Characteristics and Formation Mechanisms of Sulfate and Nitrate in Size-segregated Atmospheric Particles from Urban Guangzhou, China

Feng Jiang1,2, Fengxian Liu1,2, Qinhao Lin1, Yuzhen Fu1,2, Yuxiang Yang1,2, Long Peng1,2, Xiuwen Lian1,2, Guohua Zhang1*, Xinxi Bi1, Xinming Wang1, Guoying Sheng1

1 State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Resources Utilization and Protection, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
2 University of Chinese Academy of Sciences, Beijing 100049, China

ABSTRACT

Various water-soluble inorganic compounds, including Na+, NH4+, K+, Ca2+, Mg2+, Cl−, NO3−, PO43− and SO42−, were analyzed in 130 sets of size-segregated (< 0.49, 0.49–0.95, 0.95–1.5, 1.5–3.0, 3.0–7.2 and 7.2–10.0 µm) aerosol samples collected from March 2013 to April 2014 in Guangzhou, China. SO42− was unimodally distributed and peaked during a typical droplet mode (0.49–0.95 µm). However, the distribution of NO3− significantly varied across the four seasons. It was unimodally distributed in summer and autumn, peaking in the coarse mode (3.0–7.2 µm), and bimodally distributed in winter and spring, peaking in the size ranges of 0.49–0.95 µm and 3.0–7.2 µm, respectively. The coarse-mode NO3− was mainly related to the influence of soil/dust. The additional mode during winter and spring was attributable to the formation of ammonium nitrate. Compared to clean days, polluted days favored the formation of SO42− in summer and autumn and NO3− in winter and spring. The sulfur oxidation ratios (SORs) for < 0.49, 0.49–0.95 and 0.95–1.5 µm particles were negatively correlated with the relative humidity (RH) in spring, summer and autumn, respectively. However, the SORs for 0.49–3.0 µm particles were positively correlated with the RH in winter, implying an important contribution from the aqueous oxidation of SO2. Further analysis shows that the SO42− in < 0.49 µm particles was formed primarily through gas-phase photochemical oxidation of SO2 during all four seasons. The formation of NO3− was mainly attributable to heterogeneous reactions for 1.5–3.0 µm particles year-round and homogeneous gas-phase reactions for < 0.49 µm particles in winter. Correlation analysis also indicates a positive influence from biomass burning on the formation of nitrate and sulfate. The average pH of PM3 was calculated to be 2.6–5.6. Thus, the aqueous oxidation of SO2 by NO2 plays a limited role in the formation of sulfate in the atmosphere of Guangzhou.

Keywords: Water-soluble inorganic compounds; Sulfate; Nitrate; Sulfur oxidation ratio; Nitrogen oxidation ratio; Guangzhou.

INTRODUCTION

Atmospheric particulate matter has a significant impact on human health, air quality and climate (Poschl, 2005; Seinfeld and Pandis, 2006). Water-soluble inorganic compounds are the main constituents of particulate matter in the air and account for ~30–50% of PM10 (Lai et al., 2007; Cao et al., 2012; Wu et al., 2017). SO42− and NO3−, largely present in the forms of (NH4)2SO4 and NH4NO3 (Wang et al., 2016b), respectively, account for more than 40% of the total water-soluble inorganic ions (TWSI) (Yao et al., 2002; Yue et al., 2010; Chang et al., 2013; Yue et al., 2015). They are identified as the major drivers for the formation of haze. Consequently, reductions in SO42− and NO3− aerosols are of significance for PM2.5 pollution control and air quality improvement.

