Pollution Characteristics of Water-Soluble Inorganic Ions in PM$_{2.5}$ from a Mountainous City in Southwest China

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Abstract: In order to explore the characteristics of water-soluble inorganic ions (WSIIs) in the atmosphere of Wanzhou, a small mountainous city in Chongqing, four representative seasonal PM$_{2.5}$ samples and gaseous precursors (SO$_2$ and NO$_2$) were collected from April 2016 to January 2017. The WSIIs (including Cl$^-$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, and Ca$^{2+}$) were analyzed by ion chromatography. During the sampling period, daily PM$_{2.5}$ concentration varied from 3.47 to 156.30 g m$^{-3}$, with an average value of 33.38 g m$^{-3}$, which was lower than the second-level annual limit of NAAQS-China. WSIIs accounted for 55.6% of PM$_{2.5}$, and 83.1% of them were secondary inorganic ions (SNA, including SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$). The seasonal variations of PM$_{2.5}$ and WSIIs were similar, with the minimum in summer and the maximum in winter. PM$_{2.5}$ samples were the most alkaline in summer, weakly alkaline in spring and winter, and close to neutral in fall. The annual average ratio of NO$_3^-$/SO$_4^{2-}$ was 0.54, indicating predominant stationary sources for SNA in Wanzhou. NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$ mainly existed in the form of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$. The results of the principal component analysis (PCA) showed that the major sources of WSIIs in Wanzhou were the mixture of secondary inorganic aerosols, coal combustion, automobile exhaust (49.53%), dust (23.16%), and agriculture activities (9.68%). The results of the backward trajectory analysis showed that aerosol pollution in Wanzhou was mainly caused by local emissions. The enhanced formation of SNA through homogeneous and heterogeneous reactions contributed to the winter PM$_{2.5}$ pollution event in Wanzhou.

Keywords: PM$_{2.5}$; water-soluble inorganic ions; source apportionment

1. Introduction

Atmospheric fine particulate matter (PM$_{2.5}$, with aerodynamic diameter $\leq$ 2.5 µm particulate matter) is one of the primary air pollutants in most cities [1,2]. Due to the characteristics of small particle size, higher surface/mass ratio, and easy retention in the air, PM$_{2.5}$ easily becomes the reactant and carrier of other pollutants, thus enriching more harmful chemical components [3]. Chemical components of PM$_{2.5}$ include organic carbon (OC), elemental carbon (EC), water-soluble inorganic ions (WSIIs), crustal elements, and various trace elements. WSIIs are the main components of PM$_{2.5}$, which affect the formation of cloud condensation nuclei, atmospheric extinction coefficient, atmospheric radiation balance, and precipitation acidity, and harm human health [4–6]. Secondary inorganic ions (SNA, including SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$) are the dominant components, usually accounting for 50%–90% of WSIIs [5,7–9]. In addition, studies showed that the proportion of SNA increased significantly during severe haze periods, indicating that they play a crucial role in haze formation and visibility impairment [10–13].
Many studies related to PM$_{2.5}$ and WSIs have focused on large or megacities in China, such as Beijing, Shanghai, Guangzhou, and Tianjin [11,14–16]. Those studies showed that the concentration of WSIs was mainly determined by local emissions and regional transportation, and meteorological conditions (e.g., temperature, humidity, wind speed, etc.) can also affect the distribution and pollution characteristics of WSIs through chemical processes and physical diffusion. From the perspective of spatial distribution, the concentrations of WSIs in the Beijing–Tianjin–Hebei area (BTH) [2,17,18], Fenwei Plain [1,19], and Sichuan Basin [5,9] were higher than those in the Pearl River Delta (PRD) [20,21] and coastal region [22,23] in China. In terms of inter-annual variation, PM$_{2.5}$ concentrations in major cities have shown a downward trend since the Chinese government issued the Air Pollution Prevention and Control Action Plan (APPCAP) in 2013 [24]. The composition proportion of WSIs in PM$_{2.5}$ and source contributions of WSIs varied remarkably. For example, many studies showed that the concentration of SO$_4^{2−}$ had a declining trend in recent years due to strict strategies implemented in China, such as installing desulphurization systems in coal-fired power plants and conversion of fuel to natural gas [5,25,26]. However, the concentration of NO$_3^{−}$ was found to have an increasing trend; therefore, a transition from sulfate-driven to nitrate-driven aerosol pollution appeared in some cities [26–29]. In terms of seasonal variation, the highest concentrations of PM$_{2.5}$ and its WSIs were mostly observed in the cold seasons regardless of geographical regions in China. In winter, the enhanced emissions of coal combustion and biomass burning, as well as stagnant meteorological conditions, such as low wind speed and high relative humidity, were responsible for PM$_{2.5}$ pollution [24,30–33].

