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

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ABSTRACT

Various water-soluble inorganic compounds, including Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , PO_4^{3-} and SO_4^{2-} , were analyzed in 130 sets of size-segregated (< 0.49 , $0.49\text{--}0.95$, $0.95\text{--}1.5$, $1.5\text{--}3.0$, $3.0\text{--}7.2$ and $7.2\text{--}10.0$ μm) aerosol samples collected from March 2013 to April 2014 in Guangzhou, China. SO_4^{2-} was unimodally distributed and peaked during a typical droplet mode ($0.49\text{--}0.95$ μm). However, the distribution of NO_3^- significantly varied across the four seasons. It was unimodally distributed in summer and autumn, peaking in the coarse mode ($3.0\text{--}7.2$ μm), and bimodally distributed in winter and spring, peaking in the size ranges of $0.49\text{--}0.95$ μm and $3.0\text{--}7.2$ μm , respectively. The coarse-mode NO_3^- 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 SO_4^{2-} in summer and autumn and NO_3^- in winter and spring. The sulfur oxidation ratios (SORs) for < 0.49 , $0.49\text{--}0.95$ and $0.95\text{--}1.5$ μm particles were negatively correlated with the relative humidity (RH) in spring, summer and autumn, respectively. However, the SORs for $0.49\text{--}3.0$ μm particles were positively correlated with the RH in winter, implying an important contribution from the aqueous oxidation of SO_2 . Further analysis shows that the SO_4^{2-} in < 0.49 μm particles was formed primarily through gas-phase photochemical oxidation of SO_2 during all four seasons. The formation of NO_3^- was mainly attributable to heterogeneous reactions for $1.5\text{--}3.0$ 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 PM_3 was calculated to be 2.6–5.6. Thus, the aqueous oxidation of SO_2 by NO_2 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 $\text{PM}_{2.5}$ (Lai *et al.*, 2007; Cao *et al.*, 2012; Wu *et al.*, 2017). SO_4^{2-} and NO_3^- , largely present in the forms of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 (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 SO_4^{2-} and NO_3^- aerosols are of significance for $\text{PM}_{2.5}$ pollution control and air quality improvement.

Formation mechanisms of SO_4^{2-} and NO_3^- in the complex atmosphere are still under debate. Sulfate can be formed through the oxidation of SO_2 by gas-phase reactions with $\text{OH}\cdot$ (Stockwell and Calvert, 1983; Blitz *et al.*, 2003) and by aqueous oxidation of SO_2 with dissolved H_2O_2 or with O_2 under the catalysis of transition metal (Seinfeld and Pandis, 2006). Aqueous oxidation is regarded as the most important pathway for the formation of SO_4^{2-} (Tan *et al.*, 2009b; Huang *et al.*, 2016). A recent study found that the aqueous oxidation of SO_2 by NO_2 was the key process involved in the efficient formation of sulfate on wet aerosols or cloud droplets with NH_3 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

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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 $\text{OH}\cdot$ during daylight followed by condensation, and the heterogeneous reactions of nitrate radical ($\text{NO}_3\cdot$) or N_2O_5 during nighttime (Pun and Seigneur, 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_4NO_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_2O_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 $\text{PM}_{2.5}$ was mainly formed by homogeneous reactions under ammonium-rich conditions ($[\text{NH}_4^+]/[\text{SO}_4^{2-}] > 1.5$) 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 , $0.49\text{--}0.95$, $0.95\text{--}1.5$, $1.5\text{--}3.0$, $3.0\text{--}7.2$ and $7.2\text{--}10.0\text{ }\mu\text{m}$ at a flow rate of $1.13\text{ m}^3\text{ min}^{-1}$. 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 ($> 18.2\text{ M}\Omega$), using an ultrasonic bath for 20 min at room temperature. The extracts were filtered using a $0.45\text{ }\mu\text{m}$ 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 $0.018\text{ }\mu\text{g m}^{-3}$ 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)

were provided by the Guangdong Environmental Monitoring Center (<http://www.gdemc.gov.cn/main.html>). The precipitation data were available from <http://www.met.comanz.com>.

