Study on pollution behavior and sulfate formation during the typical haze event in Nanjing with water soluble inorganic ions and sulfur isotopes

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ABSTRACT

The typical haze event in Nanjing was selected to study pollution behavior and sulfate formation by field measurement. Based on the concentrations of water soluble inorganic ions in PM2.5, pollution characteristics of the haze were investigated with phase clustering analysis. Besides, δ34S values of SO2 and sulfate in PM2.5 were determined in order to explore sulfur sources and sulfate formation. The result showed that PM2.5 pollution during the haze event was significantly serious, which was mainly from coal combustion, vehicle exhaust emission and biomass burning. Sulfate formation was attributed to aqueous phase sulfur oxidation reactions promoted by high relative humidity and NO2 concentration under the alkaline condition. The color of sky on 22 Dec. was ascribed to the combination of sunset glow and fine particles in high-moisture atmosphere. δ34S values of SO2 are found to be lower than those of sulfate in PM2.5 indicating there was presence of sulfur isotopic fractionation during SO2 oxidation. The average contribution of SO2 homogenous oxidation to sulfate was about 51.2% during the haze events. The ratio of SO2 heterogeneous and homogeneous oxidation to sulfate was mainly attributed to the concentrations of gaseous pollutants (NO2, SO2 and O3) and relative humidity of the atmosphere.

1. Introduction

PM2.5 is a particulate matter with aerodynamics equivalent diameter ≤ 2.5 μm (GB3095–2012). Haze is defined as a pollution phenomenon which cuts atmospheric visibility to < 10 km due to the complex materials suspended in the atmosphere (China Meteorological Administration, 2010). Generally, haze is mainly related to high PM2.5 concentration, relative humidity (RH) < 90% and stable meteorological condition (Peng et al., 2016; Feng et al., 2016; Yuan et al., 2015). Chen et al. (2012) proposed a parameterization of light extinction for low visibilities on hazy days and found that a high aerosol volume concentration was responsible for low visibility. Usually, PM2.5 possesses profound impacts on human and ecosystem health, weather and climate change (Cheng et al., 2013). Although the government took great efforts to control air pollution (Cai et al., 2017; Wang et al., 2017a, 2017b), China has been suffering from haze pollution nowadays due to the massive emission of particulate matter and gaseous pollutants (Jiang et al., 2016). There exists the heaviest haze pollution observed in four regions in China: Beijing-Tianjin-Hebei (Tan et al., 2016; Gao et al., 2015; Guo et al., 2014), Yangtze River Delta (Cheng et al., 2013; Shen et al., 2015), Pearl River Delta (Tao et al., 2014) and Sichuan Basin (Wang et al., 2017a, 2017b). However, the formation mechanism of heavy haze event remains uncertain in China (Zhang et al., 2015).

Nanjing, located in Yangtze River Delta, is one of the biggest cities in China with an area of 6597 km² and permanent resident population > 8.2 millions. The annual average temperature and precipitation are about 15.4 °C and 1106 mm, respectively. Generally, the pollution of particulate matter in Nanjing is rather serious (Wang et al., 2012). Li et al. (2016) measured water soluble inorganic ions (WSIIs) and metal elements during the haze-fog events in Nanjing and identified emission sources as road dust, coal combustion and steel industry. Kong et al. (2015) studied the variation of PAHs in PM2.5 during winter haze period in Nanjing, indicating that coal combustion, traffic emission,
industrial production and petroleum were main sources of PAHs. Wang et al. (2011) determined chemical compositions and size distribution of water soluble organic compounds in particles during a heavy haze caused by field burning in Nanjing and made clear the effect of straw burning on the haze.

Sulfate is one of the prevalent components of PM$_{2.5}$. It is controversial for rapid growth of sulfate concentration during the haze in China. Wang et al. (2016) and Cheng et al. (2016) believed that the presence of NO$_2$ was obviously favorable for SO$_2$ oxidation under the conditions of high RH and NH$_3$. However, Guo et al. (2017) insisted that SO$_x$ catalytic oxidation of metal ions was main sulfate formation process. Sulfur isotope can be used for tracing sulfur source and exploring sulfate formation (Xiao et al., 2014). Therefore, it is admirable to determine sulfur isotopic composition in PM$_{2.5}$ during the haze events. Nowadays, as an effective indicator, $\delta^{34}$S has been adopted to identify sulfur sources of the atmosphere around the world. Ohizumi et al. (2014) monitored sulfur isotopic ratio in sulfate deposition for 28 years at Nagaoka indicating that $\delta^{34}$S could be applied to perceive the change of emission sources. Han et al. (2016) used sulfur and oxygen isotopes to identify the sources of Beijing aerosol suggesting that biogenic sulfur emission in summer and the increasing coal combustion in winter were the main contributions to aerosol. Sakata et al. (2013) studied $\delta^{34}$S value in aerosol from Japan Sea coast and concluded sulfur isotope was a tracer of emission during coal combustion. Besides, Leung et al. (2001) and Sinha et al. (2008) found that $\delta^{34}$S in aerosol could be employed to distinguish the mixing processes and transport pathways of sulfur-containing pollutants in the atmosphere. In the contribution, we chose the typical haze events in Nanjing from 21 Dec. 2015 to 1 Jan. 2016 to study pollution characteristics and sulfate formation. Especially, a scarcely purple sky during the haze was observed at 17:00 on 22 Dec. 2015. Many local and national news outlets reported this unusual haze event (http://news.xinhuatan.com/local/2015-12/23/c_128559783.htm). It is unclear whether there existed the difference in pollution behaviors of this haze compared to other haze events. In addition, sulfate formation during the haze was usually complicated in China. Single component analysis hardly makes clear the sources of PM$_{2.5}$ and sulfate formation during the haze event.