Wanzhou, as an important transportation hub city, is located in the border area of six provinces and cities, namely northeast Chongqing, northeast Sichuan, southern Shaanxi, western Hubei, western Hunan, and northern Guizhou. It is also the eastern opening gateway of the Chengdu–Chongqing twin city economic circle and the regional center city of northeast Chongqing Three Gorges Reservoir Area town group. It has high relative humidity and low wind speed all year round, which makes the air pollution in this area more serious [34]. Previous studies on air pollution in Wanzhou were all about PM$_{2.5}$ and its carbonaceous components. For example, Zhang et al. (2015) found that annual average PM$_{2.5}$ concentrations were 125.3 µg m$^{-3}$ in 2013 in Wanzhou, which was 3.6 times higher than the National Ambient Air Quality Standards of China (NAAQS-China, annual limit of 35 µg m$^{-3}$) [35]. Huang et al. (2020) found annual fine particle black carbon (BC) mean displayed a significantly decreasing trend in Wanzhou since the implementation of APPCAP, from 5.3 µg m$^{-3}$ in 2013 to 3.7 µg m$^{-3}$ in 2017 [36]. However, the characteristics of WSIs in Wanzhou are still unknown. In order to provide effective guidance for local governments to formulate pollution prevention and control policies for PM$_{2.5}$, a comprehensive sampling of PM$_{2.5}$ was conducted in Wanzhou from April 2016 to January 2017 to obtain the concentration data of WSIs in PM$_{2.5}$. In this study, WSIs’ mass concentration level and seasonal variation characteristics were firstly analyzed. Then, the chemical forms of main secondary ions and their formation mechanisms were discussed. Finally, the main sources of PM$_{2.5}$ were identified through principal component analysis (PCA). In addition, the formation mechanism of an air pollution event that occurred in winter was explored in this study.

2. Materials and Methods
2.1. PM$_{2.5}$ Sampling

PM$_{2.5}$ samples were collected on a rooftop of the experimental building about 27 m above the ground (30.79° N, 108.37° E) within the Chongqing Three Georges University (Figure 1) in Wanzhou, a small urban city located about 228 km northeast of the megacity Chongqing. The monitoring site is surrounded by residential and commercial areas, agricultural fields, and a main traffic road (Shalong road). There is no fixed atmospheric pollution source within 1 km of the sampling site.
Two PM$_{2.5}$ samples were collected in parallel by one sampler (URG-3000K, URG Corp., Carrboro, NC, USA) with a flow rate of 15 L·min$^{-1}$. The left channel was connected with an annular denuder and Teflon filter (diameter 47 mm), while the right channel was connected with a quartz filter (diameter 47 mm). PM$_{2.5}$ mass was the sum of the weight of the Teflon filter and quartz filter (after deducting the mass of the blank filters) and then divided by the sum of the volume of the left and right channels. PM$_{2.5}$ samples were collected for 30 days in each of the four seasons: spring (8 April to 7 May 2016); summer (7 July to 5 August 2016); fall (14 October to 12 November 2016); winter (18 December 2016 to 16 January 2017). The sampling duration was 23 h per day, from 11:00 am to 10:00 am (the next day). A total of 120 days of PM$_{2.5}$ samples were collected. The annular denuder was wetted with glycerol/citric acid solution to absorb NH$_3$ from the air. Hourly concentrations of NO$_2$ and SO$_2$ were measured by on-line gas analyzers, including Thermo 42i NO$_2$ and 43i SO$_2$ analyzers (Thermo Scientific Corp., Waltham, MA, USA). NO$_2$ and SO$_2$ were averaged in the same periods as PM$_{2.5}$. At the same time, the meteorological parameters were also collected by weather stations (WS500-UMB, Lufft Corp., Fellbach, Germany) during the sampling period, and the main meteorological parameters and air pollutant concentrations are listed in Table 1.

### Table 1. Meteorological data and air pollutant concentrations during the sampling period.

<table>
<thead>
<tr>
<th>Season</th>
<th>T/(°C)</th>
<th>RH/%</th>
<th>WS/(m·s$^{-1}$)</th>
<th>Radiation/(W·m$^{-2}$)</th>
<th>NH$_3$/($\mu$g·m$^{-3}$)</th>
<th>NO$_2$/($\mu$g·m$^{-3}$)</th>
<th>SO$_2$/($\mu$g·m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>20.61</td>
<td>76.62</td>
<td>0.95</td>
<td>151.18</td>
<td>18.86</td>
<td>44.38</td>
<td>8.55</td>
</tr>
<tr>
<td>Summer</td>
<td>30.03</td>
<td>68.28</td>
<td>1.01</td>
<td>226.82</td>
<td>14.57</td>
<td>23.60</td>
<td>12.40</td>
</tr>
<tr>
<td>Fall</td>
<td>17.41</td>
<td>83.30</td>
<td>0.73</td>
<td>65.87</td>
<td>11.98</td>
<td>31.63</td>
<td>13.23</td>
</tr>
<tr>
<td>Winter</td>
<td>10.41</td>
<td>76.27</td>
<td>0.74</td>
<td>120.89</td>
<td>14.49</td>
<td>38.37</td>
<td>12.49</td>
</tr>
<tr>
<td>Annual</td>
<td>19.69</td>
<td>76.27</td>
<td>0.86</td>
<td>120.89</td>
<td>14.49</td>
<td>38.37</td>
<td>12.49</td>
</tr>
</tbody>
</table>

T, temperature; WS, wind speed; RH, relative humidity.

2.2. Ions Analysis

The adsorbed NH$_3$ was eluted with ultrapure water, and the eluent was then filtered by a 0.45μm poresyringe filter. PM$_{2.5}$ samples were ultrasonically extracted with ultrapure water, and then the extracted solution was filtered by a 0.45μm poresyringe filter. Eight WSIIs, including SO$_4^{2-}$, NO$_3^-$, Cl$^-$, Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, and Ca$^{2+}$, were determined using ion chromatography (Dionex-600, Dionex Corp., Sunnyvale, CA, USA). The cationic column CS12A and anionic column AS11-HC were used for sample analysis. The eluent used for the determination of cations was 20 mmol·L$^{-1}$ MSA (methanesulfonic acid) at a flow rate of 1 mL·min$^{-1}$. The anionic eluent was 30 mmol·L$^{-1}$ KOH at a flow rate of 1 mL·min$^{-1}$. The reference materials were prepared with the anionic and cationic standard
solutions of O2Si from the United States, and the correlation coefficient of each standard curve can reach 0.999. Blank and standard samples were repeated every ten samples.