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, PM_3 and PM_{3-10} represent the fine and coarse particle fractions, respectively. The TWSI components were mainly concentrated in fine particles, averaging 84.4% in PM_3 and 15.2% in PM_{3-10} 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 ($75 \mu\text{g m}^{-3}$) was applied to separate the “polluted” and “clean” days in this study. Table 1 summarizes the concentrations of SO_4^{2-} and NO_3^- , gaseous precursors, and meteorological conditions on polluted and clean days. During the entire sampling period, several pollution episodes were observed. The levels of SO_2 and NO_2 on polluted days ($31.2 \pm 13.9 \mu\text{g m}^{-3}$ and $84.5 \pm 34.6 \mu\text{g m}^{-3}$) were considerably higher than those on clean days ($15.6 \pm 6.2 \mu\text{g m}^{-3}$ and $46.4 \pm 14.5 \mu\text{g m}^{-3}$). Similarly, higher O_3 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

SO_4^{2-} and NO_3^- were the most abundant TWSI components over the four seasons, as shown in Fig. 1. The mass contributions of SO_4^{2-} and NO_3^- 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 SO_4^{2-} and NO_3^- constituted 68.4% of TWSI on summer-haze days and 67.1% on winter-haze days in Guangzhou. Increased levels of SO_4^{2-} and NO_3^- were observed on polluted days in the summer, autumn and winter. This is likely due to the relatively higher production of SO_4^{2-} , as evidenced by higher SOR, O_3 and SO_2 on polluted days (Tables 1 and 2). On the contrary, an increased contribution of NO_3^- 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 NO_3^- , 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 $\pm$ SD) of gaseous precursors, meteorological factors and sulfate and nitrate in PM_3 .

	Spring			Summer			Autumn			Winter			One year		
	C	P	C	C	P	C	C	P	C	C	P	C	C	P	C
$\text{PM}_{3.0}$ ($\mu\text{g m}^{-3}$)	60.8 $\pm$ 10.9	101.1 $\pm$ 31.0	41.9 $\pm$ 14.0	84.0 $\pm$ 15.8	54.6 $\pm$ 13.5	82.3 $\pm$ 14.4	53.2 $\pm$ 15.8	116.5 $\pm$ 33.0	50.5 $\pm$ 15.1	106.2 $\pm$ 31.6					
SO_2 ($\mu\text{g m}^{-3}$)	20.9 $\pm$ 5.7	27.3 $\pm$ 5.7	13.2 $\pm$ 4.9	18.4 $\pm$ 15.1	15.6 $\pm$ 5.2	18.9 $\pm$ 4.5	16.2 $\pm$ 7.9	38.0 $\pm$ 13.5	15.6 $\pm$ 6.2	31.2 $\pm$ 13.9					
NO_2 ($\mu\text{g m}^{-3}$)	58.1 $\pm$ 10.9	83.1 $\pm$ 16.9	34.8 $\pm$ 8.9	42.6 $\pm$ 23.7	50.1 $\pm$ 12.1	53.3 $\pm$ 12.0	58.4 $\pm$ 12.6	99.0 $\pm$ 35.6	46.4 $\pm$ 14.5	84.5 $\pm$ 34.6					
O_3 ($\mu\text{g m}^{-3}$)	44.7 $\pm$ 14.5	30.2 $\pm$ 23.9	60.0 $\pm$ 44.9	89.9 $\pm$ 47.6	64.3 $\pm$ 29.7	92.8 $\pm$ 35.0	30.4 $\pm$ 15.5	51.2 $\pm$ 28.2	56.1 $\pm$ 35.0	55.0 $\pm$ 38.2					
Temperature ($^{\circ}\text{C}$)	22.6 $\pm$ 3.0	21.6 $\pm$ 3.4	29.4 $\pm$ 1.7	30.7 $\pm$ 2.8	26.0 $\pm$ 2.0	25.6 $\pm$ 1.0	12.0 $\pm$ 1.7	15.3 $\pm$ 2.9	25.1 $\pm$ 5.8	19.5 $\pm$ 5.9					
RH (%)	63.4 $\pm$ 7.2	65.1 $\pm$ 9.8	64.9 $\pm$ 8.1	56.9 $\pm$ 9.4	51.0 $\pm$ 8.6	43.3 $\pm$ 6.2	50.2 $\pm$ 19.1	39.8 $\pm$ 14.5	57.8 $\pm$ 12.3	47.7 $\pm$ 16.2					
Wind Speed (m s^{-1})	1.8 $\pm$ 0.3	1.1 $\pm$ 0.3	1.7 $\pm$ 0.4	2.2 $\pm$ 0.9	1.4 $\pm$ 0.7	1.4 $\pm$ 0.5	2.0 $\pm$ 0.4	1.6 $\pm$ 0.4	1.6 $\pm$ 0.6	1.5 $\pm$ 0.4					
SO_4^{2-} ($\mu\text{g m}^{-3}$)	10.4 $\pm$ 2.1	14.0 $\pm$ 3.8	5.2 $\pm$ 2.9	9.4 $\pm$ 5.3	12.7 $\pm$ 2.9	19.6 $\pm$ 5.7	11.1 $\pm$ 4.6	20.9 $\pm$ 6.9	9.4 $\pm$ 5.5	18.2 $\pm$ 7.2					
NO_3^- ($\mu\text{g m}^{-3}$)	6.1 $\pm$ 1.5	11.7 $\pm$ 6.8	1.7 $\pm$ 0.5	2.4 $\pm$ 1.5	2.0 $\pm$ 1.4	3.0 $\pm$ 2.2	5.8 $\pm$ 2.7	16.7 $\pm$ 8.1	3.0 $\pm$ 2.3	12.4 $\pm$ 8.8					