2. Materials and methods

2.1. Sampling site

PM$_{2.5}$ and SO$_2$ samples were collected on the roof of the library in Nanjing University of Information Science & Technology (NUIST, 32.1° N, 118.5° E), which is about 35 m above the ground. The sampling site of NUIST in Nanjing, China is depicted in Fig. 1. The site, located at the side of Ningxiu Road, is close to Nanjing chemical industry park. There are presence of many large-scale steel plants, petrochemical companies and thermal power plants, which release massive exhaust gases and particles. In addition, there exists a small amount of rice farmland around the sampling site.

2.2. Determination of particle number and spectral distribution

Wide-range Particle Spectrometer (1000XP, MSP Co., USA) was used to determine number concentration and spectral distribution of aerosol particles. The sampling flows of Differential Mobility Analyzer and Laser Particle Spectrometer were 0.3 and 0.70 L min$^{-1}$, respectively. The time resolution was set at 5 min.

2.3. Sample collection

PM$_{2.5}$ and SO$_2$ were collected using a modified sampler (TH-1000H, Tianhong Co., Wuhan) with a flow rate of 1.05m$^3$ min$^{-1}$ from 9 am to 9 pm per day from 21 Dec. 2015 to 1 Jan. 2016, which covered a complete process of haze pollution. The double sampling frames were installed in the sampler slot. The upper sampling frame was used to collect PM$_{2.5}$/PM$_{10}$, while the lower sampling frame was adopted to gather SO$_2$. Before PM$_{2.5}$ and SO$_2$ sampling, the sampler was usually calibrated to ensure the accuracy.

PM$_{2.5}$ and SO$_2$ were sampled with quartz filters (203 × 254 mm, Munktell, Sweden) and glass fiber filters (203 × 254 mm, Tisch Environment INC, USA), respectively. Before PM$_{2.5}$ and SO$_2$ sampling, the filters were firstly incinerated in a muffle furnace at 450 °C for 4 h to avoid the influence of organic matters and moisture. Then, quartz filters were directly placed in the desiccators at room temperature. The glass fiber filters were soaked in the solution of 2% K$_2$CO$_3$ and 2% glycerol for 2 h. After being dried in DGG-9070A electric oven, the filters were kept in the desiccators for 24 h at room temperature. While SO$_2$ sampling, it can be absorbed in alkaline-soaked glass fiber filters and transformed into SO$_2$ and HSO$_3$ immediately.

The sampled filters were reserved in a refrigerator for chemical analysis. During the samples treatment, H$_2$O$_2$ solution was used to oxidize SO$_2$ and HSO$_3$ into sulfate.

2.4. WSIIs analysis

After the dissolution of 1/32 sampled filter with Milli-Q water and the filtration with 0.22 μm membrane, the concentrations of the WSIIs (Na$^+$, Na$^+$, NH$_4^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Mg$^{2+}$, Cl$^-$, NO$_3^-$ and SO$_4^{2-}$) in PM$_{2.5}$ were measured by using ICS-3000 and ICS-2000 Ion Chromatography (Dionex, USA). The detection limit of each ion was lower than 0.015 μg m$^{-3}$.

2.5. Sulfur isotopic analysis

Sulfur isotopic composition was analyzed in State Key Laboratory of Biogeology and Environmental Geology in China University of Geosciences (Wuhan). Elemental analyzer (EA, Flash 2000, Thermo) and isotopic mass spectrometer (IRMS, Delta V Plus, Finningan) were used to determine $\delta^{34}$S of sulfate in PM$_{2.5}$. Specifically, 1/4 sampled filters were shredded and soaked overnight in 200 mL Milli-Q water. Dissolved sulfate in PM$_{2.5}$ was precipitated as BaSO$_4$ by adding 3 mL 1 mol L$^{-1}$ BaCl$_2$. The precipitate was then separated by 0.22 μm acetate membrane and rinsed with 150 mL Milli-Q water to remove Cl$^-$.