3. Results and Discussion

3.1. Concentrations of PM$_{2.5}$ and WSIIs

During the sampling period, daily PM$_{2.5}$ concentration varied from 3.47 to 156.30 µg·m$^{-3}$ with an average value of 33.38 µg·m$^{-3}$, which was lower than the NAAQS-China (annual limit of 35 µg·m$^{-3}$). The PM$_{2.5}$ concentration in Wanzhou was significantly lower than that in Chongqing urban areas such as Fuling, Yubei, and Beibei and lower than that in Jin Yun mountain, a rural background of Chongqing. (Table 2). In addition, compared with other cities in China, it was much lower than Handan, Taiyuan, Chengdu, and Neijiang and comparable to Nanning and Kunming. In general, the PM$_{2.5}$ concentration in Wanzhou is relatively low in China. It is worth noting that the annual average PM$_{2.5}$ concentration in this study decreased by 73.4% compared to the previous report in 2013 [35]. Since the implementation of the APPCAP in 2013, the Chongqing municipal government has taken a series of corresponding measures to improve the city’s air quality, such as eliminating yellow-labeled vehicles, installing desulphurization systems in coal-fired power plants, controlling dust pollution, and banning the open burning of straw and garbage. These measures have effectively reduced the atmospheric particulate matter concentration in Chongqing. We also found from the literature that the atmospheric particulate matter concentration in other districts of Chongqing has also decreased in recent years. For instance, Chen et al. (2019) found that the PM$_{2.5}$ level decreased by 57.3% in 2012–2013 compared to that in 2005–2006 in Yubei, Chongqing. The PM$_{2.5}$ concentration decreased by nearly 66% and 40% in 2017–2018 compared to that in 2005–2006 and in 2014–2015 in Beibei, Chongqing, respectively [7].

Table 2. Comparison of water-soluble inorganic ion (WSII) concentrations (µg·m$^{-3}$) in Wanzhou to other cities in China.

<table>
<thead>
<tr>
<th>City</th>
<th>Sampling Time</th>
<th>Na$^+$</th>
<th>NH$_4^+$</th>
<th>K$^+$</th>
<th>Mg$^{2+}$</th>
<th>Ca$^{2+}$</th>
<th>Cl$^-$</th>
<th>SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>WSIIs</th>
<th>PM$_{2.5}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wanzhou</td>
<td>2016.04–2017.01</td>
<td>1.48</td>
<td>3.66</td>
<td>0.38</td>
<td>0.10</td>
<td>0.48</td>
<td>0.66</td>
<td>7.53</td>
<td>4.05</td>
<td>18.34</td>
<td>33.16</td>
<td>This study</td>
</tr>
<tr>
<td>Fuling, Chongqing</td>
<td>2015.04–2016.01</td>
<td>6.80</td>
<td>0.57</td>
<td>1.00</td>
<td>13.70</td>
<td>6.70</td>
<td>28.77</td>
<td>66.90</td>
<td></td>
<td></td>
<td></td>
<td>[37]</td>
</tr>
<tr>
<td>Yubei, Chongqing</td>
<td>2015.12–2016.03</td>
<td>0.28</td>
<td>6.56</td>
<td>1.17</td>
<td>0.35</td>
<td>0.28</td>
<td>1.35</td>
<td>17.5</td>
<td>10.9</td>
<td>38.4</td>
<td>67.54</td>
<td>[5]</td>
</tr>
<tr>
<td>Beibei, Chongqing</td>
<td>2017.09–2018.08</td>
<td>0.22</td>
<td>4.87</td>
<td>0.87</td>
<td>0.07</td>
<td>1.51</td>
<td>0.90</td>
<td>9.81</td>
<td>7.36</td>
<td>25.61</td>
<td>43.02</td>
<td>[7]</td>
</tr>
<tr>
<td>Jin Yun mountain, Chongqing</td>
<td>2014.10–2015.07</td>
<td>5.5</td>
<td>0.48</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[38]</td>
</tr>
<tr>
<td>Chengdu</td>
<td>2012–2013</td>
<td>0.45</td>
<td>9.0</td>
<td>1.23</td>
<td>0.07</td>
<td>0.44</td>
<td>2.46</td>
<td>17.7</td>
<td>11.9</td>
<td>43.0</td>
<td>86.7</td>
<td>[39]</td>
</tr>
<tr>
<td>Neijiang</td>
<td></td>
<td>0.21</td>
<td>8.2</td>
<td>1.17</td>
<td>0.06</td>
<td>0.32</td>
<td>0.69</td>
<td>17.6</td>
<td>7.8</td>
<td>35.4</td>
<td>78.6</td>
<td>[40]</td>
</tr>
<tr>
<td>Nanning</td>
<td>2017.09–2018.08</td>
<td>0.19</td>
<td>3.23</td>
<td>0.61</td>
<td>0.08</td>
<td>2.31</td>
<td>0.44</td>
<td>9.14</td>
<td>3.08</td>
<td>19.08</td>
<td>37.02</td>
<td>[41]</td>
</tr>
<tr>
<td>Handan</td>
<td>2013</td>
<td>0.7</td>
<td>1.3</td>
<td>1.8</td>
<td>0.1</td>
<td>1</td>
<td>4.4</td>
<td>25.2</td>
<td>20.6</td>
<td>66.80</td>
<td>131</td>
<td>[18]</td>
</tr>
<tr>
<td>Kunming</td>
<td>2017.09–2018.08</td>
<td>0.13</td>
<td>2.53</td>
<td>0.44</td>
<td>0.09</td>
<td>2.49</td>
<td>0.51</td>
<td>6.84</td>
<td>2.37</td>
<td>15.40</td>
<td>30.27</td>
<td>[41]</td>
</tr>
<tr>
<td>Taiyuan</td>
<td>2015.08–2016.05</td>
<td>0.5</td>
<td>12.7</td>
<td>1.3</td>
<td>0.8</td>
<td>2.6</td>
<td>3.4</td>
<td>19.1</td>
<td>13.1</td>
<td>53.2</td>
<td>109.6</td>
<td>[42]</td>
</tr>
<tr>
<td>Xiangtan</td>
<td>2016.04–2017.01</td>
<td>5.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.8</td>
<td>14.4</td>
<td>9.6</td>
<td>40.9</td>
<td>73.6</td>
<td>[43]</td>
</tr>
</tbody>
</table>

