Characteristics, Formation Mechanisms and Potential Transport Pathways of PM$_{2.5}$ at a Rural Background Site in Chongqing, Southwest China

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ABSTRACT

Daily PM$_{2.5}$ samples were collected at a rural background station (JinYun) located in Chongqing across four consecutive seasons from October 2014 to July 2015. The major water-soluble inorganic ions (WSIs), organic carbon (OC) and elemental carbon (EC) were analyzed, and their chemical characteristics, transport pathways and potential source regions were investigated. The average annual PM$_{2.5}$ concentration was 56.2 ± 31.0 µg m$^{-3}$, of which secondary inorganic aerosol (SNA) and carbonaceous aerosols composed 41.0% and 29.4%, respectively. Higher concentrations of and contributions from SO$_4^{2-}$, which were likely caused by the secondary transformation of SO$_2$ into SO$_4^{2-}$, were observed in summer than in autumn and spring. Additionally, transportation from the urban area of Chongqing (Yubei) played an important role in elevating the SO$_4^{2-}$ during this season. Although the accumulation of PM$_{2.5}$ during pollution episodes in winter was also due to aqueous-phase reactions, based on the entire year, NO$_3^-$ formation may have been primarily driven by homogeneous gas-phase reactions. Furthermore, the aerosol environment was ammonium-rich, and NH$_4^+$ formation promoted the production of NO$_3^-$ at lower temperatures. The carbonaceous component, which consisted of 81.0–84.6% OC, exhibited higher concentrations in winter than in the other seasons; 50.0–77.2% of the total OC, in turn, was contributed by primary organic carbon (POC). Potential source contribution function (PSCF) analysis suggests that the site was mainly affected by regional pollution originating in the southwestern and northern areas of Chongqing.

Keywords: PM$_{2.5}$; Rural background site; Chemical transformation; Potential transport pathways.

INTRODUCTION

Atmospheric fine particles (PM$_{2.5}$, particulate matter with an aerodynamic diameter ≤ 2.5 µm) negatively impact human health, air quality, and atmospheric visibility (Anderson et al., 2012; Cao et al., 2012; Deng et al., 2014; Deng et al., 2016a; Fu et al., 2016). PM$_{2.5}$ levels across China have increased sharply in the past several decades due to rapid economic development, industrialization and urban expansion (Tie and Cao, 2009; Ma et al., 2016; Li et al., 2017). Although annual average PM$_{2.5}$ concentration is declining recently due to the implementation of several measures, PM$_{2.5}$ pollution was still serious in some megacities such as Beijing-Tianjin-Hebei, Yangtze River Delta, Pearl River Delta, and Sichuan Basin (Tao et al., 2017). Chongqing was one of the most important industrial cities in Sichuan Basin and had severe aerosol pollution (Tian et al., 2017a; Wang et al., 2018b). For example, the annual mean concentration of PM$_{2.5}$ was 70.9 ± 41.4 µg m$^{-3}$ during 2014–2015 at Chongqing, which was about 2 times the secondary grade limit specified in the Chinese National Ambient Air Quality Standards (NAAQS) (Wang et al., 2018b). Different from other cities, Chongqing is a
municipality with a population of 8.23 million and encircled by high mountains. Additionally, Chongqing is characterized by high relative humidity, low wind speeds, and extremely high temperature (Chen and Xie, 2013; Chen et al., 2017a). The characteristics, formation mechanisms and sources of PM_{2.5} have been investigated in this region, but mostly focused on urban areas (Yang et al., 2011; Tao et al., 2017; Tian et al., 2017b; Wang et al., 2017; Huang et al., 2018; Wang et al., 2018a, b). Results from these studies indicated that PM_{2.5} pollution was largely caused by local sources in this region. However, few studies have investigated PM_{2.5} pollution in rural areas in this region. Field study of PM_{2.5} at a rural background station can help to understand the impacts of anthropogenic activities on regional air quality, as has been done in the other regions of China (Zhang et al., 2014; Feng et al., 2015; Zhang et al., 2017; Zong et al., 2018).

In this study, PM_{2.5} filters were sampled in four consecutive seasons from October 2014 to July 2015 at a rural background station in Chongqing and analyzed for the mass concentrations and chemical compositions. The characteristics and possible formation mechanisms of PM_{2.5} and its major chemical components in different seasons were investigated. Transport pathways and potential source regions of PM_{2.5} were identified through cluster analysis and potential source contribution function (PSCF) based on backward trajectories. The results of this study have implications for better understanding the impacts of anthropogenic activities on regional pollution of PM_{2.5} in Chongqing.

