Characteristics of Aerosol Pollution Under Different Visibility Conditions in Winter in a Coastal Mega–City in China

YANG Hong-long (杨红龙)\textsuperscript{1}, ZHANG Yong (张 勇)\textsuperscript{2}, LI Lei (李 磊)\textsuperscript{1,4}, CHAN PK WAI (陈柏玮)\textsuperscript{3},
LU Chao (陆超)\textsuperscript{1}, ZHANG Li (张丽)\textsuperscript{1}

1. Shenzhen National Climate Observatory, Meteorological Bureau of Shenzhen Municipality, Shenzhen 518040 China; 2. Meteorological Observation Center, China Meteorological Administration, Beijing 100081 China; 3. Hong Kong Observatory, Hong Kong 999077 China; 4. School of Atmospheric Sciences, Sun Yat-sen University, Zhuhai 519082 China

Abstract: To investigate chemical profiles and formation mechanisms of aerosol particles in winter haze events, comprehensive measurements including hourly concentrations of PM\textsubscript{2.5} and water-soluble inorganic ions and related gas-phase precursors were conducted via an online monitoring system from January to March of 2016 in Shenzhen, a coastal mega-city in south China. In this study, high concentrations of PM\textsubscript{2.5}, NO\textsubscript{x} and lower levels of O\textsubscript{3} were observed during haze periods in comparison with clear days (Visibility>15km). The major secondary ionic species were NH\textsubscript{4}\textsuperscript{+}, NO\textsubscript{3} and SO\textsubscript{4}\textsuperscript{2}\textsuperscript{−}, which varied significantly on haze and clear days. The ratio of NO\textsubscript{2}/SO\textsubscript{4}\textsuperscript{2}\textsuperscript{−} in haze days was greater than that on clear days and tended to be larger when air pollution became more serious. At the same time, compared with previous studies, it has been found that the ratio has been increasing gradually in Shenzhen, indicating that the motor vehicle exhaust emissions have a more and more important impact on air quality in Shenzhen. Sulfur oxidation rate(SOR) and nitrogen oxidation rate(NOR) was higher during the haze period than that in clear days, indicating efficient gas to particle conversion. Further analysis shows that high concentrations of sulfate might be explained by aqueous oxidation, but gas-phase reactions might dominate nitrate formation. This study also highlights that wintertime nitrate formation can be an important contributor to aerosol particles, especially during haze periods.

Key words: air quality; haze day; Shenzhen; water-soluble inorganic ions

1 INTRODUCTION

Haze refers to the weather phenomenon in which the average daily visibility is less than 10 km (7.5 km for remote sensing) due to suspended solid, liquid particles and water vapor in the atmosphere. It is closely related to meteorological conditions and air quality \cite{1}. Haze events have adverse effects on visibility, human health, and global climate change \cite{2,3}. Fine particulates (PM\textsubscript{2.5}, aerodynamic equivalent diameter less than 2.5μm) are considered as important contributors to haze formation, due to their effects on light extinction \cite{4}. Secondary inorganic species are the important components of PM\textsubscript{2.5}, and have attracted wide attention due to their adverse impacts on visibility \cite{5,4}. Due to the characteristics of atmospheric aerosols and other influencing factors, the meteorological parameters in different regions may be different, and the formation mechanism is also different. Previous studies also have pointed out that the characteristics and formation mechanisms could be different between haze and non-haze events \cite{7,4}.