Daily WSIIs concentrations ranged from 3.59 to 106.99 µg·m$^{-3}$, with an annual average concentration of 18.34 µg·m$^{-3}$, accounting for 55.6% of PM$_{2.5}$ mass. This concentration was obviously lower than in other districts of Chongqing, slightly higher than Kunming, and only about 1/3 of WSIIs concentration in Handan and Taiyuan (Table 2). The order of annual average concentrations of the eight ions is SO$_4^{2-}$ > NO$_3^-$ > NH$_4^+$ > Na$^+$ > Cl$^-$ > Ca$^{2+}$ > K$^+$ > Mg$^{2+}$. SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ (SNA) were the most abundant components of WSIIs, accounting for 41.1%, 22.1%, and 19.9% of total WSIIs (TWSIIs), respectively.

3.2. Seasonal Variations of PM$_{2.5}$ and WSIIs

Figure 2 displays the seasonal variation of PM$_{2.5}$ with the maximum in winter (59.82 µg·m$^{-3}$), decreasing through spring (30.87 µg·m$^{-3}$) and fall (25.20 µg·m$^{-3}$), and the minimum in
summer (17.61 µg·m⁻³), which was consistent with that reported at a different site of Chongqing [9]. The pollution of PM₅.₅ was the most serious in winter, with a concentration of 3.4 times that in summer. The number of days exceeding the NAAQS-China daily limit of 75 µg·m⁻³ was 26.7% in winter, while in other seasons, it did not exceed the standard. Stagnant meteorological conditions and biomass burning by residents to keep themselves warm were the major causes of the highest PM₅.₅ mass in winter, while the lower PM₅.₅ mass concentration in summer was mainly due to abundant precipitation favoring wet scavenging [44].

Figure 2. Seasonal variations of PM₂.₅ and WSIIIs.

The seasonal variation of TWSIIIs concentration was similar to PM₂.₅ mass, and the order was winter (30.94 µg·m⁻³) > spring (18.58 µg·m⁻³) > fall (14.28 µg·m⁻³) > summer (9.96 µg·m⁻³). The proportion of WSIIIs in PM₂.₅ mass was ranked as follows: spring (60.2%) ≈ summer (56.6%) > fall (56.7%) > winter (51.7%). The concentration of SNA was the highest in winter (27.06 µg·m⁻³), followed by spring (16.43 µg·m⁻³), fall (11.38 µg·m⁻³), and summer (6.48 µg·m⁻³), which contributed 87.4%, 88.4%, 79.7%, and 65.0% to TWSIIIs, respectively. SO₄²⁻ showed the same seasonal trends as SNA, which were not consistent with those of SO₂: winter > fall > summer > spring. The reason for the highest SO₄²⁻ concentration in winter may be attributed to the formation of abundant precursor SO₂ through heterogeneous aqueous processes reaction. It is noteworthy that SO₂ concentration in spring was 1.6 times lower than that in fall, while the concentration of SO₄²⁻ in spring was 1.5 times higher than that in fall. Compared with the meteorological data (Table 1), it was found that the solar radiation and temperature were stronger in spring than in fall, which was conducive to the formation of SO₄²⁻ through a homogeneous gas phase oxidation reaction. The concentration of NO₃⁻ in winter was 2.3–8.1 times higher than in other seasons. However, there were little differences in the seasonal concentrations of its precursor NO₂, with their concentrations 1.3–1.6 times higher in spring and winter than in other seasons. The variation of NO₃⁻ concentration in particulate matter largely depends on temperature and RH [45]. High temperature and low RH in summer are not conducive to the existence of NO₃⁻ in the form of particulate matter and also cause the loss of NO₃⁻ volatilization in the sampled filter membrane [37,39]. The low temperature and high RH in winter are beneficial for nitrate stabilization. NH₃, mostly from agricultural emissions due to the intensive use of fertilizer, had higher concentrations in spring (18.86 µg·m⁻³) and summer (14.57 µg·m⁻³) than in fall (11.98 µg·m⁻³) and winter (11.65 µg·m⁻³). Abundant acidic substances in winter were conducive to the conversion of NH₃ to NH₄⁺, while high temperature and precipitation scavenging in summer decreased NH₄⁺, leading to a significantly higher concentration of NH₄⁺ in winter than in summer.
Na\(^+\) was another important ion and ranked fourth concentration in WSIIs. Mg\(^{2+}\) and Ca\(^{2+}\) usually come from soil dust, and Na\(^+\) can also come from sea salt in addition to soil dust [46]. In this study, the concentrations of Na\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\) were higher in summer than in other seasons, which may be related to the dust from the surrounding construction sites. K\(^+\) and Cl\(^-\) concentrations were highest in winter, followed by spring and fall, and lowest in summer. K\(^+\) is a representative element of biomass combustion, which reflects the phenomenon of straw and leaf burning in winter. Cl\(^-\) comes not only from biomass burning and fossil fuel burning but also from sea salt [47]. There was a significant correlation between K\(^+\) and Cl\(^-\) in winter, r = 0.97. Considering that Wanzhou does not use coal for central heating in winter and is located away from the coast, biomass burning was likely to be the main cause of higher Cl\(^-\) concentrations in winter.

