Size-segregated Characteristics and Formation Mechanisms of Water-soluble Inorganic Ions during Different Seasons in Heshan of Guangdong, China

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ABSTRACT

To identify the characteristics, sources, and formation mechanisms of aerosol particles during pollution episodes in the Pearl River Delta, 24 sets of size-segregated samples were collected in Heshan during July 2014 and January 2015 using a 10-stage Micro-Orifice Uniform Deposit Impactor (MOUDI), and nine ions, viz., Na+, NH4+, K+, Mg2+, Ca2+, Cl−, NO3−, SO42−, and SO2−3, were investigated. The Na+, Mg2+, and Ca2+ were mainly distributed in the coarse particles, and were mainly from soil, dust, and sea salt. The fine-mode K+ during winter was mostly generated by biomass burning. The coarse-mode Cl− originated from sea salt, whereas the fine-mode Cl− resulted from the conversion of NH4Cl to the particle phase. Both the SO42− and the NO3− exhibited unimodal distributions during winter but bimodal ones during summer. The coarse-mode SO42− and NO3− arose from sea salt and heterogeneous reactions, respectively. An increase in the nitrogen oxidation ratio (NOR) and a decrease in the sulfur oxidation ratio (SOR) were observed on polluted days, with the highest values occurring in the 0.56–1 µm particle size fraction. The formation of NO3− was chiefly related to homogeneous gas-phase reactions during winter and nocturnal heterogeneous reactions involving N2O5 during summer, whereas the formation of SO42− was driven by gas-phase oxidation in the 0.056–0.32 µm size range and aqueous oxidation in the 0.56–3.2 µm range. Additionally, the SOR and the NO3− concentration displayed a positive correlation in the 0.056–1.8 µm particle size fraction, indicating that the potential formation of SO42− via aqueous reactions was accelerated by NO2.

Keywords: Water-soluble inorganic ions; Size distribution; Secondary formation; SOR; NOR.

INTRODUCTION

Particulate matter has been a concern of scientists for decades because it is associated with a range of effects on the atmospheric environment, visibility, human health, and the global radiation budget (Watson, 2002; Poschl, 2005; Kang et al., 2013). The chemical composition of particulate matter includes organic carbon (OC), elemental carbon (EC), elements, and water-soluble inorganic ions (WSIs). According to previous studies, the mass concentration of WSIs could account for over 30% of PM2.5 on an annual basis (Hua et al., 2015). Under typical weather conditions or pollution episodes, the percentage of WSIs in PM2.5 can reach up to 50–60% (Yue et al., 2015b). As a major component of PM2.5, WSIs have a significant impact on the formation of the cloud condensation nuclei and aerosol acidity (Yao et al., 2003a; Shen et al., 2014;); thus, the chemical composition, size distribution, sources, and formation mechanisms need to be fully understood to determine the role of aerosols during atmospheric processes (Wang and Lu, 2006).

SO42−, NO3−, and NH4+ (sulfate, nitrate and ammonium ions [SNA]) are the most abundant species in WSIs, accounting for over 40% of WSII mass concentrations (Yao et al., 2002; Yue et al., 2010; Chang et al., 2013; Yue et al., 2015b). They are mostly from secondary formation, and their formation mechanisms have been studied. The formation mechanism of SNA is relatively clear but is still not fully understood. Generally, the formation of SNA is related to its gaseous precursors (SO2, NOx, and NH3), oxidant (O3), oxidation transformation rate (sulfur oxidation ratio [SOR]) and nitrogen...
The NO\textsuperscript{3–} formation is dominated by the reactions of NO\textsubscript{2} with OH- radical or nitric acid with NH\textsubscript{3} during daylight, or by heterogeneous hydrolysis of N\textsubscript{2}O\textsubscript{5} on aerosol surfaces during the night (Seinfeld and Pandis, 2006). SO\textsubscript{4}\textsuperscript{2–} is produced through the gas-phase oxidation of SO\textsubscript{2} by reactions with OH- radicals, or by the aqueous uptake of SO\textsubscript{2} on pre-existing particles or cloud droplets with dissolved H\textsubscript{2}O\textsubscript{2} or with O\textsubscript{2} under the catalysis of transition metals, such as Fe(III) and Mn(II) (Blitz et al., 2003; Seinfeld and Pandis, 2006). A recent study found that the aqueous oxidation of SO\textsubscript{2} by NO\textsubscript{2} was an efficient sulfate formation pathway on fine aerosols with high relative humidity or cloud conditions under NH\textsubscript{3} neutralization (Wang et al., 2016). NH\textsubscript{4}+ is mostly combined with SO\textsubscript{4}\textsuperscript{2–} and/or NO\textsubscript{3–} (Feng and Penner, 2007).