Finally, the precipitate was transferred to ceramic crucible and combusted at 800 °C in muffle furnace for 2 h to acquire high-purity BaSO$_4$ powder. BaSO$_4$ was converted into SO$_2$ in EA in the presence of Cu$_2$O. SO$_2$ from EA was ionized and $\delta^{34}$S value was measured using IRMS. The result was with respect to international standard V-CDT and the accuracy was better than ± 0.2‰.

The determination of the WSIIs and sulfur isotopic composition was carried out in duplicate and the average values were used for data analysis.

2.6. Phase clustering analysis

Phase clustering analysis can be used to describe the similarity of different sample clusters. In this study, we used three phases clustering analysis to explore the distribution of the WSIIs in PM$_{2.5}$. We firstly divided the WSIIs into three phases according to different sources. On this basis, the proportions of three phases were calculated. The proportion in different PM$_{2.5}$ samples might have a certain discrepancy, but the samples with similar proportion would assemble together.
3. Results and discussion

3.1. Pollution behavior of PM$_{2.5}$ during the haze event

3.1.1. PM$_{2.5}$ concentration

The mass concentration and number concentration of PM$_{2.5}$ during the haze events are shown in Fig. 2. It can be observed that mass concentrations of PM$_{2.5}$ ranged from 40.03 to 233.43 $\mu$g·m$^{-3}$ with an average and standard deviation of 144.67 ± 54.12 $\mu$g·m$^{-3}$, which is 1.93 times of the Second Grade National Ambient Air Quality Standard (75 $\mu$g·m$^{-3}$) and 4.13 times of the First Grade National Ambient Air Quality Standard (35 $\mu$g·m$^{-3}$) (GB3095–2012). Meanwhile, mass concentrations of PM$_{2.5}$ were beyond the safety standard of World Health Organization (10 $\mu$g·m$^{-3}$) during the observation period. In addition, we noted that average mass concentration of PM$_{2.5}$ during the haze events was higher than those in Hong Kong (55.50 $\mu$g·m$^{-3}$, Cheng et al., 2015), Guangzhou (76.80 $\mu$g·m$^{-3}$, Tao et al., 2014), Xiamen (86.20 $\mu$g·m$^{-3}$, Zhang et al., 2012), Beijing (115.80 $\mu$g·m$^{-3}$, Hu et al., 2014) and Xi’an (142.60 $\mu$g·m$^{-3}$, Wang et al., 2015), indicating that PM$_{2.5}$ pollution was very serious. As indicated in Fig. 2, mass concentrations of PM$_{2.5}$ during the haze event markedly fluctuated. The highest PM$_{2.5}$ concentration occurred on 22 Dec. 2015 with a value at 233.43 $\mu$g·m$^{-3}$, then significantly decreased to 125.39 $\mu$g·m$^{-3}$ on 23 Dec. Besides, the lowest PM$_{2.5}$ concentration was found to be 40.03 $\mu$g·m$^{-3}$ on 27 Dec. According to weather conditions of Nanjing during the haze events in Fig. 3, high PM$_{2.5}$ concentration on 22 Dec. was related to low wind speed, the continuously static and stable weather made it difficult to spread for fine particles in the atmosphere, thereby causing the accumulation of different pollutants (Ueda et al., 2016; Cuhadaroglu and Demirci, 1997). Considering relative humidity at 85% and visibility < 2 km on 22 Dec., we inferred that there was presence of a heavy haze event on 22 Dec. It can be observed from Fig. 3 that the decrease of PM$_{2.5}$ concentration on 23 Dec. was due to the precipitation. The lowest PM$_{2.5}$ concentration on 27 Dec. was mainly ascribed to high wind speed, which was favorable for the diffusion of fine particles.