3.3. Stoichiometric Analysis of Cations and Anions

Figure 3 depicts the linear relationship between cations and anions equivalents in four seasons in Wanzhou. Anion equivalent (AE) and cation equivalent (CE) were calculated as follows:

\[
\text{AE} = \frac{\text{Cl}^-}{35.5} + \frac{\text{SO}^{2-}_4}{48} + \frac{\text{NO}_3^-}{62} \quad (1)
\]

\[
\text{CE} = \frac{\text{Mg}^{2+}}{12} + \frac{\text{NH}_4^+}{18} + \frac{\text{Ca}^{2+}}{20} + \frac{\text{Na}^+}{23} + \frac{\text{K}^+}{39} \quad (2)
\]

Figure 3. Plot of cations concentration vs. anions concentration in four seasons.

As shown in Figure 3, strong correlations between AE and CE were found in all seasons, supporting that the measured eight ions were the major constituents in the PM\(_{2.5}\) ionic components. The annual mean AE/CE ratio (slope of the linear regression) was 0.90, indicating weak alkaline PM\(_{2.5}\) aerosols at Wanzhou. Similar patterns of PM\(_{2.5}\) acidity (AE/CE slope < 1) were also observed in Fuling and Beibei, both small cities of Chongqing [7,37]. Seasonally, except for fall, the slopes of the line for spring, summer, and winter were lower than 1. In summer, the slope of the line was 0.54, demonstrating an apparent deficiency of anions of PM\(_{2.5}\) samples, which can be attributed partly to the measurement of bicarbonate and carbonate as well as the elevated concentrations of alkaline dust particles in summer, such as Na\(^+\) and Ca\(^{2+}\); thus PM\(_{2.5}\) samples showed alkaline feature. In spring and winter, the slopes of the line were 0.94 and 0.86, respectively, indicating a weakly alkaline property, which can be ascribed to the high levels of acid ions of SO\(_4^{2-}\) and NO\(_3^-\) in spring and winter. In the fall, most of the samples generally showed a balance between anions and cations, and the slope of the line was almost equal to 1.
3.4. Formation Path of SO$_4^{2-}$ and NO$_3^-$

NO$_3^-$ and SO$_4^{2-}$ are mainly secondary ions formed by gaseous precursors (NO$_x$, SO$_2$) through atmospheric chemical reactions. The mass ratio of NO$_3^-$/SO$_4^{2-}$ is commonly used to assess the relative influence of mobile or stationary sources on atmospheric nitrogen and sulfur [33]. The high values of NO$_3^-$/SO$_4^{2-}$ (>1) are ascribed to the large number of mobile sources (such as motor vehicle exhaust) in China. If the NO$_3^-$/SO$_4^{2-}$ ratios are low (<1), that indicates that a fixed source (such as coal combustion) is the main source. During the sampling period, the annual average ratio of NO$_3^-$/SO$_4^{2-}$ in Wanzhou was 0.54, lower than Nanjing (1.38) and Shanghai (1.40) [48] and comparable with Fuling (0.49) [37]. The results indicated that the contribution of stationary sources to PM$_{2.5}$ was greater than that of mobile sources in Wanzhou. In addition, the seasonal average ratios of NO$_3^-$/SO$_4^{2-}$ were ranked in the order of winter (0.85) > fall (0.57) > spring (0.44) > summer (0.27). The NO$_x$ from automobile exhaust is more easily converted into NO$_3^-$ under the poor atmospheric dilution and diffusion conditions in winter, which increases the concentration of NO$_3^-$ in the atmosphere [5,45], thus resulting in the highest NO$_3^-$/SO$_4^{2-}$ ratio in winter. On the contrary, the minimum ratio appeared in summer, which may be related to the volatility of nitrate at high temperature [18].

Sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) are usually used to represent the formation and transformation process of secondary aerosols using the following equations [49]:

\[
\text{SOR} = \frac{[\text{SO}_4^{2-}]}{[\text{SO}_4^{2-}] + [\text{SO}_2]} \tag{3}
\]

\[
\text{NOR} = \frac{[\text{NO}_3^-]}{[\text{NO}_3^-] + [\text{NO}_2]} \tag{4}
\]