The Pearl River Delta region is one of the four regions with the strongest haze influence in China \cite{9}. Shenzhen is one of China's megacities with a population of 12 million. Located west of the Pearl River Estuary and the Lingdingyang Bay, Shenzhen is a hub connecting Hong Kong with the inland cities of the Pearl River Delta. Shenzhen is located in a transitional zone of the East Asian monsoon system, where the southeaster summer monsoon from the South China Sea. With the rapid growth of local industrial fuel consumption and the number of motor vehicles, Shenzhen has experienced increased air pollution, reflected in the frequency of haze events \cite{10}. The worst period was in 2004, during which there were 187 days with haze events. Compared with other parts of northern China, Shenzhen has seen significant improvement in air quality \cite{11}, but serious pollution events still occur occasionally in winter. Most existing studies were mainly based on sampling and off-
line observations, which have limitations in providing further understanding of the characteristics and the roles played by major chemical species during haze events\textsuperscript{[10, 12]}. There are few reports about the composition and formation mechanism of PM\textsubscript{2.5} in the haze formation process. In this study, a comprehensive monitoring campaign was carried out in Shenzhen to better understand the cause of haze events from Jan to Mar of 2016 through an online monitoring systems. This study aims to obtain a complete picture of pollution events and to understand formation mechanisms of secondary inorganic aerosols and their relationship with haze events.

2 DATA AND METHODS

The observation site (22°32’N, 114°0’E, altitude 63 meters) is located in Shenzhen Garden Expo Park. The surrounding region of this site is mainly commercial and living areas, without large industrial sources (Fig. 1). Ozone (O\textsubscript{3}), sulfur dioxide (SO\textsubscript{2}), nitric dioxide (NO\textsubscript{2}) and carbon monoxide (CO) are measured using online commercial analyzers (Thermo Instruments, USA, TEI 49i, 43i, 42i, and 48i respectively) with the lowest detection limit of 1 ppb (10 seconds average time) and 0.50 ppb (300 seconds average time), 0.40 ppb (60 seconds average time), 0.04 ppm (10 seconds average time) respectively. These instruments are maintained, including zero and span calibrations weekly (each lasting for 30 minutes), and a multi-point calibration every month. PM\textsubscript{2.5} is measured by ambient Particulate Monitor (Grimm 180, Grimm Aerosol Technik GmbH & Co. KG, Germany) based on laser scattering theory, which can obtain the mass concentrations in different particle size segments.

Hourly real-time concentrations of gases and particulate water-soluble inorganic ions in PM\textsubscript{2.5} are determined by the Monitor for Aerosols and Gases (MARGA, Applikon Analytical B. B. Corp., ADI2080, Netherlands). The details of MARGA system have been provided in Du et al.\textsuperscript{[13]}. MARGA includes a sampling unit and an analytical unit. The sampling unit consists of two parts: one is a wet rotating denuder (WRD) for absorbing gas (HCl, HONO, SO\textsubscript{2}, HNO\textsubscript{3}, and NH\textsubscript{3}) and the other is a steam jet aerosol collector (SJAC) for collecting particles. Ambient air is drawn through the WRD followed by the SJAC. Gaseous and particles components are collected for ion chromatographic (IC) analysis, respectively. The IC is continuously controlled by an internal calibration method using a standard lithium bromide (LiBr). In this work, the concentrations of trace gases (i.e., NH\textsubscript{3}) and water-soluble inorganic ions (i.e., NH\textsubscript{4}+, Na\textsuperscript{+}, K\textsuperscript{+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Cl\textsuperscript{-}, NO\textsubscript{3}⁻, and SO\textsubscript{4}²⁻) in PM\textsubscript{2.5} were analyzed. During the observation period, the slope of 1.02 for regression and scattering of anions (AE)and cations(CE) (see (1) and (2) for calculation formula) (Fig. 2) (\(R^2=0.99\)) indicated that the particles are neutral.

\[
\begin{align*}
\text{CE} & = \frac{\text{Na}^+}{23} + \frac{\text{NH}_4^+}{18} + \frac{\text{K}^+}{39} + \frac{\text{Mg}^{2+}}{12} + \frac{\text{Ca}^{2+}}{20} \\
\text{AE} & = \frac{\text{SO}_{4}^{2-}}{48} + \frac{\text{NO}_3^-}{62} + \frac{\text{Cl}^-}{35.5}
\end{align*}
\]

Figure 1. The sampling site in Shenzhen.