**METHODS**

**Site Description**

PM_{2.5} samples were collected on the roof of a six-floor building near the top of JinYun mountain (JY) (106°22′E, 29°49′N, 800 m a.s.l.), 35 km away from the central downtown area of urban Chongqing and 5 km away from the nearest town (Beibei). Lush vegetation dominates within a few kilometers of the site. This site is mainly influenced by regional transported pollutants and can be considered as a background site in this region (Fig. S1).

**Sample Collection**

Daily (22 h, from 12:00 a.m. to 10:00 a.m. next day) integrated ambient PM_{2.5} samples were collected from 20 October to 15 November (representative of autumn) in 2014, 6 January to 5 February (winter), 31 March to 29 April (spring), and 2 to 30 July (summer) in 2015. Two low-volume aerosol samplers (frmOMNI Ambient Air Sampler; BGI, USA), both operated at a flow rate of 5 L min^{-1}, were employed to collect PM_{2.5} samples synchronously. One sampler was loaded with 47-mm quartz-fiber filter (Whatman, UK) for water-soluble inorganic ions (WSIIs) and carbonaceous components analysis. The other one was equipped with 47-mm Teflon filter (Whatman, UK) for trace elements and PM_{2.5} mass analysis. A total of 93 samples were collected during the entire campaign with at least 15 samples in each season.

Blank filters were also prepared every 10 samples for quality control. Before sampling, all quartz-fiber filters were preheated at 450°C in a muffle furnace for 4 h to remove potential contaminants such as some organic compounds. All the sampled and blank filters were stored in clean filter boxes at approximately –18°C before analysis to avoid cross contamination and evaporation of volatile components.

During the sampling period, gaseous pollutants were continuously measured by a set of online gas analyzers, including a pulsed UV fluorescence analyzer (Model 43i SO2 Analyzer; Thermo Scientific) for SO2 and a chemiluminescence analyzer (Model 42i NO-NO2-NOx Analyzer; Thermo Scientific) for NO/NO2/NOx. Hourly meteorological parameters, including ambient temperature (T), wind speed (WS) and direction, relative humidity (RH), and pressure (P), were obtained from an automatic weather station (Luft WS501, Germany).

**Mass and Chemical Analysis**

Before and after sample collection, all the Teflon filters were equilibrated for 24 h in a temperature (20–23°C) and relative humidity (45–50%) controlled chamber and weighed for at least 3 times using an electronic microbalance with ± 0.001 mg sensitivity (MES-F; Sartorius, Germany). The differences among replicate weights should be less than 15 µg for blank filters and 20 µg for samples.

Elemental carbon (EC) and organic carbon (OC) amounts in the collected samples were measured using a DRI OC/EC Analyzer (Atmoslytic Inc., USA). The methodology for OC/EC analysis was based on the thermal-optical reflectance (TOR) method following the Interagency Monitoring of Protected Visual Environments (IMPROVE-A) protocol (Chow et al., 2007, 2011).

Five cations (Na^+, NH4^+, K^+, Mg^{2+} and Ca^{2+}) and four anions (F^-, Cl^-, SO_{4}^{2−} and NO_{3}−) in the PM_{2.5} samples were measured using an ion chromatograph analyzer (DX-600; Dionex, USA). Cations were detected using CSRS-4 suppressor with CS12A analytical column and 20 mM methanesulfonic acid (MSA) at a flow rate of 1.0 mL min^{-1}. Anions were determined with an ASRS-4 suppressor with an AS11-HC analytical column and 30 mM KOH at a flow rate of 1.0 mL min^{-1}. The QA/QC procedures for sample pretreatment, instrument analysis, and data processing were described in Wang et al. (2018b).

The trace elements, including Al, Si, Ca, Fe, and Ti, were quantified on a Teflon filter using X-ray fluorescence (ED-XRF) analyzer (Epsilon 5; PANalytical, Netherlands); the concentration of fine soil (FS) was calculated by summing Al_{2}O_{3}, SiO_{2}, CaO, FeO, Fe_{2}O_{3}, and TiO_{2} (Huang et al., 2014); the QA/QC procedures of the XRF analysis have been described in Cao et al. (2012).

**Backward Trajectory Analyses**

Forty-eight hour air mass backward trajectories, starting at 04:00, 10:00, 16:00 and 22:00 UTC every day at the height of 100 m a.g.l. (meter above ground level), were generated for the sampling period to explore the origins and transport pathways using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSLIMIT) model developed by NOAA with the 0.5° × 0.5° meteorological data (Stein et
al., 2015; Squizzato and Masiol, 2015). A total of 368 backward trajectories were produced, which were clustered into five main paths based on the total spatial variance, as detailed in previous studies (Markou and Kassomenos, 2010; Cabello et al., 2016).