where [SO$_4^{2-}$], [SO$_2$], [NO$_3^-$], and [NO$_2$] are the molar concentrations of SO$_4^{2-}$, SO$_2$, NO$_3^-$, and NO$_2$, respectively. Because of the monitoring instrument failure, NO$_2$ and SO$_2$ data in the summer were missing. Generally, the critical values of SOR and NOR are both 0.1, and higher NOR and SOR values indicate increased secondary transformation [50,51]. During the sampling period, the average value of SOR was 0.31, indicating a significant secondary transformation of SO$_2$ in the atmosphere. In addition, the value of SOR was the highest in spring (0.40), followed by winter (0.30), and the lowest in fall (0.22). The NOR values had a different seasonal pattern from SOR, which peaked in winter (0.13) and had lower values in spring and fall (both 0.06). Both sulfate and nitrate had two formation pathways, homogenous and heterogeneous reactions. Homogeneous gas-phase oxidation reaction involves SO$_2$ or NO$_2$ and OH radicals, which is a strong function of temperature. Heterogeneous transformation processes (H$_2$O$_2$/O$_3$ oxidation under the catalysis of metal or hydrolysis of N$_2$O$_5$ on preexisting particles) are correlated with RH and mass concentration of particulate matter [7,18,52]. As shown in Figure 4a, when the temperature was low (<15 °C), its concentration increased with the temperature, but when the temperature was higher than 15 °C, its concentration decreased rapidly, and NOR also presented a similar trend (Figure 4c). In winter, the temperature was usually below 15 °C, and it was found that NH$_4^+$ and NO$_3^-$ had significant correction (r = 0.84, 0.92, 0.95 in spring, fall, and winter, respectively), so it can be inferred that NO$_3^-$ was mainly formed through homogeneous meteorological reaction in winter. NO$_3^-$ is more volatile at high temperatures, which is the reason NOR is lower at high temperatures [41]. Additionally, NOR increased with RH (Figure 4d), suggesting the main formation pathway of NO$_3^-$ was a heterogeneous reaction in the fall (average RH: 83.3%). Since SOR increased with temperature and RH (Figure 4c,d), it can be speculated that SO$_4^{2-}$ was mainly formed by heterogeneous reactions in winter (lower temperature, higher relative humidity, Table 1), while both homogeneous and heterogeneous reactions existed in spring and fall.
3.5. Chemical Forms of SNA

NH₃ could react with acidic gases such as H₂SO₄ and HNO₃ to form (NH₄)₂SO₄, NH₄HSO₄, and NH₄NO₃ through homogeneous reactions. Moreover, NH₃ reacts preferentially with H₂SO₄ to form non-volatile (NH₄)₂SO₄ or NH₄HSO₄, and the excess NH₃ further reacts with HNO₃ to form relatively volatile NH₄NO₃ [53]. As shown in Figure 5, significant correlations between [NH₄⁺] and [SO₄²⁻] were found in the four seasons, with the correlation coefficient being larger than 0.90. The slopes of linear regressions higher than 2.0 indicated that there was sufficient NH₄⁺ to neutralize SO₄²⁻ to form (NH₄)₂SO₄ rather than NH₄HSO₄. In order to identify the specific existence forms of (NH₄)₂SO₄ or NH₄HSO₄ and NH₄NO₃, it can be distinguished by comparing the NH₄⁺ measured experimentally with the NH₄⁺ calculated [54]. When NO₃⁻, SO₄²⁻ and NH₄⁺ exist as the form of (NH₄)₂SO₄ and NH₄NO₃, the estimated concentration of NH₄⁺ can be expressed as ρ(NH₄⁺) (μg m⁻³) = 0.38ρ(SO₄²⁻) + 0.29ρ(NO₃⁻). The regression analysis of NH₄⁺ measured and calculated values were shown in Table 3. Assuming that NH₄⁺ existed in (NH₄)₂SO₄, the slopes of regression lines in spring, summer, fall, and winter were 0.99, 1.03, 0.93, and 1.21, respectively. When NH₄⁺ was assumed to exist as the form of NH₄HSO₄, the slopes of regression lines were 1.57, 1.74, 1.48, and 1.83, respectively. By comparison, the slopes of (NH₄)₂SO₄ in the four seasons were closer to 1, and the measured values and the calculated values were relatively consistent. Therefore, it can be concluded that NO₃⁻, SO₄²⁻, and NH₄⁺ mainly exist in the form of (NH₄)₂SO₄ and NH₄NO₃ in Wanzhou during the sampling period.

Table 3. Regression analysis between calculated values and measured values of NH₄⁺

<table>
<thead>
<tr>
<th>Season</th>
<th>In the Form of (NH₄)₂SO₄</th>
<th>In the Form of NH₄HSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Linear Regression Equation</td>
<td>R²</td>
</tr>
<tr>
<td>Spring</td>
<td>y = 0.99x – 0.54</td>
<td>0.98</td>
</tr>
<tr>
<td>Summer</td>
<td>y = 1.04x – 0.74</td>
<td>0.97</td>
</tr>
<tr>
<td>Fall</td>
<td>y = 0.93x – 0.39</td>
<td>0.99</td>
</tr>
<tr>
<td>Winter</td>
<td>y = 1.21x – 1.02</td>
<td>0.99</td>
</tr>
</tbody>
</table>

x represents NH₄⁺ measured value (μg m⁻³); y represents NH₄⁺ calculated value (μg m⁻³).
Figure 5. Correlations between [NH$_4^+$] and [SO$_4^{2-}$].