Figure 2. Scatter plots of anions and cations in PM\textsubscript{2.5}.
Meteorology variables such as wind speed, wind direction, relative humidity (RH), and temperature are observed by MAW301 (Vaisala Corp. Finland). Atmospheric visibility is also observed by a PWD20 (Vaisala Corp. Finland). The station is local in Shenzhen National Basic Synoptic station, which is 50 meters away from the observation site of air pollutants.

The observation period is from January 1 to March 30, 2016. The MARGA data from January 31 to February 3, February 25, February 28-29, and March 30 are missing due to instrumental failure.

3 RESULTS

3.1 PM$_{2.5}$, and trace gases levels under different visibility conditions

In this study, three different visibility conditions are defined: the daily visibility >15km is defined as a relatively clean condition, denoted as V1; 5 km < the daily visibility <7.5km with no precipitation is defined as haze day, denoted as V2; the daily visibility <5km with no precipitation is defined as the heavy haze day, denoted as V3. Table 1 shows the average concentrations of several atmospheric pollutants (PM$_{2.5}$, SO$_2$, NO$_x$, and O$_3$) and the meteorological conditions (visibility, temperature, relative humidity and wind speed) under different visibility conditions. During haze events, the daily of PM$_{2.5}$ are higher than the average concentration during the observation period (33.1 ± 16.2 μg m$^{-3}$), was about 2 times of that during clear days. The highest PM$_{2.5}$ hourly concentrations exceed 50 μg m$^{-3}$, with a maximum value reaching 125 μg m$^{-3}$. The mean concentration of SO$_2$ changed slightly, during haze days compared to those during clear days. The concentration of NO$_x$ increased by 64% and 89%, respectively, during haze days and heavy haze day compared to those during non-haze days. In contrast, mean O$_3$ level were much higher during clear days than during haze days, implying lower atmospheric oxidation potential during haze events. As expected, unfavorable weather conditions (high RH, low wind speed) were among the causes of haze formation as well as in many other cities [14-16].

<table>
<thead>
<tr>
<th>Species</th>
<th>Numbers (Hour)</th>
<th>PM$_{2.5}$ (μg m$^{-3}$)</th>
<th>SO$_2$ (ppb)</th>
<th>NO$_x$ (ppb)</th>
<th>O$_3$ (ppb)</th>
<th>Vis (km)</th>
<th>T (°C)</th>
<th>RH (%)</th>
<th>WS (m s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>2184 Aver.$^a$</td>
<td>32.1</td>
<td>4.16</td>
<td>25.8</td>
<td>19.0</td>
<td>10.3</td>
<td>15.7</td>
<td>75</td>
<td>1.8</td>
</tr>
<tr>
<td>V1</td>
<td>168 Aver.</td>
<td>27.6</td>
<td>5.0</td>
<td>20.2</td>
<td>27.9</td>
<td>17.2</td>
<td>14.7</td>
<td>53</td>
<td>2.0</td>
</tr>
<tr>
<td>V2</td>
<td>216 Aver.</td>
<td>53.6</td>
<td>4.5</td>
<td>39.8</td>
<td>20.1</td>
<td>5.7</td>
<td>16.9</td>
<td>77</td>
<td>1.4</td>
</tr>
<tr>
<td>V3</td>
<td>72 Aver.</td>
<td>64.6</td>
<td>5.1</td>
<td>46.8</td>
<td>24.7</td>
<td>5.0</td>
<td>18.4</td>
<td>77</td>
<td>1.3</td>
</tr>
<tr>
<td>V1/V2</td>
<td>0.5</td>
<td>1.1</td>
<td>0.51</td>
<td>1.4</td>
<td>0.9</td>
<td>0.7</td>
<td>0.7</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>V1/V3</td>
<td>0.4</td>
<td>1.0</td>
<td>0.4</td>
<td>1.1</td>
<td>0.8</td>
<td>0.7</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ the average concentration. $^*$ standard deviation.