Formation mechanisms of SO42− and NO3− in the complex atmosphere are still under debate. Sulfate can be formed through the oxidation of SO2 by gas-phase reactions with OH· (Stockwell and Calvert, 1983; Blitz et al., 2003) and by aqueous oxidation of SO2 with dissolved H2O2 or with O2 under the catalysis of transition metal (Seinfeld and Pandis, 2006). Aqueous oxidation is regarded as the most important pathway for the formation of SO42− (Tan et al., 2009b; Huang et al., 2016). A recent study found that the aqueous oxidation of SO2 by NO2 was the key process involved in the efficient formation of sulfate on wet aerosols or cloud droplets with NH3 neutralization (Cheng et al., 2016; Wang et al., 2016). However, Guo et al. (2017) and Liu et al. (2017b) suggested that the above aqueous oxidation pathway for sulfate production may not be
relevant in China due to the acidic nature of aerosol, with a pH range of 3.0 to 4.9. NO$_3^-$ formation is dominated by the gas-phase reactions of NO$_2$ with OH· during daylight followed by condensation, and the heterogeneous reactions of nitrate radical (NO$_3$) or N$_2$O$_5$ during nighttime (Pun and Seinfeld, 2001; Seinfeld and Pandis, 2006).

Particle size could be a very useful indicator to understand the formation mechanisms of SO$_4^{2-}$ and NO$_3^-$ (Liu et al., 2008). Condensation-mode SO$_4^{2-}$ is mainly formed by gas-to-particle conversion, while droplet-mode SO$_4^{2-}$ is mainly attributed to cloud processing (Meng and Seinfeld, 1994). Fine-mode NO$_3^-$ is formed by nitric acid with ammonia, and coarse-mode NO$_3^-$ is mainly formed by heterogeneous reactions of nitric acid or NO$_2$ with coarse particles, such as sea-salt, dust or soil particles (Seinfeld and Pandis, 2006). Such distinct processes could lead to different size-segregated characteristics of SO$_4^{2-}$ and NO$_3^-$ (Wang et al., 2017). In addition, their dominant pathways may vary with regions and seasons, depending on various factors, including temperature, atmospheric oxidation capacity, levels of gaseous precursors, aerosol size, water content and acidity. High temperature facilitates the oxidation of SO$_2$ to SO$_4^{2-}$ and the dissociation of NH$_4$NO$_3$ in particulate matter (Tai et al., 2010). Aerosol pH is also an important parameter for the acidity-dependent heterogeneous chemical processes on aerosol surfaces, such as the oxidation of SO$_2$ and the hydrolysis of N$_2$O$_5$ (Fu et al., 2015; Cheng et al., 2016). In addition, aerosol water content is a ubiquitous contributor to the aerosol fraction and significantly influences the chemistry involving both organic and inorganic species (Herrmann et al., 2015; Nguyen et al., 2016).

Various field measurements highlight the increased and more efficient production of SO$_4^{2-}$ and NO$_3^-$ during severe haze events in mega-cities (i.e., Beijing, Shanghai and Guangzhou) over China (Sun et al., 2013; Huang et al., 2014; Liu et al., 2017a). The ratios of SO$_4^{2-}$ and NO$_3^-$ to TWSI increased most dramatically in summer and autumn during polluted periods in Beijing, respectively (Huang et al., 2016). Guangzhou, a mega-city in the Pearl River Delta (PRD) region, has long suffered from air pollution (Han et al., 2014; Fu et al., 2015; Yue et al., 2015). While the level of pollution has been reduced in recent years, high production and contribution of secondary aerosol components to fine particles are still observed (Liu et al., 2017a; Li et al., 2018). SO$_4^{2-}$ was mainly formed by aqueous-phase reactions (Zheng et al., 2015) and NO$_3^-$ in PM$_{2.5}$ was mainly formed by homogeneous reactions under ammonium-rich conditions ([NH$_4^+$/[SO$_4^{2-}$] > 1.5] in Guangzhou (Pathak et al., 2009; Huang et al., 2011). The increased contribution of the SO$_4^{2-}$ to PM$_{10}$ from clean to hazy days was higher than the corresponding value for NO$_3^-$ in Guangzhou during summer (Han et al., 2014). The degrees of oxidation of SO$_2$ and NO$_2$ to SO$_4^{2-}$ and NO$_3^-$, represented as sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR), respectively, were generally higher on hazy days than clean days (Tan et al., 2009a). SOR was found to be positively correlated with relative humidity (RH) and O$_3$ during haze episodes in Beijing and Guangzhou (Tao et al., 2012; Yang et al., 2015; Wang et al., 2016). NOR was significantly correlated with particle surface area, RH and temperature (Liu et al., 2015; Huang et al., 2016; Ge et al., 2017). However, the formation mechanisms of SO$_4^{2-}$ and NO$_3^-$ in size-segregated particles in the PRD region are still not well understood. In addition, previous studies were mainly based on short-term observations, which did not consider the seasonal information. In the present study, water-soluble inorganic ions from size-segregated aerosol particles in Guangzhou were analyzed over different seasons. The main objective of this study was to investigate the effects of O$_3$, RH, temperature and aerosol acidity on the size-resolved formation of SO$_4^{2-}$ and NO$_3^-$.