The number concentrations of PM$_{2.5}$ during the observation period varied from 6067.8 to 21,225.3 #·cm$^{-3}$ with an average and standard deviation of 13,165.7 ± 4714.7#·cm$^{-3}$ (Fig. 2). It is noteworthy that there existed the uncertainty between mass concentration and number concentration of PM$_{2.5}$. For instance, high mass concentration corresponded to the relatively high number concentration of PM$_{2.5}$. For instance, high mass concentration corresponded to the relatively high number concentration of PM$_{2.5}$ on 22 Dec. While on 29 Dec., there existed low mass concentration and rather high number concentration. Generally, mass concentration of PM$_{2.5}$ was mainly dominated by the larger particles, while number concentration of PM$_{2.5}$ was mainly affected by fine particles. Therefore, the
discrepancy between mass concentration and number concentration of PM$_{2.5}$ was chiefly ascribed to different particle number size distribution. As shown in Fig. 4, the particle number size distribution on 22 Dec. (Fig. 4a) mainly concentrated below 500 nm and peak value of number concentration at 150 nm was about 650 $\text{# cm}^{-3}$. However, the particle number size distribution was below 400 nm and peak value of number concentration at 100 nm was about 800 $\text{# cm}^{-3}$ on 29 Dec. (Fig. 4b). This indicated that there were more superfine particles on 29 Dec. compared to those on 22 Dec. It is noted that there existed high relative humidity (85%) and lots of fine particles in the atmosphere on 22 Dec. When sunlight passed through small water drops and fine particles, it could be resolved into different kinds of monochromatic light, thereby causing the appearance of the sky color. Therefore, the color of sky on 22 Dec. was just a physical phenomenon from the combination of sunset glow with water drops and fine particles.

3.1.2. WSIIs of PM$_{2.5}$

The concentrations of WSIIs in PM$_{2.5}$ during the haze events are compared in Table 1 and concentration distribution for each ion is shown in Fig. 5. The average value and standard deviation of Na$^+$, NH$_4^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Mg$^{2+}$, Cl$^-$, NO$_3^-$ and SO$_4^{2-}$ were 0.75 ± 0.40, 21.30 ± 10.51, 1.84 ± 0.89, 0.86 ± 0.30, 0.35 ± 0.26, 4.81 ± 2.67, 26.46 ± 11.51 and 19.01 ± 6.78 $\mu$g·m$^{-3}$, respectively. The predominant ions in PM$_{2.5}$ during the haze events were NO$_3^-$, NH$_4^+$ and SO$_4^{2-}$, accounting for 86.58% of the WSIIs. NO$_3^-$ and SO$_4^{2-}$ were the dominant anions, the concentrations of which were much higher compared to that of Cl$^-$, NH$_4^+$ was the most important cation in PM$_{2.5}$, the concentrations of K$^+$, Ca$^{2+}$, Na$^+$ and Mg$^{2+}$ were relatively lower.

Three phases clustering analysis was used to interpret the distribution of the WSIIs in PM$_{2.5}$ during the haze events. NO$_3^-$, NH$_4^+$ and SO$_4^{2-}$ were the typically secondary pollutants, there was presence of good correlations between NH$_4^+$ and NO$_3^-$ ($r = 0.87$), NH$_4^+$ and SO$_4^{2-}$ ($r = 0.80$), NO$_3^-$ and SO$_4^{2-}$ ($r = 0.92$). Considering NH$_4^+$ was mainly from nitrogen utilization, livestock’s and the secondary formation of exhaust gas from fuel combustion and vehicle emission (Ge et al., 2011), NO$_3^-$ was chiefly from the conversion of NOx (Pastuszka and Wawroś, 2003) and SO$_4^{2-}$ mainly came from coal combustion and the oxidation of SO$_2$ (Lu et al., 2010; Karthikeyan and Balasubramanian, 2006), we classified NH$_4^+$, NO$_3^-$ NO$_3^-$ and SO$_4^{2-}$ together as the first phase. Besides, it is known that K$^+$ was an indicator of biomass burning (Yang et al., 2015) and Cl$^-$ was usually from coal combustion and biomass burning (Zhou et al., 2016). So we put K$^+$ and Cl$^-$ together as the second phase. Finally, we defined Na$^+$, Mg$^{2+}$ and Ca$^{2+}$ as the third phase due to these ions were mainly from natural sources such as dust and sea salt. On this basis, three phases clustering

![Fig. 2. The mass concentrations and number concentrations of PM$_{2.5}$ during the observation period.](image)

![Fig. 3. The weather conditions during the observation period.](image)
The ten days of a-II concentrated on high level area of the secondary ions with an average of 74.23%. In addition, there existed a good correlation between the secondary ions and PM$_{2.5}$ was as high as 89.39%. While the other two days of a-I was at low level area of the secondary ions with an average of 15.82%. Besides, PM$_{2.5}$ had relatively high correlation coefficients with Cl$^-$ (r = 0.54) and K$^+$ (r = 0.61), which indicated that biomass burning was a source for PM$_{2.5}$ during the haze events.