3.6. Source Apportionment of WSIIs

3.6.1. Principal Component Analysis (PCA) of WSIIs

In this study, principal component analysis (PCA) was used to analyze the sources of WSIIs during the observation period. PCA can extract several potential factors from the mass concentration data, which can be used to explain the relationship between the measured samples [55]. PCA was conducted for 11 variables (Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$, NH$_3$, SO$_2$, NO$_2$), and the KMO test value was 0.753, greater than 0.5, indicating that it was suitable for factor analysis. Based on the PCA method, three factors (potential sources) were identified as principal components (PC) at Wanzhou (Table 4). PC1 explained 49.5% of the total variance, and was mainly affected by NH$_4^+$ (0.96), K$^+$ (0.98), Cl$^-$ (0.95), NO$_3^-$ (0.89), SO$_4^{2-}$ (0.96), NO$_2$ (0.56), and SO$_2$ (0.65). NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$ are the typical traces of secondary sources [56,57]. K$^+$ and Cl$^-$ are associated with coal combustion and biomass burning. SO$_2$ and NO$_2$ are derived from coal burning and automobile exhaust emissions, respectively. Therefore, PC1 was attributed to the mixture of secondary origin aerosol, biomass burning, coal combustion, and automobile exhaust. PC2, responsible for 23.2% of the total variance, was characterized by high loadings of Na$^+$ (0.87), Mg$^{2+}$ (0.70), and Ca$^{2+}$ (0.86). Since Na$^+$, Mg$^{2+}$, and Ca$^{2+}$ are principal markers of dust emissions [58,59], PC2 was identified as construction dust and road dust source in the present study. PC3 explained 9.68% of the total variance with obvious loading of NH$_3$ (0.93) and NH$_3$, which mainly came from agriculture activities. In view of there being several agricultural fields to the west of the sampling site, PC3 was regarded as agricultural activity.

Table 4. Results of principal component analysis.

<table>
<thead>
<tr>
<th>PCA Source Loadings</th>
<th>PC1</th>
<th>PC2</th>
<th>PC3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>0.13</td>
<td>0.87</td>
<td>−0.05</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>0.96</td>
<td>−0.04</td>
<td>0.16</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.98</td>
<td>0.07</td>
<td>0.02</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.33</td>
<td>0.70</td>
<td>−0.52</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>−0.21</td>
<td>0.86</td>
<td>0.03</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.95</td>
<td>0.01</td>
<td>−0.06</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.89</td>
<td>−0.03</td>
<td>0.29</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>0.96</td>
<td>−0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>0.19</td>
<td>−0.08</td>
<td>0.93</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>0.56</td>
<td>−0.44</td>
<td>0.27</td>
</tr>
</tbody>
</table>
3.6.2. Regional Transport

To analyze the effects of air mass on atmospheric quality, 72 h backward trajectories arriving in Wanzhou during the sampling period were calculated by the TrajStat [60]. The starting time of trajectory calculation per day was 10:00 am (UTC), with the arrival level at 500 m AGL (Above Ground Level). The cluster analysis was based on the 72 h backward trajectories and grouped into five clusters (Figure 6). Cluster 1 mainly came from the southwest pathway, originating from Burma, through the Yunnan Province, and the junction of Chongqing and Guizhou Province. Cluster 3 represented the southern pathway which originated from Guangxi Province and passed through Guizhou Province. Clusters 1 and 3 (accounting for 8.8% and 17.7%, respectively) had mid-distance air mass trajectories and carried with the lowest PM$_{2.5}$ and WSIIs concentrations. However, Clusters 1 and 3 showed high proportions of dust ions (Na$^+$, Mg$^{2+}$, and Ca$^{2+}$), accounting for 22.3% and 25.5%, respectively. In terms of the origins and pathways, these air masses were expected to bring in relatively clean air passing through some sparsely populated, thus contributing toward pollution alleviation in Wanzhou. Cluster 2 was the dominant trajectory in Wanzhou (accounting for 63.7%), which mainly originated from the local southeastern area. Since Wanzhou’s large-scale industrial complexes, including chemical plants, cement plants, and power plants, are located southeast of the sampling site, the southeast wind brought in a large number of pollutants from the industrial activities from this region’s sources [61]. Cluster 5 (accounting for 7.9%) had long-range air masses originating from southern Xinjiang Province through the Tibet Autonomous Region, Qinghai, and Sichuan Provinces. The air masses in Clusters 2 and 5 carried higher concentrations of PM$_{2.5}$ and WSIIs, and their ionic compositions were similar, with the proportion of SNA reaching 84.8% and 85.6% of WSIIs, respectively. Cluster 4 (accounting for 1.8%) reflected the ultra-long-distance and polluted air masses transported from Saudi Arabia. This cluster corresponded to the highest concentrations of PM$_{2.5}$ and WSIIs, with the highest contribution (average 87.3%) from SNA. Since Cluster 4 mainly occurred in winter, it can be inferred that the transport of air mass from this pathway may be related to the air pollution in winter.