EXPERIMENT AND METHODS

Collection of Size-segregated Particles

The sampler was set up on the rooftop of a 15-m-high building at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The site is surrounded by heavily trafficked roads and dense residential areas, representing a typical urban location. Seasonal size-segregated PM filter samples were collected using a cascade impactor (Model SA235; Andersen Instruments, Inc.) with cut-off points at < 0.49, 0.49–0.95, 0.95–1.5, 1.5–3.0, 3.0–7.2 and 7.2–10.0 µm at a flow rate of 1.13 m$^3$ min$^{-1}$. Before sampling, filters were preheated at 600°C for 4 h. The filters were also conditioned (at 25°C and 50% RH) before and after sampling in an electronic hygrothermostat for 24 h.

The details of the samples are listed in Table S1. Seasonal samples consisted of 34 sets of samples in summer (16 June–14 July 2013), 36 sets of samples in autumn (15 September–16 October 2013), 37 sets of samples in winter (13–17 December 2013 and 20 December 2013–20 January 2014), and 23 sets of samples in spring (15–29 March and 10–15 April 2014). The sample collection lasted for 12 h, 24 h or 48 h.

Ions Analysis

A part of the filter was extracted twice with a total of 10 mL ultrapure water (> 18.2 MΩ), using an ultrasonic bath for 20 min at room temperature. The extracts were filtered using a 0.45 µm Teflon filter. Then the solution was transferred to 25 mL plastic bottles, and stored in a refrigerator before analysis. The ionic components were analyzed by ion chromatograph (883 Basic IC plus; Metrohm). The limits of detection were 0.014, 0.014, 0.046, 0.017, 0.041, 0.022, 0.032, 0.136 and 0.018 µg m$^{-3}$ for Na$^+$, NH$_4^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Cl$^-$, NO$_3^-$, PO$_4^{3-}$ and SO$_4^{2-}$, respectively. Field and laboratory blanks were analyzed in the same way as the field samples. Ion balance was used as a quality control check in the cation/anion analysis. A good linear correlation ($R^2 = 0.94$) was observed between cations and anions, with a slope of 0.79 (Fig. S1 in the supporting materials), which indicates that the ion analysis method is reliable.

Gaseous Pollutants and Meteorological Data

Hourly meteorological data (temperature, RH and wind speed) and gaseous pollutants data (SO$_2$, NO$_2$ and O$_3$)
RESULTS AND DISCUSSION

Since a cut-off size of 2.5 µm is not available in the Anderson sampler, 3 µm was defined as the boundary between fine and coarse particles in this paper. Thus, PM3 and PM3-10 represent the fine and coarse particle fractions, respectively. The TWSI components were mainly concentrated in fine particles, averaging 84.4% in PM3 and 15.2% in PM3-10 in this study, in accordance with other studies (Liu et al., 2008; Li et al., 2013; Huang et al., 2016).

The national second level for fine particles (75 µg m⁻³) was applied to separate the “polluted” and “clean” days in this study. Table 1 summarizes the concentrations of SO₄²⁻ and NO₃⁻, gaseous precursors, and meteorological conditions on polluted and clean days. During the entire sampling period, several pollution episodes were observed. The levels of SO₂ and NO₂ on polluted days (31.2 ± 13.9 µg m⁻³ and 84.5 ± 34.6 µg m⁻³) were considerably higher than those on clean days (15.6 ± 6.2 µg m⁻³ and 46.4 ± 14.5 µg m⁻³). Similarly, higher O₃ was observed on polluted days, except during spring. Higher RH on clean days, rather than hazy days, was also observed in summer, autumn and winter, most likely due to more precipitation. The seasonal pattern of pollution was similar to previous studies (Yue et al., 2015) and was mainly attributed to the influence of both the local meteorological conditions and air masses. Generally, Guangzhou mainly experienced polluted days from autumn to early spring (Yu et al., 2017), under the influence of northern air masses (Tan et al., 2009a).