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 $\pm$ SD) on clean and hazy days over the four seasons.

		Spring		Summer		Autumn		Winter	
		C	P	C	P	C	P	C	P
< 0.49 μm	SOR	0.10 $\pm$ 0.02	0.09 $\pm$ 0.02	0.12 $\pm$ 0.04	0.18 $\pm$ 0.05	0.18 $\pm$ 0.09	0.23 $\pm$ 0.06	0.15 $\pm$ 0.08	0.12 $\pm$ 0.04
	NOR	0.02 $\pm$ 0.00	0.03 $\pm$ 0.01	0.01 $\pm$ 0.01	0.02 $\pm$ 0.02	0.01 $\pm$ 0.01	0.01 $\pm$ 0.00	0.03 $\pm$ 0.01	0.04 $\pm$ 0.02
0.49–0.95 μm	SOR	0.13 $\pm$ 0.04	0.13 $\pm$ 0.04	0.08 $\pm$ 0.03	0.13 $\pm$ 0.05	0.20 $\pm$ 0.11	0.22 $\pm$ 0.06	0.20 $\pm$ 0.12	0.14 $\pm$ 0.07
	NOR	0.03 $\pm$ 0.01	0.04 $\pm$ 0.02	0.01 $\pm$ 0.00	0.01 $\pm$ 0.01	0.01 $\pm$ 0.00	0.01 $\pm$ 0.04	0.03 $\pm$ 0.01	0.05 $\pm$ 0.02
0.95–1.5 μm	SOR	0.07 $\pm$ 0.04	0.06 $\pm$ 0.04	0.03 $\pm$ 0.01	0.02 $\pm$ 0.01	0.08 $\pm$ 0.06	0.11 $\pm$ 0.04	0.11 $\pm$ 0.09	0.08 $\pm$ 0.05
	NOR	0.02 $\pm$ 0.01	0.02 $\pm$ 0.01	0.01 $\pm$ 0.00	0.01 $\pm$ 0.00	0.01 $\pm$ 0.00	0.01 $\pm$ 0.00	0.01 $\pm$ 0.01	0.03 $\pm$ 0.01
1.5–3.0 μm	SOR	0.03 $\pm$ 0.02	0.03 $\pm$ 0.01	0.02 $\pm$ 0.01	0.02 $\pm$ 0.01	0.03 $\pm$ 0.02	0.03 $\pm$ 0.01	0.03 $\pm$ 0.03	0.02 $\pm$ 0.02
	NOR	0.02 $\pm$ 0.01	0.02 $\pm$ 0.01	0.02 $\pm$ 0.01	0.01 $\pm$ 0.01	0.01 $\pm$ 0.01	0.01 $\pm$ 0.01	0.01 $\pm$ 0.00	0.01 $\pm$ 0.01
PM_{10}	SOR	0.31 $\pm$ 0.08	0.31 $\pm$ 0.08	0.24 $\pm$ 0.08	0.34 $\pm$ 0.09	0.49 $\pm$ 0.26	0.59 $\pm$ 0.12	0.48 $\pm$ 0.33	0.35 $\pm$ 0.16
	NOR	0.08 $\pm$ 0.02	0.10 $\pm$ 0.03	0.04 $\pm$ 0.01	0.05 $\pm$ 0.03	0.03 $\pm$ 0.02	0.04 $\pm$ 0.02	0.07 $\pm$ 0.02	0.12 $\pm$ 0.05