SNA have strong hygroscopicity, and can change the atmospheric visibility significantly and the heterogeneous reactions on the particle’s surface, affecting aerosol size distribution (Liu et al., 2008; Lee and Hieu, 2013). For example, sub-mode NO\textsubscript{3–} is mostly combined with nitric acid and ammonia, coarse-mode NO\textsubscript{3–} is mainly formed by heterogeneous reactions of nitric acid or NO\textsubscript{2} with coarse particles, such as sea salt, dust, or soil particles (Seinfeld and Pandis, 2006). Coarse-mode SO\textsubscript{4}\textsuperscript{2–} is mainly formed by gas-to-particle conversion, while droplet-mode SO\textsubscript{4}\textsuperscript{2–} is mainly attributed to cloud processing (Meng and Seinfeld, 1994). Many other studies also show that the dominant formation pathway of SNA varied with the research locations and the sampling periods (Wang et al., 2009; Ye et al., 2011).

The Pearl River Delta (PRD) region is one of the most economically developed in China. With highly intensive pollutant emissions caused by the rapid economic growth and continuous metropolitan expansion and high humidity, the PRD region has been experiencing frequent haze pollution, leading to low visibility and severe health effects. Although air quality has improved significantly in recent years, regional pollution processes still occur. There have been many studies on the WSIs of aerosols in the PRD region. Gong et al. (2012) revealed that SO\textsubscript{4}\textsuperscript{2–} has the highest content in the Heshan region followed by NO\textsubscript{3–}. Dai et al. (2013) found that WSIs were over 50% of the PM\textsubscript{2.5} in Shenzhen. He et al. (2014) found that in a haze episode in Guangzhou, SNA accounted for 76% of the total inorganic ions in the fine particles. Huang et al. (2014) investigated atmospheric particles collected in the Heshan Kaiping region in 2008 and found that SO\textsubscript{4}\textsuperscript{2–} and NO\textsubscript{3–} contributed 44% of the total PM\textsubscript{2.5} due to the high emission of SO\textsubscript{2} and NO\textsubscript{2}. Liu et al. (2019) found that the photochemical process is a critical factor affecting the formation of secondary ions in Guangzhou, and the SOR and NOR values were higher in winter than in summer. The size distribution and chemical composition of aerosols are essential to understanding the impact of their emission, migration, formation, and the conversion of secondary aerosols (Haywood et al., 2008; Liu et al., 2008; Asmi et al., 2016; Kuang et al., 2016). There has also been some research on size-resolved chemical compositions in this region. For example, Liao et al. (2015) found that SNA showed a distinct triple-peak pattern while other ions showed double- or single-peak structures in the fine-particle mode in South China. Gao et al. (2016) resolved trimodal size distributions of major chemical components using the Positive Matrix Factorization (PMF) model. They discussed the possible sources in different modes and found that secondary SO\textsubscript{4}\textsuperscript{2–}, engine exhaust, shipping, coal/biomass burning, and industrial sources were the main contributors to fine particles in Hong Kong. Jiang et al. (2019) compared pollution days and clean days and found that in summer and autumn, the SO\textsubscript{4}\textsuperscript{2–} showed higher formation rate, while the NO\textsubscript{3–} showed higher production rate in winter and spring. Moreover, different formation mechanisms were found in different size ranges and seasons. Previous studies were focused on urban areas and based on short-term monitoring in a single season. The seasonal characteristics, sources of WSIs, and size-segregated formation mechanisms of SO\textsubscript{4}\textsuperscript{2–} and NO\textsubscript{3–} are still not well understood. Furthermore, previous studies on the impact of various possible factors on the formation mechanism of SNA are not adequate.

Size-segregated aerosol samples were collected at the Heshan Supersite (using a 10-stage Micro-Orifice Uniform Deposit Impactor (MOUDI)) in July 2014 and January 2015 to obtain a comprehensive understanding of the characteristics in the concentration variation, size distribution, sources, and formation mechanism of WSIs during the pollution days in different seasons in the PRD region, which shows regional and complex air pollution characteristics. The Heshan Supersite is in the downwind area 50–100 km from the concentrated emission area of the pollution sources in Guangzhou, Foshan, and Dongguan, which is an ideal area to study the characteristics of regional air pollution. WSIs from size-segregated aerosol particles in summer and winter were analyzed. The main aim of this study was to investigate the characteristics and sources of main inorganic ions in different size ranges and gain more knowledge on the formation pathways of SNA and the causes of pollution weather.

METHODS

Sample Collection

The sampling site is located at the Guangdong Atmospheric Supersite, a suburban site of Heshan city in the PRD region, surrounded mainly by villages and forests with no noticeable industrial sources around. The site is about 50 and 100 km southwest of Foshan and Guangzhou, respectively; both cities are densely industrial areas. The supersite is designed to monitor the air quality of the Pearl River Delta.