Characteristics and Size Distributions of Sulfate and Nitrate

SO₄²⁻ and NO₃⁻ were the most abundant TWSI components over the four seasons, as shown in Fig. 1. The mass contributions of SO₄²⁻ and NO₃⁻ to TWSI were 67.8%, 60.1%, 63.7% and 66.9% on clean days and 65.4%, 64.4%, 70.3% and 70.9% on polluted days in the spring, summer, autumn and winter, respectively. Similarly, Tan et al. (2009a) found that SO₄²⁻ and NO₃⁻ constituted 68.4% of TWSI on summer-haze days and 67.1% on winter-haze days in Guangzhou. Increased levels of SO₄²⁻ and NO₃⁻ were observed on polluted days in the summer, autumn and winter. This is likely due to the relatively higher production of SO₄²⁻, as evidenced by higher SOR, O₃ and SO₂ on polluted days (Tables 1 and 2). On the contrary, an increased contribution of NO₃⁻ to the TWSI was observed on polluted days in winter and spring. This is consistent with higher NOR on polluted days than clean days (Table 2). This indicates that winter and spring periods facilitate the formation of NO₃⁻, particularly, on polluted days. Values of the SOR and NOR were calculated by the following equations using the corresponding molar concentrations (n⁻).

### Table 1. Average values (mean ± SD) of gaseous precursors, meteorological factors and sulfate and nitrate in PM₃.

<table>
<thead>
<tr>
<th>Season</th>
<th>C (Clean)</th>
<th>P (Polluted)</th>
<th>One year</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PM₃.0 (µg m⁻³)</strong></td>
<td>60.8 ± 10.9</td>
<td>101.1 ± 31.0</td>
<td>82.3 ± 14.4</td>
</tr>
<tr>
<td><strong>SO₂ (µg m⁻³)</strong></td>
<td>20.9 ± 5.7</td>
<td>27.3 ± 5.7</td>
<td>18.9 ± 4.5</td>
</tr>
<tr>
<td><strong>NO₂ (µg m⁻³)</strong></td>
<td>58.1 ± 10.9</td>
<td>83.1 ± 16.9</td>
<td>62.0 ± 23.9</td>
</tr>
<tr>
<td><strong>O₃ (µg m⁻³)</strong></td>
<td>44.7 ± 14.5</td>
<td>30.2 ± 23.9</td>
<td>29.4 ± 14.5</td>
</tr>
<tr>
<td><strong>PM₃ (µg m⁻³)</strong></td>
<td>41.9 ± 14.0</td>
<td>101.1 ± 15.1</td>
<td>75.2 ± 15.1</td>
</tr>
<tr>
<td><strong>SO₄²⁻ (µg m⁻³)</strong></td>
<td>6.1 ± 1.5</td>
<td>14.5 ± 6.9</td>
<td>12.4 ± 8.8</td>
</tr>
<tr>
<td><strong>NO₃⁻ (µg m⁻³)</strong></td>
<td>1.1 ± 0.3</td>
<td>2.0 ± 0.5</td>
<td>1.7 ± 0.2</td>
</tr>
</tbody>
</table>

C, clean days; P, polluted days.
Fig. 1. The ratio of water-soluble inorganic ions to TWSI over the four seasons during (a) clean and (b) polluted days, respectively.

Table 2. Summary of SOR and NOR (mean ± SD) on clean and hazy days over the four seasons.