Figure 3 shows the diurnal variation of the hourly averaged SO$_2$, NO$_x$, and PM$_{2.5}$ under different visibility conditions. For gas-phase compounds (SO$_2$, CO, and NO$_x$) are mainly affected by near-surface direct emissions, while O$_3$ is mainly affected by photochemical reactions. We observe very different diurnal variations between the two types of species. The concentrations of NO$_x$ are relatively high during the morning and evening rush hours, and the concentration rapidly decreases around 10:00 p.m.. In addition, the height of the atmospheric boundary layer (PBL) is also the main factor affecting the change of NO$_x$ concentrations [17]. In the morning, the PBL is lower, and the NO$_x$ concentrations are higher. With the gradual elevation of the PBL, the NO$_x$ concentrations reach the lowest level at noon. In contrast, SO$_2$ shows one distinct peak, with peaks occurring at 18:00, because SO$_2$ is mainly affected by long-distance transport and elevation of the PBL [18]. As photochemical reaction is the main source of ozone [15], O$_3$ shows the highest concentrations at around noon.

Under different visibility conditions (V1, V2, and V3), the gas-phase compounds and PM$_{2.5}$ exhibit different behavior. The difference is mainly reflected in the magnitudes of concentrations. All gas and PM$_{2.5}$ (except for O$_3$) show higher concentrations under low visibility. In contrast, O$_3$ level in haze events presents a consistent low concentration and stable daily variation. The relatively low levels of O$_3$ under low visible conditions might be due to the decreased photochemical production. It should be noted that the concentration of O$_3$ in V3 is relatively higher than that in V2, due to ozone pollution at night. Because nocturnal low-level jets (LLJs) will enhance vertical mixing between the
Diurnal variation of the hourly averaged SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}\textsuperscript{-}, O\textsubscript{3}, and PM\textsubscript{2.5} under different visibility conditions for the whole measurement period.

### 3.2 Chemical compositions of PM\textsubscript{2.5}

The mean concentrations of water-soluble inorganic ions (WSIs) during the observation period is 12.4±1.4 μg m\textsuperscript{-3}, accounting for 37% of PM\textsubscript{2.5} mass concentration. SO\textsubscript{4}\textsuperscript{2-} is the most abundant species in water-soluble inorganic ions, with an average of 5.1 ± 4.1 μg m\textsuperscript{-3}, followed by NO\textsubscript{3}\textsuperscript{-} (3.5±4.5 μg m\textsuperscript{-3}) and NH\textsubscript{4}\textsuperscript{+} (2.8±2.6 μg m\textsuperscript{-3}), accounting for 41%, 29% and 23% of the total concentrations, respectively. The sum of the three components accounts for 93% of the total concentration of the WSIs, which is close to that of Beijing and Suzhou\textsuperscript{16, 19}. Except for the three ions, the proportions of Na\textsuperscript{+} (0.10±0.17 μg m\textsuperscript{-3}), Cl\textsuperscript{-} (0.53±0.50 μg m\textsuperscript{-3}), K\textsuperscript{+} (0.14±0.31 μg m\textsuperscript{-3}), Mg\textsuperscript{2+} (0.02±0.05 μg m\textsuperscript{-3}) and Ca\textsuperscript{2+} (0.15±0.11μg m\textsuperscript{-3}) are lower than 3%.