MOUDI (Model 110; MSP, USA) was installed on the roof of the main building of the supersite, approximately 10 m above the ground. Atmospheric particles with the size of 0.056, 0.10, 0.18, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6, 10.0, and 18.0 μm were collected on 47 mm quartz fiber filters (QFFs; Whatman) preprocessed at a flow rate of 30 L min\textsuperscript{−1}. The details of the filter processing method have been illustrated in published articles (Gan et al., 2015). Sampling was done from 9:00 a.m. to 8:30 a.m. of the next day in the periods July 22–August 1, 2014, and January 14–February 2, 2015.
(except for January 22–24). Overall, 10 and 14 sets of samples were collected in summer and winter, respectively, and blank field membranes were also collected. Before and after sampling, the filters were kept at constant temperature (25°C) and relative humidity (RH; 50%) for 24 h before weighing. They were wrapped with annealed aluminum foil and stored in a refrigerator at −40°C until analysis.

Sample Processing and Chemical Analysis

Each sample filter was cut to a certain size and put into a centrifuge tube with 5 mL ultra-pure water and was extracted using an ultrasonic bath for 40 min. The extract was filtered using a 0.45 µm pore size filter. Then the process above was repeated. Only the ultrasonic extracted time was changed to 20 min. Both extraction solutions were mixed, resulting in a 10 mL solution, which was stored in a refrigerator until analysis. Ice was placed into the water bath to prevent the loss of ammonium due to the increase of the bath temperature. Concentrations of WSIIs were determined using the Dionex ICS-90 ion chromatogram instrument. In total, five cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) and four anions (Cl⁻, NO₃⁻, NO₂⁻, SO₄²⁻) were analyzed. The detection limits were 0.020, 0.009, 0.005, 0.010, 0.016, 0.008, 0.007, 0.005, and 0.022 mg L⁻¹ for Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, NO₂⁻, and SO₄²⁻, respectively. The spike recovery test showed that recoveries of all ions were over 98% after a 60 min extraction. The precision of the analysis was calculated by duplicating the measurement of the same sample 7 times, and it yielded relative standard deviation (RSD) of 0.49%, 1.23%, 0.97%, 1.41%, 1.14%, 0.50%, 2.24, 1.73%, and 1.33% for Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, NO₂⁻, and SO₄²⁻, respectively. The same method was used to analyze the blank membranes. The concentration of ions in the blank samples accounted for 4.33%, 4.44%, 2.85%, 5.63%, 4.49%, 0.86%, 7.83%, 1.72%, and 0.24% of the ambient samples for Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, NO₂⁻, and SO₄²⁻ in the summer samples, respectively, and the values were 7.32%, 1.31%, 1.40%, 11.71%, 4.89%, 0.37%, 3.37%, 0.24%, and 0.16% for winter samples. The blank deduction was applied for all samples before data analysis.

The ion balance was checked to evaluate the data quality and acidity of the samples following Eqs. (1)–(2) below.

\[
\text{CE (Cation Equivalent)} = [\text{Na}^+] / 23 + [\text{NH}_4^+] / 18 + [\text{K}^+] / 39 + [\text{Mg}^{2+}] / 12 + [\text{Ca}^{2+}] / 2
\]  

(1)

\[
\text{AE (Anion Equivalent)} = [\text{Cl}^-] / 35.5 + [\text{NO}_2^-] / 46 + [\text{NO}_3^-] / 62 + [\text{SO}_4^{2-}] / 48
\]  

(2)

Because MOUDI does not have a 2.5 µm cut size, we define particles with a size range of 0.056–3.2 µm as fine particles and 3.2–10 µm as coarse particles. As shown in Fig. 1, good linear correlations were observed between cations and anions in most size ranges, indicating that the analysis method is reliable. Most fine-particle samples reached equilibrium or showed excess anions except for the two smallest size ranges, while most of the coarse samples showed excess cations, which means that fine particles were more acidic than the coarse particles. The huge gap between anions and cations in size ranges smaller than 0.18 µm might be the result of incomplete detection of ions in these size ranges.

RESULTS AND DISCUSSION

Characteristics of WSIIs During Clean and Pollution Days of Summer and Winter

Fig. 2 shows the temporal variation of the WSI mass concentrations in summer and winter in the Heshan region. Fine particles (PM₁₀) were dominant during the sampling periods, with average mass concentrations of 69.85 (± 26.45) µg m⁻³ and 103.4 (± 49.33) µg m⁻³ in summer and winter, respectively. WSIIs were mostly in fine particles, with 80.8% and 85.7% distributed in PM₁₀ in summer and winter, respectively. The mass concentrations of WSIIs were 21.61 (± 5.90) µg m⁻³ and 59.86 (± 24.13) µg m⁻³ in summer and winter, accounting for 32.1 (± 8.5%) and 60.6 (± 16.4%) of the PM₁₀ mass concentration. SO₄²⁻, NO₃⁻, and NH₄⁺ were major components of WSIIs. In summer, SNA/WSIIs were 58.4 ± 10.4% and 44.7 ± 13.1% in fine and coarse particles, respectively. In winter, SNA/WSIIs were 81.3 ± 5.6% and 58.5 ± 8.1% in fine and coarse particles, respectively. SNA are mainly a result of secondary transformation (Yao et al., 2003b; Lin et al., 2012). In 2013, Yue et al. (2015a) investigated the SNA of atmospheric particles in winter in the Heshan region, finding that its mean contribution in PM₂.₅ was 64.3%. Liu et al. (2015) focused on the atmospheric particles in Guangzhou from 2010 to 2012 and found that in the haze episode, SNA accounts for 55% of the total mass of PM₂.₅. In this paper, the percentages of SNA/PM₁₀ in summer and winter were 18.8 ± 5.8% and 48.8 ± 11.4%, respectively, which were lower than the two results mentioned above.