C: clean days; P: polluted days.

$$\text{SOR} = n\text{-SO}_4^{2-} / (n\text{-SO}_4^{2-} + n\text{-SO}_2) \quad (1)$$

$$\text{NOR} = n\text{-NO}_3^- / (n\text{-NO}_3^- + n\text{-NO}_2) \quad (2)$$

Higher SOR and NOR indicate that more gaseous SO_2 and NO_2 in the atmosphere are oxidized to SO_4^{2-} and NO_3^- , respectively. The Pearson correlation analysis also shows that SO_2 had a positive correlation with SO_4^{2-} ($R > 0.56$, $p < 0.01$) and NO_2 had a positive correlation with NO_3^- ($R > 0.64$, $p < 0.01$) in each size range. It indicates that the formation of SO_4^{2-} and NO_3^- was influenced by SO_2 and NO_2 from local emissions. Size-segregated NO_3^- and SO_4^{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 SO_4^{2-} and NO_3^- over the four seasons. SO_4^{2-} was unimodally distributed and peaked at 0.49–0.95 μm . This is a typical droplet mode for SO_4^{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 SO_4^{2-} was likely due to the limited influence of sea-salt or dust on the formation of SO_4^{2-} at this site. However, correlations of SO_4^{2-} with Ca^{2+} and Mg^{2+} in coarse particles (Table S2) still indicated the influence of sea-salt and dust on the formation of SO_4^{2-} (Yeaman *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 SO_4^{2-} , the distribution of NO_3^- 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 NO_3^- was mainly related to soil/dust, with high correlations of NO_3^- with Ca^{2+} ($R = 0.89$, $p < 0.01$) and Mg^{2+} ($R = 0.88$, $p < 0.01$). PMF analysis further showed that ~60% of the modelled nitrate in coarse particles were most likely associated with dust (Fig. S4). In addition, NO_3^- 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, NO_3^- 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

Fig. 2. Size distribution of NO_3^- and SO_4^{2-} over the four seasons: (a) spring, (b) summer, (c) autumn, (d) winter.

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 NH_4NO_3 , which might explain the absence of NO_3^- peak at 0.49–0.95 μm in summer and autumn (Tai *et al.*, 2010). Likewise, the correlations of NO_3^- and NH_4^+ 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 NO_3^- and NH_4^+ in $\text{PM}_{2.5}$ was higher in winter and spring than in summer and autumn in Guangzhou. It indicated that the NO_3^- 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 O_3

The relationships of SOR and NOR versus O_3 are illustrated in Fig. 3. It can be seen that SOR was moderately correlated ($R = 0.44$, $p < 0.01$) with O_3 at < 0.49 μm . The median values of SOR at < 0.49 μm increased from 0.09 to 0.20 with increasing O_3 (Fig. 3(a)). This result indicates that SO_4^{2-} in < 0.49 μm particles was contributed by gas-phase photochemical oxidation of SO_2 . 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 O_3 . Therefore, SO_4^{2-} in this size range may be formed through the aqueous oxidation of SO_2 , which was less dependent on the level of O_3 . In previous work, SO_4^{2-} 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 O_3 ($R = 0.45$, $p < 0.01$) in winter. NOR at 0.49–0.95 μm and 0.95–1.5 μm was weakly correlated with O_3 and RH in winter. In addition, $\text{PM}_{0.49}$ in 35 out of 37 samples was in an ammonium-rich ($[\text{NH}_4^+]/[\text{SO}_4^{2-}] > 1.5$) condition (Fig. 4). NO_3^- was highly correlated ($R = 0.64$, $p < 0.01$) with ammonium in this size range. Therefore, the formation of NO_3^- was most likely via homogeneous gas-phase reactions, in the form of NH_4NO_3 . Similarly, Pathak *et al.* (2009) and Huang *et al.* (2011) found that NH_4NO_3 in $\text{PM}_{2.5}$ 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 O_3 ($R = 0.26$, $p < 0.01$), temperature ($R = 0.22$, $p < 0.05$) and RH ($R = 0.20$, $p < 0.05$). It indicates that the formation of NO_3^- at this size range had limited dependence on temperature, O_3 and RH. Instead, high correlations of NO_3^- with Ca^{2+} ($R = 0.64$, $p < 0.01$) and Mg^{2+} ($R = 0.80$, $p < 0.01$) were observed. This result might suggest that NO_3^- was in the forms of $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ in this size range, most likely via heterogeneous reactions