<table>
<thead>
<tr>
<th>WSIs</th>
<th>NO\textsubscript{3}</th>
<th>SO\textsubscript{4}\textsuperscript{2-}</th>
<th>NH\textsubscript{4}</th>
<th>Na\textsuperscript{+}</th>
<th>K\textsuperscript{+}</th>
<th>Mg\textsuperscript{2+}</th>
<th>Ca\textsuperscript{2+}</th>
<th>Cl\textsuperscript{-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>can (μg m\textsuperscript{-3})</td>
<td>1.72</td>
<td>3.40</td>
<td>1.47</td>
<td>0.02</td>
<td>0.48</td>
<td>0.06</td>
<td>0.08</td>
<td>0.37</td>
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</table>

<table>
<thead>
<tr>
<th>WSIs</th>
<th>NO\textsubscript{3}</th>
<th>SO\textsubscript{4}\textsuperscript{2-}</th>
<th>NH\textsubscript{4}</th>
<th>Na\textsuperscript{+}</th>
<th>K\textsuperscript{+}</th>
<th>Mg\textsuperscript{2+}</th>
<th>Ca\textsuperscript{2+}</th>
<th>Cl\textsuperscript{-}</th>
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<tr>
<td>can (μg m\textsuperscript{-3})</td>
<td>6.75</td>
<td>9.73</td>
<td>5.40</td>
<td>0.32</td>
<td>0.30</td>
<td>0.06</td>
<td>0.25</td>
<td>1.26</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>WSIs</th>
<th>NO\textsubscript{3}</th>
<th>SO\textsubscript{4}\textsuperscript{2-}</th>
<th>NH\textsubscript{4}</th>
<th>Na\textsuperscript{+}</th>
<th>K\textsuperscript{+}</th>
<th>Mg\textsuperscript{2+}</th>
<th>Ca\textsuperscript{2+}</th>
<th>Cl\textsuperscript{-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>can (μg m\textsuperscript{-3})</td>
<td>8.22</td>
<td>10.06</td>
<td>5.88</td>
<td>0.56</td>
<td>0.61</td>
<td>0.13</td>
<td>0.28</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Figure 3. Diurnal variation of the hourly averaged SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}\textsuperscript{-}, O\textsubscript{3}, and PM\textsubscript{2.5} under different visibility conditions for the whole measurement period.

Figure 4. Water-soluble inorganic ion species under different visibility conditions.
The average concentration of WSIs in V1 was 10.4±5.1 μg m⁻³, while the concentration of WSIs in V2 and V3 was 2.8 and 3.2 times as much as that in V1, respectively. The mean concentrations of SO₄²⁻ and NO₃ during V1 are 3.40 μg m⁻³ and 1.72 μg m⁻³, respectively, accounting for 44.7% and 22.7%, and the ratio NO₃ / SO₄²⁻ is 0.50. With decreasing visibility, the ratios of NO₃/SO₄²⁻ increased. During V2 and V3, the ratios of NO₃/SO₄²⁻ increases markedly, with 0.69 and 0.82 respectively, the corresponding concentrations of NO₃ and SO₄²⁻ are 6.74 μg m⁻³, 8.21 μg m⁻³ and 9.73 μg m⁻³, 10.06 μg m⁻³. The ratio of NO₃/SO₄²⁻ during the pollution period is greater than that during the non-haze days, and the result is in agreement with the results in Guangzhou and Suzhou⁹, 20. In the present study, NO₃ concentration greatly exceeded that of SO₂ during haze periods. Under high NO₃ condition, concentration of OH and H₂O₂ were reduced, further decreasing the possibility of SO₄²⁻ formation⁸. Thus, the elevation of NO₃ concentration under worse visibility conditions is greater than that of SO₄²⁻ and contribute higher to the reduction of visibility. At the same time, the ratio of NO₃ / SO₄²⁻ tend to be larger when air pollution became more serious. For examples, the ratio of NO₃/SO₄²⁻ during V1 (clean day), V2 (haze day) and V3 (heavy haze day) increases gradually.