**Potential Source Contribution Function (PSCF)**

PSCF represents a conditional probability for a pollutant of interest having concentrations above a given value and passing through a grid cell during transport processes arriving at the receptor site. Grid cells with high PSCF values are identified as potential source locations (Hopke et al., 1995; Polissar et al., 1999).

The PSCF normalized value can be defined as follows:

\[
PSCF_{ij} = \frac{m_{ij}}{n_{ij}}
\]

where \(n_{ij}\) is the total number of endpoints falling into the grid cell \((i,j)\) and \(m_{ij}\) is the number of endpoints having a pollutant concentration above the given threshold value in the same cell. In order to minimize the PSCF uncertainties with small \(n_{ij}\) values, a weighting function \(w_{ij}\) was defined as follows, where \(n_{ave}\) is considered as the average number of endpoints in each grid cell (Polissar et al., 1999; Zhang et al., 2017; Wang et al., 2018b).

\[
w_{ij} = \begin{cases} 
1.00 & n_{ij} > 3n_{ave} \\
0.70 & 1.5n_{ave} < n_{ij} \leq 3n_{ave} \\
0.42 & n_{ave} < n_{ij} \leq 1.5n_{ave} \\
0.20 & n_{ij} \leq n_{ave} 
\end{cases}
\]

In this study, PSCF values of daily PM\(_{2.5}\) and other pollutants were evaluated over trajectory covered area, which was in the range of 20–40°E longitude and 90–117°N latitude. The area was gridded at a resolution of 0.5° × 0.5°. The threshold value for each pollutant was set as its mean observed value.

**RESULTS AND DISCUSSION**

**PM\(_{2.5}\) Mass Concentrations**

The temporal variations of meteorological parameters and concentrations of gaseous pollutants and PM\(_{2.5}\) observed at JY during the sampling period are given in Fig. 1. Daily PM\(_{2.5}\) mass concentrations ranged from 11.3 to 162.5 µg m\(^{-3}\), with an annual average of 56.2 ± 31.0 µg m\(^{-3}\), which was 1.6 times of the Chinese NAAQS (35 µg m\(^{-3}\)). PM\(_{2.5}\) concentrations were significantly lower at rural background site (JY) than at urban area of Chongqing (YB) (Table S1), likely due to strong influence of anthropogenic sources in YB (Chen et al., 2017b; Wang et al., 2018b). However, the annual average of PM\(_{2.5}\) at JY site was higher than those observed at the other rural sites in China (except the rural sites of Zhejiang and Bohai Sea), even at some urban sites (e.g., Deyang and Zunyi) (Table S1), which is not only due to the source emissions but also due to the regional transported contribution (e.g., from Yubei area) (Zhang and Cao, 2015; Liu et al., 2018). Furthermore, the climate of Chongqing is characterized by stagnant weather with weak wind and relatively low boundary layer height, leading to favorable atmospheric conditions for accumulation and formation of aerosols (Liao et al., 2018; Wang et al., 2018b).