Fig. 3. (a) SOR at $< 0.49 \mu m$ and NOR at $1.5-3.0 \mu m$ versus (b) the concentration of O_3 and (c) RH, respectively. The color scale in the legend represents temperature ($^{\circ}C$).

Fig. 4. The relationship between the ratios of $[NH_4^+]/[SO_4^{2-}]$ and $[NO_3^-]/[SO_4^{2-}]$ for $PM_{1.5-3}$ 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, $\text{PM}_{1.5-3.0}$ in 89 out of 130 samples was assigned as ammonium-poor (Fig. 4), indicating the limited formation of NO_3^- as NH_4NO_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 $< 0.49 \mu\text{m}$ ($R = -0.66$, $p < 0.01$), $0.49\text{--}0.95 \mu\text{m}$ ($R = -0.43$, $p < 0.01$) and $0.95\text{--}1.5 \mu\text{m}$ ($R = -0.3$, $p < 0.01$). 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 $0.49\text{--}3.0 \mu\text{m}$ increased with increasing RH (Fig. 5(b)) in dry seasons (winter). SOR was positively correlated with RH in the range of $0.49\text{--}0.95 \mu\text{m}$ ($R = 0.65$, $p < 0.01$), $0.95\text{--}1.5 \mu\text{m}$ ($R = 0.62$, $p < 0.01$) and $1.5\text{--}3.0 \mu\text{m}$ ($R = 0.57$, $p < 0.01$). 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 $0.43\text{--}0.65 \mu\text{m}$ ($R = 0.68$, $p < 0.01$), $0.65\text{--}1.1 \mu\text{m}$ ($R = 0.75$, $p < 0.01$) and $1.1\text{--}2.1 \mu\text{m}$ ($R = 0.77$, $p < 0.01$) 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 $\text{NH}_4^+ - \text{K}^+ - \text{Ca}^{2+} - \text{Na}^+ - \text{Mg}^{2+} - \text{SO}_4^{2-} - \text{NO}_3^- - \text{H}_2\text{O}$ (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 $0.49\text{--}0.95 \mu\text{m}$, 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 $< 0.49 \mu\text{m}$. 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 $0.49\text{--}0.95 \mu\text{m}$ versus RH over the four seasons.

Table 3. H^+_{air} and pH (mean $\pm$ SD), and correlation coefficients of SOR and NOR with H^+_{air} and pH in size-segregated aerosols.

Size-segregated aerosol	H^+_{air} (nmol m^{-3})	pH	Correlation coefficients		
				H^+_{air}	pH
$< 0.49 \mu\text{m}$	3.0 ± 11.0	5.6 ± 3.0	SOR	0.09	0.08
			NOR	0.08	−0.04
$0.49\text{--}0.95 \mu\text{m}$	10.2 ± 27.7	2.6 ± 3.4	SOR	0.11	−0.21*
			NOR	0.53**	−0.29*
$0.95\text{--}1.5 \mu\text{m}$	3.7 ± 14.8	4.8 ± 3.4	SOR	0.12	−0.29**
			NOR	0.57**	−0.58**
$1.5\text{--}3.0 \mu\text{m}$	0.6 ± 2.5	5.6 ± 3.0	SOR	−0.05	0.13
			NOR	0.20	−0.13

** $p < 0.01$. * $p < 0.05$.

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_2 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 $< 0.49 \mu\text{m}$, 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 ($\text{pH} = 2.6\text{--}5.6$). 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 $< 0.49 \mu\text{m}$ 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 $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ 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 $< 0.49 \mu\text{m}$ 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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