NO₃⁻ and SO₄²⁻ represent the secondary aerosol from transformation of the precursors of NOₓ and SO₂⁹. The study in the Yangtze River Delta showed that the emission ratio of NO₃ / SO₄ for motor vehicles is 17.2-52.6, while the ratio of NOₓ / SO₂ for stationary sources, such as factories, etc., is 0.527-0.804¹⁹. Thus, the ratio of NO₃ / SO₄²⁻ is used as an important indicator of relative importance of mobile versus stationary sources of sulfur and nitrogen in atmosphere ²¹. The ratio of NO₃ / SO₄²⁻ during the observation period in this study is 0.65 and the ratio of NO₃ / SO₂ is 6.2, indicating that both the automobile exhaust and the stationary sources are very important in Shenzhen. The ratios of NO₃ / SO₄²⁻ in Shenzhen is greater than that of some other areas in China, such as Shanghai (0.43), Qingdao (0.35), Taiwan (0.2), Guiyang (0.13), Suzhou (0.59) ²⁰, 22-23. At the same time, previous studies had shown that the ratios of NO₃ / SO₄²⁻ in Shenzhen in 2004 and in 2009 were 0.26 and 0.62 respectively ²⁷, lower than the results in this study, indicating that the ratio of NO₃ / SO₄²⁻ had gradually increased. From 2004 to 2017, the number of car ownership in the Shenzhen area had continuously increased from 660,000 to 3.4 million. The Pearl River Delta region had taken desulfurization measures starting from the “Eleventh Five-Year Plan”, which may be one reason for the increase in the ratio of NO₃ / SO₄²⁻, indicating that the automobile exhaust emissions may have increasingly important impacts on pollution in Shenzhen.

![Figure 5. Distribution of wind direction and the ratio of NO₃⁻ (a), SO₄²⁻ (b), NO₃/SO₄²⁻ (c) on haze days.](image)

![Figure 6. Time series of water soluble inorganic icons, wind speed, wind direction and RH from January 1 to January 2, 2016.](image)
The relationship between the ratio of NO$_3^-$/SO$_4^{2-}$ and wind direction during haze events is illustrated in Fig. 5. The result shows that the ratio of NO$_3^-$/SO$_4^{2-}$ is relatively large, when the sea breezes (southerly wind and westerly winds). But when the land breezes (northerly and easterly wind), the ratio of NO$_3^-$/SO$_4^{2-}$ is relatively lower. It indicates that the land and sea breeze could affect the formation of pollution in Shenzhen, though the regional transportation from the inland area of Pearl River Delta is still important to the formation of the pollution events. To take the haze event (shown in Fig. 6) as an example, the haze event occur from January 1 to January 2, 2016. A weak northerly wind started and lasted from the night of December 31, 2015 to 10:00 a.m on January 1, 2016. Subsequently, the direction of wind turned to south and the sea breezes gradually dominated. As the wind became sea breezes, the ratio of NO$_3^-$/SO$_4^{2-}$ was large. Previous studies have indicate that the land breezes (northerly winds) can transport the local pollutants in Shenzhen to the sea, and the sea breezes can transport the pollutants back to Shenzhen$^{[23]}$. The higher relative humidity was a beneficial factor for heterogeneous reactions when sea breezes occur. At the same time, high NO$_3^-$ concentration further reduces the possibility of SO$_4^{2-}$ generation$^{[5]}$.

3.3 Conversion from gas to particle phases

Sulfur oxidation rate (SOR=($n$(SO$_4^{2-}$)/($n$(SO$_4^{2-}$) + $n$(SO$_3$))) and nitrogen oxidation rate (NOR=$n$(NO$_3^-$)/($n$(NO$_3^-$) + $n$(NO$_2$))) can be used to estimate the transformation degree of sulfates and nitrates$^{[29]}$. During haze days, the values of NOR and SOR in Shenzhen are 2.5 and 2.2 times higher than those in clean days (V1), implying more significant transformation of sulfates and nitrates and more elevated secondary aerosols during haze days.