<table>
<thead>
<tr>
<th></th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
<th>Winter</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>P</td>
<td>C</td>
<td>P</td>
<td>C</td>
</tr>
<tr>
<td>&lt; 0.49 µm</td>
<td>SOR 0.10 ± 0.02</td>
<td>0.09 ± 0.02</td>
<td>0.12 ± 0.04</td>
<td>0.18 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>NOR 0.02 ± 0.00</td>
<td>0.03 ± 0.01</td>
<td>0.01 ± 0.01</td>
<td>0.02 ± 0.02</td>
</tr>
<tr>
<td>0.49–0.95 µm</td>
<td>SOR 0.13 ± 0.04</td>
<td>0.13 ± 0.04</td>
<td>0.08 ± 0.03</td>
<td>0.13 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>NOR 0.03 ± 0.01</td>
<td>0.04 ± 0.02</td>
<td>0.01 ± 0.00</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>0.95–1.5 µm</td>
<td>SOR 0.07 ± 0.04</td>
<td>0.06 ± 0.04</td>
<td>0.03 ± 0.01</td>
<td>0.02 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>NOR 0.02 ± 0.01</td>
<td>0.02 ± 0.01</td>
<td>0.01 ± 0.00</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td>1.5–3.0 µm</td>
<td>SOR 0.03 ± 0.02</td>
<td>0.03 ± 0.01</td>
<td>0.02 ± 0.01</td>
<td>0.02 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>NOR 0.02 ± 0.01</td>
<td>0.02 ± 0.01</td>
<td>0.02 ± 0.01</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>PM3</td>
<td>SOR 0.31 ± 0.08</td>
<td>0.31 ± 0.08</td>
<td>0.24 ± 0.08</td>
<td>0.34 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>NOR 0.08 ± 0.02</td>
<td>0.10 ± 0.03</td>
<td>0.04 ± 0.01</td>
<td>0.05 ± 0.03</td>
</tr>
</tbody>
</table>

C: clean days; P: polluted days.

SOR = n-SO4^2−/(n-SO4^2− + n-SO2) (1)

NOR = n-NO3−/(n-NO3− + n-NO2) (2)

Higher SOR and NOR indicate that more gaseous SO2 and NO2 in the atmosphere are oxidized to SO4^2− and NO3−, respectively. The Pearson correlation analysis also shows that SO2 had a positive correlation with SO4^2− (R > 0.56, p < 0.01) and NO2 had a positive correlation with NO3− (R > 0.64, p < 0.01) in each size range. It indicates that the formation of SO4^2− and NO3− was influenced by SO2 and NO2 from local emissions. Size-segregated NO3− and SO4^2− also showed high correlations with K+, with the correlation coefficients ranging from 0.48 to 0.87 (p < 0.01) and 0.36 to 0.86 (p < 0.01), respectively.

Fig. 2 displays the size distributions of SO4^2− and NO3− over the four seasons. SO4^2− was unimodally distributed and peaked at 0.49–0.95 µm. This is a typical droplet mode for SO4^2−, which was mainly formed by aqueous/cloud processing (Seinfeld and Pandis, 2006). Similarly, the value of SOR was higher at 0.49–0.95 µm than at other size ranges, except for summer. In contrast, a previous study reported a coarse mode at 3.2–5.6 µm, in addition to a droplet mode for a coastal site in Guangzhou, due to substantial influence of sea-salt (Liu et al., 2008). The absence of coarse mode for SO4^2− was likely due to the limited influence of sea-salt or dust on the formation of SO4^2− at this site. However, correlations of SO4^2− with Ca2+ and Mg2+ in coarse particles (Table S2) still indicated the influence of sea-salt and dust on the formation of SO4^2− (Yeatman et al., 2001). Through PMF analysis (Figs. S3 and S4), ~40% and ~35% of the modelled sulfate (> 60%) in coarse particles can be explained by the influence of dust and sea-salt, respectively.

