more sensitive to variations in T and RH than ε(NO₃⁻). The increasing TCI had little effect on ε(Cl⁻) in spring, summer, and autumn because NH₃ was more abundant in these three seasons than in winter (Fig. 5).

3. Summary and conclusions

The hourly mass concentrations of the inorganic components in PM₂.₅ (SO₄²⁻, NO₃⁻, NH₄⁺, K⁺, Cl⁻, Na⁺, Ca²⁺, and Mg²⁺) and gaseous precursors (SO₂, NH₃, HNO₃, HONO, and HCl) were measured online with a MARGA instrument from 2016 to 2018 at an urban site in Beijing. The hourly PM₂.₅ concentrations were 55.05, 40.94, 50.39, and 35.01 μg/m³ in the spring, summer, autumn, and winter measurement periods, respectively. The SO₄²⁻ concentration has remarkably decreased owing to the significant reduction in SO₂, and the relative contribution of NO₃⁻ to PM₂.₅ and WSIs have notably increased in recent years. The SOR was high in summer (0.82) and autumn (0.73), while the SOR was the lowest in winter (0.24). There was no significant difference in the average SO₄²⁻ concentration between the day- and nighttime. The heterogeneous reaction of SO₂ was a crucial mechanism for sulfate formation in all four seasons, especially in autumn and winter. More than 80% of the TNO₃ generated by the oxidation of NO₂ occurred in the aerosol phase (NO₃⁻) due to the excess ammonia. Most TNH₃ is present as gaseous NH₃, (TNH₃) Rich reached its lowest median value (2.43) in winter and its highest median value (6.21) in summer, and (TNH₃) Rich was very high under clean conditions compared to that under polluted conditions in all seasons. The TCI concentration was the highest in winter, which mainly came from coal combustion for heating. HONO increased significantly in Beijing compared with previous results, and its hourly concentration was highly correlated with NH₃.

According to the gas-particle partitioning sensitivity test, a lower T and higher RH could contribute to the conversion of more TNH₃, TNO₃, and TCI into the particle phase, while ε(Cl⁻) was more sensitive to the variations in T and RH than to those in ε(NO₃⁻).

In summary, with the rapid decrease of sulfate and the excessive concentration of TNH₃, nitrate becomes more important in the aerosol pollution of NCP. The concentration levels, seasonal differences, and diurnal variations of secondary inorganic ions had changed compared with those in the previous studies. Most HNO₃ and HCl existed in the form of particles, and the gas-particle partitioning process was mainly affected by the temperature and relative humidity. There was a strong correlation between HONO and ammonia. The concentration of HONO was higher than before, which played an important role in the enhancement of atmospheric oxidation.

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Appendix A. Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.08.031.

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