As the main ions of PM$_{2.5}$, NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ may constitute inorganic aerosol system with H$_2$O in the particle where NO$_3^-$ and SO$_4^{2-}$ can compete for NH$_4^+$ (Seinfeld and Pandis, 1998). Thus, it is favorable for studying their mutual relations to make clear the characteristics of the secondary pollution. Therefore, three phases clustering analysis of NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ was conducted and the proportions of each ion in the system were calculated. The corresponding results are shown in Fig. 7. The whole observation days could be classified into three categories named as b-I, b-II and b-III, respectively. There existed a large difference in the proportions of three ions in the system. The proportions of SO$_4^{2-}$, NH$_4^+$ and NO$_3^-$ in b-I followed a decreasing order with the values of 50.45%, 29.55% and 20.00%, respectively. However, the proportion of SO$_4^{2-}$, NH$_4^+$ and NO$_3^-$ in b-II fit an increasing order with the values of 28.15%, 33.26% and 38.59%. In b-III, the proportions of SO$_4^{2-}$, NH$_4^+$ and NO$_3^-$ were 29.70%, 21.89% and 48.41%, respectively. The discrepancies in the proportions of NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ might be ascribed to the precursors from different pollution sources and the combination mode of NO$_3^-$, SO$_4^{2-}$ with NH$_4^+$. [NO$_3^-$]/[SO$_4^{2-}$] has been used as an indicator to evaluate the importance of stationary and mobile sources (Arimoto et al., 1996). High [NO$_3^-$]/[SO$_4^{2-}$] ratio (> 1) indicated the predominance of mobile sources over stationary sources. [NO$_3^-$]/[SO$_4^{2-}$] value in b-I was 0.40 suggesting that stationary sources were at the more important position. While [NO$_3^-$]/[SO$_4^{2-}$] values in b-II and b-III were 1.39 and 1.64, respectively, indicating that mobile sources made the more contribution to PM$_{2.5}$. NH$_4^+$ can be transformed into (NH$_4$)$_2$SO$_4$, NH$_4$HSO$_4$ and NH$_4$NO$_3$ via the reactions with NO$_3^-$ and SO$_4^{2-}$. When NH$_4^+$ was in the forms of NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$, the calculated [NH$_4^+$] = 0.38[SO$_4^{2-}$] + 0.29[NO$_3^-$]NO$_3^-$; While NH$_4^+$ was in the forms of NH$_4$NO$_3$ and NH$_4$HSO$_4$, the calculated [NH$_4^+$] = 0.19[SO$_4^{2-}$] + 0.29[NO$_3^-$] (Kang et al., 2004). It is obtained that the correlation coefficient between the measured [NH$_4^+$] during the haze events and the calculated [NH$_4^+$] based on the first equation was 0.85. Similarly, the correlation coefficient between the

![Fig. 4. The particle number size distribution on 22 and 29Dec.2015.](image)

<table>
<thead>
<tr>
<th>Date</th>
<th>Na$^+$</th>
<th>NH$_4^+$</th>
<th>K$^+$</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Cl$^-$</th>
<th>NO$_3^-$</th>
<th>SO$_4^{2-}$</th>
<th>NO$_2$</th>
<th>O$_3$</th>
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<td>12-21</td>
<td>0.77</td>
<td>35.89</td>
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<td>1.09</td>
<td>0.11</td>
<td>8.71</td>
<td>40.62</td>
<td>23.74</td>
<td>21</td>
<td>71</td>
</tr>
<tr>
<td>12-22</td>
<td>0.62</td>
<td>38.93</td>
<td>2.89</td>
<td>0.65</td>
<td>0.07</td>
<td>5.61</td>
<td>39.78</td>
<td>23.51</td>
<td>25</td>
<td>91</td>
</tr>
<tr>
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<td>18.44</td>
<td>1.89</td>
<td>0.63</td>
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<td>4.68</td>
<td>18.9</td>
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<td>1.80</td>
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measured [NH₄⁺] and the calculated [NH₄⁺] according to the second equation was 0.86. A good correlation between the measured [NH₄⁺] and the two calculated [NH₄⁺] indicated that NH₄⁺ existed in the forms of (NH₄)₂SO₄, NH₄HSO₄ and NH₄NO₃ in PM2.5 during the haze events.

High SO₄²⁻ and NO₃⁻ concentrations in PM2.5 showed that there existed serious secondary pollution during the haze events. Besides, a good positive correlation between the concentrations of SO₄²⁻ and NO₃⁻ indicated that sulfate formation was accompanied by the increased NO₃⁻ concentration. This is mainly ascribed to SO₂ oxidation to sulfate in the presence of NO₂ under the alkaline condition. We studied the acid-base property of PM2.5 using the ratio of anions (A) and cations (C) (Hassan and Khoder, 2017). A and C can be calculated by A = NO₃⁻/62 + SO₄²⁻/48 + Cl⁻/35.5 and C = Na⁺/23 + NH₄⁺/18 + K⁺/39 + Mg²⁺/12 + Ca²⁺/20, respectively. A/C values were generally lower than 1 indicating the alkalinity of PM2.5 during the observation period. The lowest A/C value of 0.56 illustrated the strongest alkalinity on 22 Dec., which was favorable for SO₂ oxidation of high-concentration NO₂ (Hassan and Khoder, 2017; Sarwar et al., 2013). This can be confirmed by the results in Table 1.