Different from SO4^2−, the distribution of NO3− clearly varied over the four seasons (Fig. 2). It was unimodally distributed in summer and autumn, peaking at coarse mode (3.0–7.2 µm). The coarse-mode NO3− was mainly related to soil/dust, with high correlations of NO3− with Ca2+ (R = 0.89, p < 0.01) and Mg2+ (R = 0.88, p < 0.01). PMF analysis further showed that ~60% of the modelled nitrate in coarse particles were most likely associated with dust (Fig. S4). In addition, NO3− also appeared with potassium (R = 0.76, p < 0.01) and ammonium (R = 0.80, p < 0.01) in coarse particles. In winter and spring, NO3− was observed to be bimodally distributed, with an additional peak at 0.49–0.95 µm. Correspondingly, the mean values (0.03, 0.04) of NOR at 0.49–0.95 µm were relatively higher in these seasons. These distributions were consistent with those
observed in previous studies in Guangzhou (Liu et al., 2008). A relatively higher temperature (25.6–30.7°C) resulted in the dissociation of particulate NH₄NO₃, which might explain the absence of NO₃⁻ peak at 0.49–0.95 µm in summer and autumn (Tai et al., 2010). Likewise, the correlations of NO₃⁻ and NH₄⁺ at < 0.49 µm, 0.49–0.95 µm and 0.95–1.5 µm were relatively higher in spring and winter (R = 0.75, 0.84 and 0.83; p < 0.01), compared to those in summer and autumn (R = 0.16, 0.53 and 0.36; p < 0.01), as shown in Table S2. Similarly, Yue et al. (2015) found that the linear correlation between NO₃⁻ and NH₄⁺ in PM2.5 was higher in winter and spring than in summer and autumn in Guangzhou. It indicated that the NO₃⁻ formed at these size ranges most probably co-existed with ammonium in spring and winter (Pathak et al., 2009).

Factors Influencing the Formation of Sulfate and Nitrate O₃

The relationships of SOR and NOR versus O₃ are illustrated in Fig. 3. It can be seen that SOR was moderately correlated (R = 0.44, p < 0.01) with O₃ at < 0.49 µm. The median values of SOR at < 0.49 µm increased from 0.09 to 0.20 with increasing O₃ (Fig. 3(a)). This result indicates that SO₄²⁻ in < 0.49 µm particles was contributed by gas-phase photochemical oxidation of SO₂. Similarly, Liu et al. (2008) reported that sulfate in the size range of 0.32–0.56 µm was formed by gas-particle conversion in the PRD region, China. The median of SOR in 0.49–3.0 µm particles had no obvious increase with increasing O₃. Therefore, SO₄²⁻ in this size range may be formed through the aqueous oxidation of SO₂, which was less dependent on the level of O₃. In previous work, SO₄²⁻ in the range of 0.56–1.0 µm was mainly attributed to in-cloud processing (Liu et al., 2008).

NOR at < 0.49 µm was correlated with O₃ (R = 0.45, p < 0.01) in winter. NOR at 0.49–0.95 µm and 0.95–1.5 µm was weakly correlated with O₃ and RH in winter. In addition, PM0.49 in 35 out of 37 samples was in an ammonium-rich ([NH₄⁺]/[SO₄²⁻] > 1.5) condition (Fig. 4). NO₃⁻ was highly correlated (R = 0.64, p < 0.01) with ammonium in this size range. Therefore, the formation of NO₃⁻ was most likely via homogeneous gas-phase reactions, in the form of NH₄NO₃. Similarly, Pathak et al. (2009) and Huang et al. (2011) found that NH₄NO₃ in PM2.5 partly resulted from homogeneous gas-phase reactions in Guangzhou, China.

As shown in Figs. 3(b)–3(c), NOR at 1.5–3.0 µm had limited correlations with O₃ (R = 0.26, p < 0.01), temperature (R = 0.22, p < 0.05) and RH (R = 0.20, p < 0.05). It indicates that the formation of NO₃⁻ at this size range had limited dependence on temperature, O₃ and RH. Instead, high correlations of NO₃⁻ with Ca²⁺ (R = 0.64, p < 0.01) and Mg²⁺ (R = 0.80, p < 0.01) were observed. This result might suggest that NO₃⁻ was in the forms of Ca(NO₃)₂ and Mg(NO₃)₂ in this size range, most likely via heterogeneous reactions.
Fig. 3. (a) SOR at < 0.49 µm and NOR at 1.5–3.0 µm versus (b) the concentration of O₃ and (c) RH, respectively. The color scale in the legend represents temperature (°C).