Polluting weather occurred in both seasons and the WSI composition showed significant differences in the different pollution episodes. Therefore, we separated the samples into clean days and pollution days according to the Ambient Air Quality Standard published by the Ministry of Ecology and Environment of China (2012), using 75 µg m⁻³ as a standard for particulate matter. As listed in Table 1, during both seasons the pollution days had higher concentrations of SO₂ and O₃ than the clean days and a higher temperature was observed during the former. RH was slightly higher on winter pollution days but low on summer pollution days. Visibility significantly degraded from the summer clean days (20.4 km) to pollution days; however, it was lower on summer pollution days. Unlike winter, visibility was high on winter pollution days but low on summer pollution days. Visibility significantly degraded from the summer clean days (20.4 km) to pollution days (6.5 km); it was accompanied by a significant increase in the proportion of SNA in WSIIs, which increased from 51% to 83%. Strong negative correlations were found between visibility and SNA, with correlation coefficients of −0.819 (p < 0.01), −0.868 (p < 0.01), and −0.911 (p < 0.01) for NO₃⁻, SO₄²⁻, and NH₄⁺, respectively.

Fig. 3 shows the ion composition of fine and coarse particles during different periods in the two seasons. The corresponding SOR and NOR values are also given by Eqs. (3)–(4) below.

\[
\text{SOR} = [\text{SO}_4^{2-}] / ([\text{SO}_4^{2-}] + [\text{SO}_2])
\]  

(3)
Fig. 1. Ion balance of WSII s in samples of different sizes.

Fig. 2. Temporal variation of WSII mass concentrations in summer and winter.
As shown in Fig. 3, SNA were the most abundant species in both fine and coarse particles except on clean summer days. The proportion of SO$_4^{2-}$ were significantly higher in the fine particles, while those of NO$_3^-$ and crustal ions such as Na$^+$ and Ca$^{2+}$ were much higher in the coarse particles. The difference in the ion composition between the clean and pollution days showed similar trends for fine and coarse particles; however, they were distinctly different between summer and winter. In both fine and coarse particles, the proportion of SO$_4^{2-}$ increased significantly from the clean days to the pollution days in summer; in winter, the proportion of NO$_3^-$ increased. In both seasons, the SOR decreased during pollution days but the concentration of SO$_4^{2-}$ still increased significantly because of the rapid increase of SO$_2$, particularly during the summer pollution days. When the concentration of SO$_2$ tripled, the proportion of SO$_4^{2-}$ increased significantly. The NOR showed higher values on the pollution days than on the clean days. In winter, particularly, the NOR value of 0.23 during the pollution days was almost at the same level of SOR (0.31). High NOR and NO$_2$ concentrations during the winter pollution days resulted in a rapid rise in the concentration and proportion of NO$_3^-$. Vehicle emissions and coal combustion are significant contributors to NO$_3^-$ and SO$_4^{2-}$, respectively (Huang et al., 2014). Thus, the mass concentration of NO$_3^-$/SO$_4^{2-}$ has often been used to evaluate the relative contribution of vehicle emission and coal combustion to aerosol particles (Huang et al., 2016). In this study, the NO$_3^-$/SO$_4^{2-}$ mass ratio in PM$_{1.2}$ ranged from 0.08 to 1.76, with average values of 0.18, 0.14, 0.56, and 1.04 during the summer clean days, summer pollution days, winter clean days, and winter pollution days, respectively. The NO$_3^-$/SO$_4^{2-}$ mass ratios were significantly higher in winter than in summer, indicating that a greater proportion of fine particles originated from vehicle emissions in winter. In summer, the values were much smaller than the ratios in Guangzhou (Liu et al., 2019) but were at the same level as Guangzhou in winter. This was possibly the result of different prevailing wind directions during the two seasons. Back trajectory analysis showed that marine south winds dominated in summer, bringing clean air to Heshan, resulting in low NO$_3^-$/SO$_4^{2-}$ mass ratios during summer. In winter, air masses were mostly from or passed through heavily polluted areas located in the northeast or northwest of Heshan, such as Dongguan, Guangzhou, and Foshan. These cities have many cars, resulting in higher NO$_3^-$/SO$_4^{2-}$ ratios in winter, particularly during the winter pollution days.