Our observation was in agreement with Community Multiscale Air Quality (CMAQ) model simulation under NO₂-rich environment, which improved sulfate production up to 20% in wintertime (Sarwar et al., 2013). However, low NO₂ concentration (51 μg·m⁻³) and high SO₄²⁻ content (28.65 μg·m⁻³) were found on 25 Dec. According to RH and the concentrations of gaseous pollutants in Fig. 3 and Table 1, we inferred that this was related to high O₃ concentration (47 μg·m⁻³) and low RH (38%), which was helpful for the photochemical reactions from SO₂ to sulfate. On the contrary, very low O₃ concentration and high RH resulted in large amounts of sulfate on 22, 26 and 31 Dec. This was mainly attributed to the presence of very high NO₂ concentration and the strong alkalinity of PM2.5 in the atmosphere, which facilitated sulfate formation via aqueous phase sulfur oxidation reactions (Wang et al., 2016; Xie et al., 2015). This mechanism of sulfate formation was possibly dominated during the serious wintertime haze due to low O₃ concentration and the weak photochemical activity. Therefore, the
measured high NO$_3^-$ concentrations were partly attributed to an enhanced heterogeneous conversion of NO$_2$ to NO$_3^-$. At the early stage of the haze events (21 Dec.), the conversion of SO$_2$ to sulfate was mainly controlled by photochemical processes and accompanied with aqueous reactions due to high O$_3$ concentration (43 µg m$^{-3}$) and relatively high NO$_2$ concentration (71 µg m$^{-3}$) and RH (55%). With the aggregation of the haze on 22 Dec., the highest concentrations of PM$_{2.5}$, SO$_4^{2-}$ and NO$_3^-$ were mainly acquired by aqueous phase chemical reactions.

3.2. Sulfur isotopic fractionation during the haze events

3.2.1. Sulfur isotopic compositions of sulfate and SO$_2$

The regional characteristics of $\delta^{34}$S value made it meaningful to identify sulfur sources in the atmosphere (Han et al., 2016; Guo et al., 2010). Sulfur isotopic compositions of sulfate and SO$_2$ during the haze events were determined and the values of $\delta^{34}$S-SO$_4^{2-}$ and $\delta^{34}$S-SO$_2$ are compared in Fig. 8. It can be observed that the values of $\delta^{34}$S-SO$_4^{2-}$ were higher compared to those of $\delta^{34}$S-SO$_2$ during the haze events. $\delta^{34}$S-SO$_4^{2-}$ values were within the range from 3.7‰ to 6.8‰ with an average and standard deviation at 5.6 ± 1.0‰, while $\delta^{34}$S-SO$_2$ values ranged from −0.8‰ to 3.1‰ with an average and standard deviation at 1.5 ± 1.4‰. The discrepancy in the values of $\delta^{34}$S-SO$_4^{2-}$ and $\delta^{34}$S-SO$_2$ is due to sulfur isotopic fractionation effect during SO$_2$ oxidation to sulfate. The oxidation of SO$_2$ resulted in the change of sulfur isotopic composition, which was mainly due to equilibrium or kinetic discrimination between SO$_2$ and sulfate during the oxidation processes. The influence of different oxidants on sulfur isotopic fractionation needed to be further investigated. It should be pointed out that the variation tendencies of $\delta^{34}$S-SO$_4^{2-}$ and $\delta^{34}$S-SO$_2$ values were basically consistent indicating that sulfur sources of sulfate and SO$_2$ in the atmosphere were similar. Guo et al. (2016) determined $\delta^{34}$S-SO$_4^{2-}$ values with an average at 4.2‰ during the Youth Olympic Games in Aug. 2014. The discrepancy of $\delta^{34}$S-SO$_4^{2-}$ value with this study illustrated different contribution of pollution sources. In addition, we compared the values of $\delta^{34}$S-SO$_4^{2-}$ and $\delta^{34}$S-SO$_2$ with other cities in China. It is noted there existed an obviously regional difference. The values of $\delta^{34}$S-SO$_4^{2-}$ and $\delta^{34}$S-SO$_2$ in Nanjing were comparative to those in Shanghai, but lower than those in Beijing and Changchun, higher than those in Guiyang and Wuhan. Generally, the values of $\delta^{34}$S-SO$_4^{2-}$ and $\delta^{34}$S-SO$_2$ in southern China were lower compared to those in northern China.