3.7. Air Pollution Event

There was a long-lasting pollution event that occurred from 31 December 2016 to 5 January 2017, with average PM$_{2.5}$ concentration reaching 126.51 µg·m$^{-3}$, exceeding the NAAQS-China daily limit of 75 µg·m$^{-3}$ by a factor of 1.8. The time series of daily meteorological parameters, gaseous precursors, PM$_{2.5}$, and WSIIs concentrations are depicted in Figure 7. The whole sampling campaign was divided into three stages according to PM$_{2.5}$ concentrations, namely, the pre-pollution stage (P1), the pollution occurred stage (P2), and the post-pollution stage (P3). The P1 phase was from 27 to 30 December 2016, when the average PM$_{2.5}$, NO$_2$, and SO$_2$ concentrations were 34.46, 46.25, and 14.00 µg·m$^{-3}$. The P2 phase covered the period (31 December 2016 to 5 January 2017) of the long-lasting pollution event, when the average PM$_{2.5}$, NO$_2$, and SO$_2$ concentrations were 126.51, 52.83, and 22.33 µg·m$^{-3}$. Compared with those in P1, the temperature and relative humidity increased by 23% and 17%, respectively, while the wind speed decreased from 0.71 to 0.62 m·s$^{-1}$. During this period, PM$_{2.5}$ gradually accumulated and peaked on 4 January 2017 to the level of 156.30 µg·m$^{-3}$, while NO$_2$ and SO$_2$ peaked at 65 and 26 µg·m$^{-3}$ on 31 December 2016, and 2 January 2017, respectively. The P3 phase was from 6 to 7 January 2017, when PM$_{2.5}$ concentration decreased rapidly due to the removal of air pollutants by rainfall.
As shown in Figure 7, the concentrations of PM$_{2.5}$, WSIIS, and all the measured gaseous precursors were observably higher during the pollution phase (P2) than before (P1) and after the pollution event (P3). Taking P1 as the reference phase, PM$_{2.5}$ concentration in P2 increased 3.7 times, and the total amount of SNA increased 4.5 times. SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ increased 4.3, 4.1, and 5.3 times, from a low of 6.13, 4.28, and 3.23 µg·m$^{-3}$ (P1) to 26.37, 17.23, and 17.12 µg·m$^{-3}$ (P2), respectively. SOR and NOR were also enhanced by a factor of 1.8 and 2.8 in P2, respectively (from 0.24 to 0.42, 0.07 to 0.20, respectively). However, their gaseous precursors SO$_2$ and NO$_2$ only increased by 1.6 and 1.1 times in P2, respectively.

It is evident that this air pollution event was mainly caused by the enhanced chemical transformation of gaseous precursors to SNA. Compared to P1, the temperature increased by 1.2 $^\circ$C in P2 (from 9.26 to 11.41 $^\circ$C), which promoted stronger photochemical reactions. A good correlation was found between temperature and SOR ($r = 0.65$) or NOR ($r = 0.85$), suggesting homogeneous reactions as the main formation mechanism for the high level of SO$_4^{2-}$ and NO$_3^-$.

At the same time, the average relative humidity increased from 71% in P1 to 83% in P2. The relative humidity also had a good correlation with SOR and NOR, and the correlation coefficients were 0.73 and 0.95, respectively, indicating that heterogeneous reaction also contributed to the increase of SO$_4^{2-}$ and NO$_3^-$ concentrations. The strong enhancement of NH$_4^+$ concentration in P2 was apparently attributed to those of SO$_4^{2-}$ and NO$_3^-$. In addition, the concentration of K$^+$ and Cl$^-$ also increased significantly during the P2 stage, which increased by 3.6 and 4.7 times, respectively, but the proportion of K$^+$ and Cl$^-$ in WSIIs varied little. The elevated concentration of K$^+$ and Cl$^-$ may be related to straw burning in the surrounding farmland. The concentrations of Na$^+$, Mg$^{2+}$, and Ca$^{2+}$ did not vary significantly during the whole sampling period, indicating that the source strength was relatively stable. Combined with the little variation of concentration of primary pollutants SO$_2$ and NO$_2$, it can be inferred that this air pollution event was mostly caused by the enhanced formation of SNA through homogeneous and heterogeneous reactions.
Figure 7. The time series of daily meteorological parameters, gaseous precursors, PM$_{2.5}$, and WSIIs concentrations from 27 December 2016 to 7 January 2017.
4. Conclusions

From April 2016 to January 2017, PM$_{2.5}$ samples were collected in four months (each month represented a season) to analyze the characteristics and sources of WSIIs in Wanzhou. Statistical results displayed that the annual average value in Wanzhou was 33.38 µg·m$^{-3}$, which was lower than the National Ambient Air Quality Standards of China (NAAQS-China, annual limit of 35 µg·m$^{-3}$). SO$_{4}^{2-}$, NO$_{3}^{-}$, and NH$_{4}^{+}$ were the dominating water-soluble ions, with corresponding percentage contributions to the total WSIIs of 41.1%, 22.1%, and 19.9%, respectively. PM$_{2.5}$ and WSIIs showed the highest concentrations in winter and lowest concentrations in summer. Ion balance analysis showed that PM$_{2.5}$ was alkaline in summer, weakly alkaline in spring and winter, and close to neutral in fall. The annual average ratio of NO$_{3}^{-}$/SO$_{4}^{2-}$ in Wanzhou was 0.54, demonstrating that the contribution of stationary sources to PM$_{2.5}$ was greater than that of mobile sources in Wanzhou. NO$_{3}^{-}$ was mainly formed through homogeneous meteorological reactions in winter and heterogeneous reactions in fall. SO$_{4}^{2-}$ was mainly formed by heterogeneous reactions in winter, while both homogeneous and heterogeneous reactions existed in spring and fall. NO$_{3}^{-}$, SO$_{4}^{2-}$, and NH$_{4}^{+}$ mainly exist in the form of (NH$_{4}$)$_{2}$SO$_{4}$ and NH$_{4}$NO$_{3}$ in Wanzhou during the sampling period. Three main sources of WSIIs in PM$_{2.5}$ in Wanzhou were analyzed by PCA, which were the mixture of secondary origin aerosol, biomass burning, coal combustion, construction dust and road dust, and agriculture activities, respectively. The 72 h backward trajectory analysis indicated that the local emissions had a significant influence on the atmosphere of Wanzhou, and the ultra-long-distance transport from the southwest air masses carrying the highest PM$_{2.5}$ and WSIIs may cause air pollution in winter. An air pollution event that occurred in winter was mostly caused by the enhanced formation of SNA through homogeneous and heterogeneous reactions.

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