Size Distribution and Sources of WSIIs

Fig. 4 displays the size-resolved WSII composition in summer and winter. The size distribution of WSII showed distinct differences between the two seasons. In summer, WSII were bimodally distributed, with the dominant peak in the range of 0.56–1 μm, and a small peak in the range of 1.8–3.2 μm. In winter, WSII were unimodally distributed and peaked in the range of 0.56–1 μm. SO$_4^{2-}$ was predominant in the summer samples, while SO$_4^{2-}$ and NO$_3^-$ were mainly in the winter samples.
Fig. 5 shows the size distribution of single ions during different periods in summer and winter. According to the size distribution, the nine ions could be classified into three categories. The first class includes Na\(^+\), Mg\(^{2+}\), and Ca\(^{2+}\), among which Mg\(^{2+}\) and Ca\(^{2+}\) showed similar size distributions. These two ions were almost equally distributed in all size categories. The second class includes Cl\(^-\), K\(^+\), NH\(_4\)^+ and SO\(_4^{2-}\), which showed similar size distributions. The third class includes NO\(_3^-\) and NO\(_2^-\), with NO\(_2^-\) showing a much smaller size distribution. The size distribution of PM\(_{3.2}\) shows that the concentration of SOR and NOR values during different periods in summer and winter. PM\(_{3.2-10}\) is shown to have a higher concentration in winter than in summer. The size distribution of PM\(_{3.2-10}\) shows that the concentration of SOR and NOR values during different periods in summer and winter. PM\(_{3.2-10}\) is shown to have a higher concentration in winter than in summer.

**Fig. 3.** Ion composition of fine and coarse particles. SOR and NOR values during different periods in different seasons.

**Fig. 4.** Size-resolved WSI composition in summer and winter.
Fig. 5. Size distribution of single ions during different periods in summer and winter.

ranges in summer, with a tiny peak in the range of 3.2–5.6 µm, whereas in winter, they were mostly distributed in the coarse mode, with a single peak in size range of 3.2–5.6 µm. The two ions were strongly correlated with each other in both seasons (R > 0.8, p < 0.01), indicating the same origin from the soil or dust (Li et al., 2011). Na⁺ was mainly distributed in the coarse mode during the clean days of both seasons (although in summer, it had two small peaks in fine particles), while during the pollution days in both seasons, it was bimodally distributed, with the first peak appearing in size range of 0.56–1 µm, and the secondary peak in size range of 3.2–5.6 µm in winter and 5.6–10 µm in summer. The distribution pattern in the pollution days was similar to that of the previous study (Huang et al., 2016), which found a bimodal distribution of Na⁺, peaking at 0.43–0.65 µm and 4.7–5.8 µm. A moderate correlation was found between Na⁺ and Cl⁻ in size range of 5.6–10 µm (R > 0.6, p < 0.01). Back trajectory analysis indicated that 61% of the air masses during the summer sampling period were from the sea, indicating the contribution of sea salt to the coarse mode of Na⁺. Moreover, Na⁺ was strongly correlated with Ca²⁺ (R = 0.399, p > 0.05 in summer; R = 0.779, p < 0.01 in winter) and Mg²⁺ (R = 0.771, p < 0.01 in summer; R = 0.541, p < 0.05 in winter) in size range of 0.56–1 µm, indicating the crustal source of this size range.

The secondary class includes K⁺, Cl⁻, and NO₂⁻, which were unimodally distributed during winter pollution days, peaking at the size range of 0.56–1 µm. K⁺ was mainly distributed in fine-mode aerosols, and it was unimodally distributed in winter and bimodally distributed in summer. K⁺ in fine mode is considered as a major feature of biomass burning (Arimoto et al., 1995). Furthermore, global fire maps from the NASA Moderate Resolution Imaging Spectroradiometer (MODIS) and Visible Infrared Imaging Radiometer Suite (VIIRS) (https://firms.modaps.eosdis.nasa.gov/map) showed a significant increase of the fire spots over South China and Southeast Asia during the winter sampling period, which was many times more than during the summer sampling period. Many more fire spots and a higher K⁺ concentration in winter suggested more serious emission of biomass burning in winter. Cl⁻ was mainly associated with fine particles during the winter pollution days with a mono-distribution peaking at 0.56–1.0 µm. However, Cl⁻ was multimodally distributed during the other three periods, with a mass concentration mostly distributed in coarse particles. Coarse-mode Cl⁻ in size ranges larger than 3.2 µm was strongly correlated to Na⁺ (R > 0.6, p < 0.01) and Mg²⁺ (R > 0.7, p < 0.01), suggesting a marine source (Li et al., 2010). Cl⁻ from the size range of 0.56–1.0 µm was highly correlated to SNA and K⁺, with the correlation coefficients of 0.903 (p
Previous research implied that sea salt reacting with acid gas or precursor could generate \( \text{HCl} (g) \), \( \text{Na}_2\text{SO}_4 \), and \( \text{NaNO}_3 \). \( \text{HCl} (g) \) could possibly react with \( \text{NH}_3 \), generating \( \text{NH}_4\text{Cl} \), which could be redistributed into particle phases or condensed into cloud droplets (Kulmala et al., 1995). This would result in the good correlation between \( \text{Cl}^- \) and \( \text{SNA} \), and the fine mode of \( \text{Cl}^- \), which was the possible formation mechanism of \( \text{Cl}^- \) in the size range of 0.56–1 \( \mu \)m in this study.