According to $\delta^{34}$S values of potential sulfur sources in Nanjing presented in Fig. 8, $\delta^{34}$S values of primary sulfate from direct emission of coal combustion, vehicle exhaust and straw burning range from 6.15‰ to 6.63‰, 4.6‰ to 9.7‰ and 5.2 to 7.9‰, respectively (Guo et al., 2016). The average $\delta^{34}$S value of sulfate in PM$_{2.5}$ was about 5.6‰, which was similar to those from coal combustion. This showed that coal combustion was a sulfur source in PM$_{2.5}$ during the haze events. Besides, the average $\delta^{34}$S value of sulfate in PM$_{2.5}$ was within the scope of $\delta^{34}$S from vehicle exhaust and biomass burning, indicating direct emission of these two sources also played a certain role on PM$_{2.5}$. We took 22 Dec. as an example to quantitatively analyze the contributions of coal combustion, vehicle exhaust and biomass burning to PM$_{2.5}$. According to Eq. (1) (Zhang et al., 2010), we obtained that K$^+$ concentration of non-sea salt ([K$^+$/PM$_{2.5}$]) was 2.87 µg/m$^3$ on 22 Dec. On this basis, the contribution of biomass burning (f$_{bb}$) to PM$_{2.5}$ on 22 Dec. was 8.08‰ by Eq. (2). Of which, ((K$^+$/PM$_{2.5}$)$_{source}$ was 0.15 (Li et al., 2007; Zhang et al., 2007).

\[
\frac{[K^+]}{[PM_{2.5}]} = [K^+ - 0.0355[Na^+]]
\]

\[
f_{bb} = \frac{([K^+]/[PM_{2.5}])_{sample}/([K^+]/[PM_{2.5}])_{source} \times 100}{2.5}
\]

Then, the contributions of coal combustion and vehicle exhaust were calculated based on Eqs. (3) and (4) (Han et al., 2016). Considering $\delta^{34}$S value of sulfate in PM$_{2.5}$ was 6.85‰ on 22 Dec., we calculated the contributions of vehicle exhaust and coal combustion were 50.12‰ and 41.80‰, respectively.

\[
\delta^{34}S_{sample} = f_{ve}\delta^{34}S_{ve} + f_{cc}\delta^{34}S_{cc} + f_{bb}\delta^{34}S_{bb}
\]

\[
f_{ve} + f_{cc} + f_{bb} = 1
\]

where f$_{ve}$, f$_{cc}$ and f$_{bb}$ represent the contributions of vehicle exhaust, coal combustion and biomass burning, respectively. $\delta^{34}S_{ve}$, $\delta^{34}S_{cc}$ and $\delta^{34}S_{bb}$ are sulfur isotopic values of typical vehicle exhaust, coal combustion and biomass burning in Nanjing region, which were 7.7‰, 6.15‰ and 5.20‰, respectively.

It is noted that the sources of PM$_{2.5}$ based on the study of $\delta^{34}$S values were in accordance with those from phase clustering analysis of the WSIs in PM$_{2.5}$. Moreover, $\delta^{34}$S value showed that primary sulfate made a great contribution to PM$_{2.5}$ during the haze event. It is noted that $\delta^{34}$S values of sulfate in PM$_{2.5}$ on 23, 25 and 26 Dec. were 4.2‰, 3.7‰ and 4.4‰, respectively, which were lower than the minimum $\delta^{34}$S value (4.6‰) of primary sulfate from direct emission of potential sources in Nanjing. This indicated that there existed other sulfur sources and the corresponding $\delta^{34}$S value of sulfate should be lower than 3.7‰. It is reported that $\delta^{34}$S signature of biogenic sulfur from the organism release in anoxic surface environment to the atmosphere was about −2.4‰ (Mast et al., 2001). High soil moisture and temperature were
the premises for forming anoxic environment in rice farmland near the sampling site. Therefore, low temperature during the haze events made it negligible for the contribution of biogenic sulfur to PM$_{2.5}$. Considering lower $\delta^{34}$S values of SO$_2$ in the atmosphere, we speculated low $\delta^{34}$S values in PM$_{2.5}$ were possibly related to the secondary sulfate from SO$_2$ oxidation during the haze events.