As shown in Fig. S2, there was an apparent seasonal variation in PM\(_{2.5}\) at JY. The highest seasonal average concentration of PM\(_{2.5}\) was seen in winter (80.4 ± 39.5 µg m\(^{-3}\)), significantly higher than those in the other three seasons (p < 0.05). This is consistent with the typical ones observed in urban areas of China (He et al., 2001; Wang et al., 2015). The highest PM\(_{2.5}\) mass in winter was caused not only by the meteorological conditions with calm winds and shallow planetary boundary layer height, but also by the strong source emissions and atmospheric processes (Wang et al., 2017; Liao et al., 2018) (Fig. 1). Different from the typical seasonal pattern observed in the urban areas of China, i.e., lowest in summer (He et al., 2001; Wang et al., 2015; Wang et al., 2018b; Qiao et al., 2019), the seasonal average concentration of PM\(_{2.5}\) was higher in summer (52.1 ± 9.4 µg m\(^{-3}\)) than in spring (43.9 ± 18.0 µg m\(^{-3}\)) and autumn (39.0 ± 17.5 µg m\(^{-3}\)) at JY, though it was not significant (p > 0.05) (Fig. S2, Table 1). The sampling site (JY) was a forest site and surrounded by lush vegetation. Previous researches have demonstrated that the emissions of monoterpene and isoprene, the major precursors of secondary organic carbon, were stronger in summer than in other seasons at forest sites (Wang et al., 2007; Shen et al., 2015). Therefore, the slightly higher PM\(_{2.5}\) concentration in summer might be related to the high biogenic emissions at JY (e.g., emission from vegetation), consistent with the previous research at forest site (Liu et al., 2017). In addition, regional transport might be another reason for the slightly higher PM\(_{2.5}\) concentration in summer. It is worth mentioning that the contribution of SO\(_4^{2-}\) was highest in summer (Fig. 2(a)). Previous research indicated that the transformation of SO\(_2\) to SO\(_4^{2-}\) would occur within transporting air masses and can be an important source of SO\(_4^{2-}\) aerosols in summer (Wasiuta et al., 2015; Liu et al., 2018). As shown in Fig. 2(b), the prevailing wind at JY in summer was from southeast direction, where the urban area of Chongqing (YB) is located (Fig. S1). In addition, high concentration and contribution of SO\(_4^{2-}\) in summer at YB were also observed, similar to the seasonal pattern at JY (Wang et al., 2018b). These results suggested the impact of the aerosol pollution in YB on JY. In addition, the influence of the pollution at YB on JY could be partly justified by the correlation between these two sites. The concentration of SO\(_4^{2-}\) and SO\(_2\) in JY showed higher correlation coefficients with that in YB in summer (R\(^2\) = 0.883, 0.749), and the slopes of the linear regression were closer to 1 (0.96, 0.91) in summer (Figs. 2(c) and 2(d)). These results indicated that the regional transport of SO\(_4^{2-}\) and SO\(_2\) from urban area (YB) could be an important source of SO\(_4^{2-}\) aerosols at JY site in summer. Besides, these results also suggested the significant impact of YB on the relatively high PM\(_{2.5}\) concentration at JY site in summer.
Fig. 1. Temporal variations of meteorological parameters, gaseous pollutants and PM$_{2.5}$ during the sampling period at JY. The long-lasting heavy pollution period is highlighted by shaded area.

Table 1. Concentrations (mean ± standard deviation) of PM$_{2.5}$, its major chemical components, and gaseous pollutants at JY.

<table>
<thead>
<tr>
<th></th>
<th>Autumn</th>
<th>Winter</th>
<th>Spring</th>
<th>Summer</th>
<th>Annual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample number</td>
<td>23</td>
<td>30</td>
<td>21</td>
<td>18</td>
<td>92</td>
</tr>
<tr>
<td>PM$_{2.5}$ (µg m$^{-3}$)</td>
<td>39.0 ± 17.5</td>
<td>80.4 ± 39.5</td>
<td>43.9 ± 18.0</td>
<td>52.1 ± 9.4</td>
<td>56.2 ± 31.0</td>
</tr>
<tr>
<td>OC (µgC m$^{-3}$)</td>
<td>7.3 ± 3.3</td>
<td>17.1 ± 10.0</td>
<td>8.8 ± 3.4</td>
<td>5.6 ± 2.6</td>
<td>10.5 ± 7.8</td>
</tr>
<tr>
<td>EC (µgC m$^{-3}$)</td>
<td>1.7 ± 0.6</td>
<td>3.5 ± 2.2</td>
<td>1.9 ± 0.7</td>
<td>1.1 ± 0.7</td>
<td>2.2 ± 1.6</td>
</tr>
<tr>
<td>OC/EC</td>
<td>4.4 ± 0.8</td>
<td>4.9 ± 0.7</td>
<td>4.8 ± 1.2</td>
<td>5.7 ± 1.2</td>
<td>4.9 ± 1.0</td>
</tr>
<tr>
<td>SOC (µgC m$^{-3}$)</td>
<td>1.8 ± 1.7</td>
<td>4.5 ± 2.8</td>
<td>4.4 ± 2.1</td>
<td>1.5 ± 0.8</td>
<td>3.2 ± 2.5</td>
</tr>
<tr>
<td>SOC/OC (%)</td>
<td>21.8 ± 12.7</td>
<td>25.8 ± 10.4</td>
<td>47.7 ± 14.7</td>
<td>30.1 ± 15.3</td>
<td>30.6 ± 16.1</td>
</tr>
<tr>
<td>NH$_4^+$ (µg m$^{-3}$)</td>
<td>4.2 ± 2.4</td>
<td>7.5 ± 4.3</td>
<td>4.7 ± 3.5</td>
<td>4.5 ± 2.2</td>
<td>5.5 ± 3.6</td>
</tr>
<tr>
<td>K$^+$ (µg m$^{-3}$)</td>
<td>0.26 ± 0.21</td>
<td>0.65 ± 0.45</td>
<td>0.58 ± 0.39</td>
<td>0.36 ± 0.29</td>
<td>0.48 ± 0.39</td>
</tr>
<tr>
<td>SO$_4^{2-}$ (µg m$^{-3}$)</td>
<td>9.7 ± 5.7</td>
<td>14.4 ± 6.6</td>
<td>10.7 ± 6.6</td>
<td>13.5 ± 5.6</td>
<td>12.2 ± 6.4</td>
</tr>
<tr>
<td>NO$_3^-$ (µg m$^{-3}$)</td>
<td>5.3 ± 2.5</td>
<td>9.0 ± 6.7</td>
<td>4.1 ± 2.4</td>
<td>2.0 ± 1.2</td>
<td>5.6 ± 4.9</td>
</tr>
<tr>
<td>SNA (µg m$^{-3}$)</td>
<td>19.3 ± 10.1</td>
<td>30.9 ± 17.3</td>
<td>19.5 ± 11.7</td>
<td>20.0 ± 8.5</td>
<td>23.3 ± 13.9</td>
</tr>
<tr>
<td>SNA/PM$_{2.5}$ (%)</td>
<td>48.0 ± 5.8</td>
<td>36.4 ± 7.0</td>
<td>42.8 ± 11.4</td>
<td>37.8 ± 12.8</td>
<td>41.0 ± 10.3</td>
</tr>
<tr>
<td>Sions (µg m$^{-3}$)</td>
<td>20.4 ± 10.8</td>
<td>32.6 ± 18.0</td>
<td>21.9 ± 12.2</td>
<td>21.1 ± 8.7</td>
<td>24.8 ± 14.4</td>
</tr>
<tr>
<td>Sions/PM$_{2.5}$ (%)</td>
<td>50.6 ± 6.8</td>
<td>38.8 ± 6.3</td>
<td>48.2 ± 9.8</td>
<td>39.9 ± 12.7</td>
<td>44.1 ± 10.1</td>
</tr>
<tr>
<td>FS (µg m$^{-3}$)</td>
<td>0.82 ± 0.45</td>
<td>0.98 ± 0.53</td>
<td>1.72 ± 1.23</td>
<td>1.62 ± 0.90</td>
<td>1.23 ± 0.88</td>
</tr>
</tbody>
</table>