The third class consists of \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), and \( \text{NH}_4^+ \), which were typical secondarily generated ions. The three ions showed similar size distribution patterns in winter, with a single peak in size range of 0.56–1.0 \( \mu \)m. However, for size ranges of 0.56–1 and 1–1.8 \( \mu \)m, the concentration increment of \( \text{NO}_3^- \) was higher than those of \( \text{SO}_4^{2-} \) and \( \text{NH}_4^+ \) during winter pollution days. This is likely due to the higher production of \( \text{NO}_3^- \) in these size ranges during the latter, as evidenced by significantly higher NOR values in these two size bins (Fig. 6). During the winter pollution days, the NOR in the two size ranges almost doubled more than during the winter clean days, resulting in a sharp increase of \( \text{NO}_3^- \) in the two size bins. Correlation analysis showed that \( \text{NO}_3^- \) was highly correlated to \( \text{NH}_4^+ \) (\( R > 0.837, p < 0.01 \)) and \( \text{K}^+ \) (\( R > 0.9, p < 0.01 \)) in these two size ranges, indicating the possible existence of \( \text{NH}_4\text{NO}_3 \) and \( \text{KNO}_3 \) in these size ranges in winter. The distribution pattern of \( \text{NO}_3^- \) in summer varied significantly compared to winter, showing a bimodal distribution, peaking at the size range of 3.2–5.6 \( \mu \)m and 0.56–1 \( \mu \)m. \( \text{NH}_4\text{NO}_3 \) is thermally unstable, with an average temperature of 29.8 \( \pm 1.5^\circ \)C. \( \text{NH}_4\text{NO}_3 \) could be dissociated into \( \text{NH}_3 (g) \) and \( \text{HNO}_3 (g) \); then \( \text{HNO}_3 \) could be easily adsorbed on the coarse particles, which had weaker acidity than fine particles, and it could react with \( \text{CaCO}_3 \) or other species in coarse particles (Huang et al., 2013). Correlation analysis showed high correlations of \( \text{NO}_3^- \) with \( \text{Ca}^{2+} \) (\( R = 0.855, p < 0.01 \)) and \( \text{Mg}^{2+} \) (\( R = 0.951, p < 0.01 \)) in this size range, which confirmed the speculation. As Fig. 6 shows, in size ranges for 0.18–3.2 \( \mu \)m, the NOR values were systematically higher in winter than in summer, while in size ranges of 3.2–10 \( \mu \)m, the NOR values showed no significant difference between the two seasons. In ultra-fine size ranges of 0.056–0.18 \( \mu \)m and the largest size range of 10–18 \( \mu \)m, the NOR values were higher in summer than in winter. This was not in agreement with previous studies (Huang et al., 2013), which discovered higher NOR values in summer for
all size ranges in Beijing. In both seasons, the NOR during the pollution days were higher than during the clean days for all size ranges, which was in agreement with previous studies in Guangzhou (Liu et al., 2015) and Beijing (Huang et al., 2013). Moreover, the size distribution of NOR was different from previous researches in Guangzhou (Jiang et al., 2019), Beijing (Huang et al., 2013), and Tianjin (Yao et al., 2017). Huang et al. (2013) found a multimodal distribution of NOR in summer in Beijing. The highest NOR value appeared in the largest size range in summer, while in winter, the highest NOR was found to be in the smallest size range. Yao et al. (2017) found a trimodal distribution of the NOR during the clean days, and a bimodal distribution during the heavy pollution days, with the highest NOR in the size range of 1.1–2.1 μm. In this study, the NOR showed a bimodal distribution in both clean and pollution days in summer, with high values in size ranges of 0.56–1 μm and 3.2–5.6 μm. In winter, NOR was unimodally distributed with the highest value appearing in the size range of 0.056–1 μm.