### 3.2.2. Heterogeneous and homogeneous oxidation of SO$_2$

$\delta^{34}$S value might reflect to formation processes of the secondary sulfate in the atmosphere during SO$_2$ oxidation due to that $\delta^{34}$S value may change when SO$_2$ is converted into sulfate via different homogeneous and heterogeneous oxidation reactions. The measured fractionation with respect to SO$_2$ is about $-9\%$ for homogeneous oxidation (Saltzman et al., 1983; Tanaka et al., 1994) and up to $+16.5\%$ for heterogeneous oxidation (Eriksen, 1972a, 1972b). Assuming sulfate was from SO$_2$ oxidation and following the mass balance of $\delta^{34}$S value (Seal, 2006), we might calculate the contribution of SO$_2$ heterogeneous and homogeneous oxidation to sulfate based on Eqs. (5) and (6).

\[
\delta^{34}\text{SO}_2 + 16.5a - 9b = \delta^{34}\text{SO}_4^{2-} \tag{5}
\]

\[
a + b = 1 \tag{6}
\]

where $\delta^{34}\text{SO}_2$, $\delta^{34}\text{SO}_4^{2-}$ are sulfur isotopic compositions of SO$_2$ and sulfate, respectively. $a$ and $b$ represent the ratio of SO$_2$ heterogeneous and homogeneous oxidation to sulfate.

It can be observed from Fig. 9 that the contributions of SO$_2$ heterogeneous and homogeneous oxidation fluctuated significantly during the haze events. SO$_2$ heterogeneous oxidation predominated on 21 and 22 Dec., however, SO$_2$ heterogeneous oxidation dominated on 23 and 24 Dec. During the period from 25 to 28 Dec., the ratios of heterogeneous oxidation of SO$_2$ were higher with an average of 53.22%. Besides, we noted that the contribution of SO$_2$ heterogeneous oxidation reached the maximum value of 58.82% on 30 Dec. Zheng et al. (2015a, 2015b) added heterogeneous reactions to WRF-CMAQ model to evaluate the impact of heterogeneous chemistry and meteorological anomaly on regional haze formation, and found there existed a significant role of heterogeneous chemistry in regional haze formation. In addition, Zheng et al. (2015a, 2015b) observed that heterogeneous reactions played an important role in accelerating production rate of secondary aerosols during the severe pollution event.

The homogeneous oxidation of SO$_2$ is mainly motivated by OH radicals (Tanaka et al., 1994), while heterogeneous oxidation of SO$_2$ is related to SO$_2$ dissolution in cloud and droplet, which was further oxidized by H$_2$O$_2$, O$_3$, O$_2$ and NO$_2$ (Hung and Ho, 2015; He et al., 2014; Harris et al., 2013; Eriksen, 1972b). Cheng et al. (2016) investigated sulfate production during Jan. 2013 winter haze event in Beijing, and found that the missing source of sulfate and particulate matter could be explained by reactive nitrogen chemistry in aerosol water. According to Table 1, high O$_3$ concentration on 21 Dec. was favorable for heterogeneous oxidation of SO$_2$. Besides, the relatively high NO$_2$ concentration and RH accelerated SO$_2$ heterogeneous oxidation. Different from that on 21 Dec., large amount of sulfate was produced mainly by SO$_2$ heterogeneous oxidation in the presence of the highest NO$_2$ concentration on 22 Dec. On the contrary, low O$_3$ and NO$_2$ concentrations inhibited SO$_2$ heterogeneous oxidation to sulfate on 23 and 24 Dec. although there existed the highest RH in the atmosphere. Similarly, high ratios of SO$_2$ heterogeneous and homogeneous oxidation on 25, 26 and 30 Dec. were ascribed to high RH and O$_3$ concentration as well as high NO$_2$ concentration. Especially, very low A/C value (0.66) on 30 Dec. indicated the strong alkaline of PM$_{2.5}$, thereby further promoting SO$_2$ heterogeneous oxidation in the presence of O$_3$ and NO$_2$. Considering the solubility of SO$_2$ decreased with the increase of temperature, we inferred that the temperature might exert an influence on heterogeneous oxidation. It is noteworthy that the maximum temperature on 28 and 30 Dec. were 6°C and 12°C. However, the corresponding contributions of SO$_2$ heterogeneous oxidation were 54.0% and 58.8%, respectively. Compared with the temperature, we believed the concentrations of gaseous pollutants, A/C value and RH were the more important factors in affecting SO$_2$ heterogeneous oxidation.

### 4. Conclusions

There was presence of serious PM$_{2.5}$ pollution during the haze events, and the pollutants were mainly from coal combustion, vehicle exhaust release and biomass burning. The contributions of coal combustion, vehicle exhaust and biomass burning to PM$_{2.5}$ on 22 Dec. were 41.80%, 50.12% and 8.08%, respectively. The secondary sulfate in PM$_{2.5}$ was ascribed to aqueous phase sulfur oxidation promoted by high NO$_2$ concentration and RH under the alkaline condition. According to sulfur isotopic fractionation between $\delta^{34}$S-SO$_4^{2-}$ and $\delta^{34}$S-SO$_2$, we calculated that the average contribution of SO$_2$ heterogeneous oxidation to sulfate was about 48.8% during the haze events.
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