Fig. 4. The relationship between the ratios of $[\text{NH}_4^+] / [\text{SO}_4^{2-}]$ and $[\text{NO}_3^-] / [\text{SO}_4^{2-}]$ for PM$_{1.5-3.0}$ over the four seasons and PM$_{0.49}$ for winter, respectively.
between NO$_2$/HNO$_3$ and these alkaline compositions (Pathak et al., 2009; Tao et al., 2016). Correspondingly, PM$_{1.5-3.0}$ in 89 out of 130 samples was assigned as ammonium-poor (Fig. 4), indicating the limited formation of NO$_3^–$ as NH$_4$NO$_3$ (Pathak et al., 2009).

**RH**

Guangzhou is influenced by the subtropical monsoon climate, with rainy seasons from April to September while the remaining months belong to dry season. Therefore, spring, summer and autumn are regarded as rainy seasons. During rainy seasons, SOR was negatively correlated with RH (Fig. 5(a)) in the range of < 0.49 µm (R = −0.66, p < 0.01), 0.49–0.95 µm (R = −0.43, p < 0.01) and 0.95–1.5 µm (R = −0.3, p < 0.01). This was not in agreement with the corresponding values reported in previous studies (Tan et al., 2009a; Qin et al., 2015). In the present study, relatively higher humidity air masses originated from southeast air masses (Fig. S2) and more precipitation during the rainy seasons (Table S1) could remove the particulate matter (Tao et al., 2016). In contrast, the median of SOR at 0.49–3.0 µm increased with increasing RH (Fig. 5(b)) in dry seasons (winter). SOR was positively correlated with RH in the range of 0.49–0.95 µm (R = 0.65, p < 0.01), 0.95–1.5 µm (R = 0.62, p < 0.01) and 1.5–3.0 µm (R = 0.57, p < 0.01). This result suggests that the aqueous oxidation of SO$_2$ was an important pathway. Similarly, higher concentrations of droplet-mode sulfate were associated with higher RH in Hong Kong (Zhuang et al., 1999).

Huang et al. (2016) found that RH had a highly positive correlation with SOR in the range of 0.43–0.65 µm (R = 0.68, p < 0.01), 0.65–1.1 µm (R = 0.75, p < 0.01) and 1.1–2.1 µm (R = 0.77, p < 0.01) during 2013–2014 in Beijing.

**H$^+$** _air, pH and NO$_2$

Aerosol pH and H$^+$ _air was calculated by the ISORROPIA II model, which is a thermodynamic equilibrium model for NH$_4^+$–K$^+$–Ca$^{2+}$–Na$^+$–Mg$^{2+}$–SO$_4^{2–}$–NO$_3^{–}$–H$_2$O (Fountoukis and Nenes, 2007). H$^+$ _air (nmol m$^{-3}$) refers to the hydronium ion concentration per volume air. The H$^+$ _air, pH, and their correlation coefficients with SOR and NOR in the size-segregated fraction are listed in Table 3. Average H$^+$ _air and pH ranged from 0.6 to 10.2 and 2.6 to 5.6, respectively. The calculated pH was not in agreement with previous studies which reported an average aerosol pH < 1 in Guangzhou, calculated by AIM-II model (Pathak et al., 2009; Fu et al., 2015). This might be attributed to the underestimation of aerosol pH with AIM-II (Yao et al., 2006).

It is expected that the highest acidity (highest H$^+$ _air/lowest pH) was obtained in the size range of 0.49–0.95 µm, which was most likely due to the favorable formation of SO$_4^{2–}$ in this size range, as previously discussed. H$^+$ _air and pH had no clear correlation with NOR and SOR at < 0.49 µm. This is consistent with previous discussions that the formation of SO$_4^{2–}$ and NO$_3^{–}$ at this size range was via homogeneous gas-phase reactions followed by condensation. This pathway is not likely to be influenced by aerosol acidity. On the contrary, there was a high abundance of ammonium

**Fig. 5.** SOR at 0.49–0.95 µm versus RH over the four seasons.

**Table 3.** H$^+$ _air and pH (mean ± SD), and correlation coefficients of SOR and NOR with H$^+$ _air and pH in size-segregated aerosols.