Gaseous SO$_3$ is converted to particulate sulfate through gas-phase oxidation by H$_2$O and OH radical or aqueous reactions $^{[29]}$. It has been reported in many studies that the oxidation of aqueous SO$_3$ catalyzed by transition metals are more efficient during winter haze, compared to gas-phase oxidation. Our measurements also suggest that aqueous oxidation is an important sulfate formation pathway in the region of study. As shown in Fig. 7, during haze events, the concentrations of RH, NH$_3$, and NO$_x$ increase rapidly, especially RH and NOx. For example, from V1 to V2, RH and NO$_x$ increase rapidly from 53% and 20.2 ppb to 77% and 39.8 ppb, respectively $^{[31]}$, indicating that high RH and the elevation of NH$_3$ concentration can provide suitable conditions for aqueous oxidation of SO$_3$. The high level of NO$_3^-$ enhances the atmospheric oxidizing capability during hazy events. Therefore, the aqueous oxidation may be an important way to form sulfate in Shenzhen in winter.

![Figure 7. Box plot of aerosol precursors (SO$_2$, NO$_x$, NH$_3$, O$_3$, and RH during V1 (red), V2 (blue) and V3 (yellow) and specify the quartiles represented and the meaning of the black dot and the white line in the boxes.)](image)
indicating efficient gas to the concentrations were higher (\textit{...}), which especially. At the same time, O\textsubscript{3} in clear days and tend to be larger when air is greater than 0, with a linear correlation with the nitrate concentration, indicating that the gas-phase homogeneous reaction between the ambient ammonia and nitric acid is responsible for forming nitrate\textsuperscript{[15, 20]}. The ratio of major secondary ionic species during the sum of the three components accounts for 93\% of the total WSIIs. The sum of the major secondary ionic species during haze periods was about 2.8 times of that during clear days. During the haze period, SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}- and NH\textsubscript{4}+ increased significantly, especially NO\textsubscript{3}-. The ratio of NO\textsubscript{3}-/SO\textsubscript{4}\textsubscript{2-} is 0.50 in clear days and tend to be larger when air pollution became more seriously. At the same time, compared with previous studies, it is found that this ratio has been gradually increasing, indicating that vehicle emissions have an increasingly impacts on pollution.

During haze events, the gas-phase and aerosol components showed higher concentrations, especially major aerosol components (SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}- and NH\textsubscript{4}+), which were mainly from secondary sources. When visibility became lower, the concentrations were higher. Furthermore, SOR and NOR was higher during the haze period than that in clean days, indicating efficient gas to particle conversion. Further analysis shows that high concentrations of sulfate might be explained by aqueous oxidation, but gas-phase homogeneous reactions might dominate the formation of nitrate.

4 CONCLUSIONS

Haze events frequently occurred in Shenzhen in 2016, with a total of nine haze days in total from January to March. The PM\textsubscript{2.5} concentration during haze days was higher than the average value during the entire observation, with the highest value reaching 125 \textmu g m\textsuperscript{-3}. The high concentrations of NO\textsubscript{2} and lower levels of O\textsubscript{3} were observed during haze periods in comparison with clear days. Unfavorable meteorological conditions, such as low wind speed and high humidity, together with pollutants accumulation and secondary formation of aerosol are responsible for these haze formations.

The mean concentration of the WSIIs during the observation period was 12.4\pm11.4 \textmu g m\textsuperscript{-3}, accounting for 37\% of PM\textsubscript{2.5}, among which SO\textsubscript{4}\textsuperscript{2-} was the highest element, followed by NO\textsubscript{3}- and NH\textsubscript{4}+. The sum of the three components accounts for 93\% of the total WSIIs. The sum of the major secondary ionic species during haze periods was about 2.8 times of that during clear days. During the haze period, SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}- and NH\textsubscript{4}+ increased significantly, especially NO\textsubscript{3}-.

![Figure 8. Nitrate to sulfate molar ratio as a function of ammonium to sulfate molar ratio (left) and the relationship between molar concentrations of nitrate and excess ammonium (right).](image-url)