The distribution of SO$_2^{2-}$ in the summer pollution days showed a bimodal pattern with peaks at 0.56–1.0 μm and 1.8–3.2 μm, while in other periods it showed a unimodal distribution with a major peak at 0.56–1.0 μm. It is reported that SO$_2^{2-}$ in the coarse mode are possibly formed by reactions with sea salt or soil (Gao et al., 2016), which might also be the source of SO$_2^{2-}$ in the size of 1.8–3.2 μm in summer in this study, considering the marine prevailing wind directions in this season. The size range of 0.56–1 μm is a typical droplet mode for SO$_2^{2-}$, in which SO$_2^{2-}$ was mainly formed through aqueous oxidation of SO$_2$ (Seinfeld and Pandis, 2006). Similarly, the highest NOR value appeared in this size range in both clean and pollution days in both seasons. As shown in Fig. 6, only in size ranges of 0.56–1 μm and 1–1.8 μm, the NOR values were significantly higher in winter than in summer, while in size ranges smaller than 0.56 μm and size ranges larger than 3.2 μm, the NOR values were systematically higher in summer. This was in accordance with previous research in Guangzhou (Jiang et al., 2019), which also found increasing NOR values in winter in the size range of 0.49–1.5 μm but showed different trends in Beijing (Huang et al., 2013), which discovered higher NOR values in summer for all size ranges. Unlike the NOR, which showed higher values during the pollution days in all size ranges in both seasons, NOR values decreased during the pollution days, except for the size range of 1.8–5.6 μm in summer, and the size ranges of 0.18–0.32 μm and 0.56–1.0 μm in winter. The results were consistent with previous research in Guangzhou (Liu et al., 2015), which found decreased NOR values during the haze processes, different from Beijing, which showed higher NOR values during the pollution days.

The size distribution of the NOR showed different characteristics between summer and winter. In summer, smaller size ranges (0.18–1 μm) had a higher NOR, while in winter, the distribution shifted toward larger sizes. Higher NOR values were found to appear in the size range of 0.56–3.2 μm. This may indicate different formation mechanisms of the NOR in different seasons. Unlike NO$_3^-$ and SO$_2^{2-}$, NH$_4^+$ was unimodally distributed during all the monitoring periods, peaking at the size range of 0.56–1 μm. It was found to be strongly correlated with NO$_3^-$ (R = 0.955, p < 0.01), SO$_2^{2-}$ (R = 0.900, p < 0.01), Cl$^-$(R = 0.784, p < 0.01), K$^+$(R = 0.921, p < 0.01), and Ca$^{2+}$(R = 0.513, p < 0.05).

**Secondary Formation of Nitrate and Sulfate**

Fig. 7 shows the relationship between the ratios of [NH$_4^+$]/[SO$_2^{2-}$] and [NO$_3^-$]/[SO$_2^{2-}$] for all size-segregated samples. Considering [NH$_4^+$]/[SO$_2^{2-}$] > 1.5 as ammonium-rich (AR) and [NH$_4^+$]/[SO$_2^{2-}$] < 1.5 as ammonium-poor (AP), the summer samples were almost all ammonium-poor, with the [NH$_4^+$]/[SO$_2^{2-}$] ratio of 1.13 ± 0.38, indicating that NH$_4^+$ in summer aerosols mainly existed in the form of NH$_4$HSO$_4$, and limited formation of NO$_3^-$ as NH$_4$NO$_3$. Therefore, homogeneous gas-phase reactions should not be the main formation pathway of NO$_3^-$ in the summer in Heshan. It is reported that NO$_3^-$ could also be generated by heterogeneous reactions of NO$_3$ and N$_2$O$_5$ during the night on the surface of aerosols under the conditions of high relative humidity and high concentration of NO$_3$ and O$_3$ (Wang et al., 2009). During the sampling period in summer, the concentration of NO$_3$ was 25 ± 2.6 μg m$^{-3}$ at night, which was higher than 14.3 ± 6.4 μg m$^{-3}$ in the daytime. Moreover, the relative humidity was 81.6 ± 4.0%, which was also significantly higher than that of 64.0 ± 5.3% during the day, making a suitable environment for the heterogeneous reactions to happen. In winter, most of the samples in the size range of 0.18–3.2 μm were ammonium-rich, accounting for 50.7% of total winter samples. NO$_3^-$ was highly correlated with ammonium in these size ranges. The NOR in winter showed a strong correlation with O$_3$ in size range of 0.056–0.56 μm (R > 0.539, p < 0.05). Therefore, the formation of NO$_3^-$ in winter was most likely through homogeneous gas-phase reactions, in the form of NH$_2$NO$_3$, which was in accordance with the result in Guangzhou (Jiang et al., 2019).