<table>
<thead>
<tr>
<th>Size-segregated aerosol</th>
<th>H$^+$ _air (nmol m$^{-3}$)</th>
<th>pH</th>
<th>Correlation coefficients</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
</tr>
<tr>
<td>&lt; 0.49 µm</td>
<td>3.0 ± 11.0</td>
<td>5.6 ± 3.0</td>
<td>SOR 0.09</td>
</tr>
<tr>
<td>0.49–0.95 µm</td>
<td>10.2 ± 27.7</td>
<td>2.6 ± 3.4</td>
<td>NOR 0.08</td>
</tr>
<tr>
<td>0.95–1.5 µm</td>
<td>3.7 ± 14.8</td>
<td>4.8 ± 3.4</td>
<td>SOR 0.11</td>
</tr>
<tr>
<td>1.5–3.0 µm</td>
<td>0.6 ± 2.5</td>
<td>5.6 ± 3.0</td>
<td>NOR 0.53**</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SOR 0.12</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>NOR 0.57**</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SOR −0.05</td>
</tr>
<tr>
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<td>NOR 0.20</td>
</tr>
</tbody>
</table>

**p < 0.01. * p < 0.05.**
to neutralize the condensed acids. However, in ammonium-
poor samples at 0.49–1.5 µm, the formation of SO$_4^{2-}$ and
NO$_3^-$ could acidify aerosols ($R = -0.29, -0.29, -0.58; p <$
0.01; and $R = -0.21, p < 0.05$).

Wang et al. (2016) and Cheng et al. (2016) found that
aqueous oxidation of SO$_2$ by NO$_3^-$ was essential for the
efficient formation of sulfate in fine aerosols under high
RH or cloud conditions with NH$_3$ neutralization. However,
our data show that SOR at $< 0.49$ µm, 0.49–0.95 µm,
0.95–1.5 µm and 1.5–3.0 µm had no significant variation
with increasing NO$_2$ (Fig. S6), due to the acidic nature of
these particles (pH = 2.6–5.6). This result also indicates that
this pathway is probably unimportant in the atmosphere of
these particles (pH = 2.6–5.6). This result also indicates that
this pathway is probably unimportant in the atmosphere of
Guangzhou (Guo et al., 2017; Liu et al., 2017b).

**CONCLUSION**

The formation mechanisms of size-resolved samples of
SO$_4^{2-}$ and NO$_3^-$ from the atmosphere of Guangzhou across
the four seasons were investigated. The main factors
influencing the formation of SO$_4^{2-}$ and NO$_3^-$, including the
O$_3$, RH, aerosol acidity and gaseous pollutants, were
evaluated. It was found that SO$_4^{2-}$ and NO$_3^-$ accounted for
more than 60% of the total water-soluble inorganic
compounds in PM$_3$. An abundance of clean air and rainfall
during the rainy seasons resulted in a negative correlation
between the SOR and the RH. However, due to the
important role of the aqueous oxidation of SO$_2$ in forming
SO$_4^{2-}$, the SOR showed a positive correlation with the RH
during the dry season (winter). The size-resolved analysis
shows that the SO$_4^{2-}$ in $< 0.49$ µm particles was mainly
formed through the oxidation of SO$_2$ by gas-phase
photochemical reactions, whereas the SO$_4^{2-}$ in larger
particles (0.49–3.0 µm) was highly influenced by the RH.
The formation of NO$_3^-$ as Ca(NO$_3$)$_2$ and Mg(NO$_3$)$_2$ in 1.5–
3.0 µm particles was primarily attributable to heterogeneous
reactions during all four seasons. Winter facilitated the
formation of NO$_3^-$ in particles $< 0.49$ µm as ammonium
nitrate via homogeneous gas-phase reactions. The inclusion
of size-resolved and seasonal characteristics improves our
understanding of the formation of sulfate and nitrate and enables us to distinguish the controlling mechanisms or
factors.

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**SUPPLEMENTARY MATERIAL**

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

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