Sulfate could be formed through gas-phase oxidation and aqueous-phase heterogeneous reactions with its precursor gas, SO$_2$ (Zhang et al., 2015). Moreover, Wang et al. (2016) found that in China, the oxidation of SO$_2$ by NO$_3$ in aqueous media was an important pathway for sulfate generation, but it is pH-dependent. In this study, size-segregated Aerosol [H$^+$]$_{in situ}$ were calculated using the Extended AIM Aerosol Thermodynamic Model II (http://www.aim.env.uea.ac.uk/aim/model2/model2a.php), which is an equilibrium thermodynamic model of the system H$^+$ - NH$_4^+$ - SO$_2^{2-}$ - NO$_3^-$ - H$_2$O. pH was then calculated using Eq. (5) as follows:

$$pH = -\log\left(\gamma \times \frac{[H^+]|_{in\, situ}}{V} \times \frac{1000}{V}\right)$$

(5)

where $\gamma$ represents hydrogen activity coefficients and $V$ represents the volume of aqueous solutions, which could all be given by the model. Average [H$^+$]$_{in\, situ}$ in PM$_{1.2}$ was 45.7 nmol m$^{-3}$ in summer and 70.6 nmol m$^{-3}$ in winter, with pH values of 2.3 in summer and 2.6 in winter, indicating the acidic nature of the fine particles in both seasons.

Photochemical reactions are influenced by temperature, humidity, and radiation intensity (Seinfeld and Pandis, 2006).
The SOR was found to be moderately correlated with temperature in size range of 0.056–0.32 μm (R > 0.546, p < 0.01), indicating that in this size range, the formation of SO$_4^{2-}$ was controlled by the gas-phase photochemical oxidation of SO$_2$, which was similar to results of previous studies, which found a dominant gas-particle conversion mechanism in size ranges < 0.49 μm and 0.32–0.56 μm in Guangzhou (Jiang et al., 2019) and PRD region (Liu et al., 2008), respectively. In size ranges 0.56–1 μm, 1–1.8 μm, and 1.8–3.2 μm, the SOR showed weak positive correlation with relative humidity, with the correlation coefficients of 0.22, 0.29, and 0.18, respectively, indicating that in these size ranges, SO$_4^{2-}$ may be formed through the aqueous oxidation of SO$_2$. The result was also similar to previous studies (Jiang et al., 2019), which attributed SO$_4^{2-}$ in the size range of 0.49–3.0 μm to the result of aqueous oxidation. However, although E-AIM gave out low pH in both seasons, a moderate correlation between SOR and NO$_2$ was observed in the former two size ranges, with correlation coefficients of 0.545 (p < 0.01) and 0.534 (p < 0.01), respectively, which was not observed by Jiang et al. (2019). Thus, we came into the deduction that aqueous reactions accelerated by NO$_2$ might also be a possible pathway of sulfate production in Heshan, although the pathway may not be as important as in other heavily polluted areas in China, and should be further researched in future studies.

CONCLUSIONS

To identify the differences between clean and polluted days, including their seasonal attributes, in the Pearl River Delta, this study investigated the size-resolved sources of the major WSIIs and the formation pathways of SNA in Heshan, a typical suburban site representing the complex pollution characteristics of this region. Additionally, the contribution of meteorological parameters, gaseous pollutants, and other significant factors to the formation of SO$_4^{2-}$ and NO$_3^-$ was explored. The Na$^+$, Mg$^{2+}$, and Ca$^{2+}$ mainly arose from soil, dust, and sea salt. The higher concentration of K$^+$ in winter was due to the increased biomass burning during this season. The coarse-mode Cl$^-$ originated from sea salt, whereas the fine-mode Cl$^-$ resulted from the conversion of NH$_4$Cl to the particle phase. The WSII composition displayed significant differences between winter and summer, with a higher proportion of NO$_3^-$ on polluted days during the former and a higher proportion of SO$_4^{2-}$ on polluted days during the latter. Furthermore, increased NORs but decreased SORs were observed on the polluted days of both seasons. The 0.56–1 μm and 1.0–1.8 μm particle size ranges exhibited the highest SORs and NORs on polluted days during winter; however, the 0.056–1 μm and 1–3.2 μm fractions showed higher ratios during summer. The formation of NO$_3^-$ was primarily driven by homogeneous gas-phase reactions during winter and nocturnal heterogeneous reactions involving N$_2$O$_5$ during summer. A moderate positive correlation between the SOR and the temperature was found for the 0.056–0.32 μm particles, indicating the predominance of gas-phase oxidation, and a weak positive correlation between the SOR and the relative humidity was found for the 0.56–3.2 μm particles, suggesting the influence of aqueous oxidation. Moreover, the SOR and the NO$_2$ concentration displayed a positive correlation in the 0.056–1.8 μm particle size fraction, indicating that the potential formation of SO$_4^{2-}$ via aqueous reactions was accelerated by NO$_2$. Our results, which encompass the size-resolved compositions and sources of ions as well as the seasonal characteristics of their formation pathways during polluted and clean days in Heshan, enhance our understanding of air pollution in this area.

Fig. 7. The relationship between the ratios of [NH$_4^+$]/[SO$_4^{2-}$] and [NO$_3^-$]/[SO$_4^{2-}$] for all size-segregated samples, as well as the proportion of ammonium-rich (AR) samples and ammonium-poor (AP) samples in different size ranges (w before the size ranges stands for “winter”).
region and enable us to establish effective control measures according to the season.

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