**Carbonaceous Components**

The annual mean concentrations of OC and EC were 10.5 ± 7.8 and 2.2 ± 1.6 µgC m$^{-3}$ at JY, accounting for 18.3% and 3.9% of PM$_{2.5}$, respectively (Table 1). The highest seasonal average of OC and EC were both exhibited in winter with values of 17.1 ± 10.0 and 3.5 ± 2.2 µgC m$^{-3}$, respectively, which were more than 3 times of the lowest seasonal average value found in summer. Stagnant weather conditions with calm winds and shallow planetary boundary layer height were the major causes of the highest OC and EC concentrations in winter (Fig. 1) (Liao et al., 2018). Besides, stronger source emissions in winter, such as biomass burning, may also contribute to the relatively high OC and EC concentrations in winter, noting that biomass burning events occurred frequently in Sichuan Basin (Tao et al., 2013; Chen and Xie, 2014). Actually, biomass burning activities have been observed in the wintertime domestic heating season at this background rural site. K$^+$ is usually regarded as a tracer of biomass burning (Tao et al., 2016). As shown in Figs. 3 and S2, higher K$^+$ concentration and its stronger correlation with OC ($R^2 = 0.90$) and EC ($R^2 = 0.91$) in winter than other
Fig. 2. (a) Seasonal contributions of chemical components to PM$_{2.5}$ at JY and Yubei (YB), (b) seasonal direction of wind at JY, and seasonal correlations (c) between concentration of SO$_4^{2-}$ at JY and that at YB, and (d) between concentration of SO$_2$ at JY and that at YB.

Fig. 3. Correlations (a) between OC and EC, (b) between K$^+$ and OC or (c) EC.
seasons have been observed, suggesting that biomass burning might contribute to the elevated OC and EC concentration in winter.

The OC/EC ratio was much larger than 2.0, indicating the occurrence of secondary organic carbon (SOC) formation (Table 1). The EC tracer method was generally used to estimate SOC, which can be defined as (Castro et al., 1999):

\[
OC = EC \times (OC/EC)_{\text{air}}
\]

\[
SOC = OC - EC \times (OC/EC)_{\text{air}}
\]

where \(OC/EC\) was the minimum ratio in each season. The highest concentration of SOC was observed in winter, which was similar to that of OC (Fig. S2 and Table 1). Relatively high SOC mass fraction (SOC/OC) occurred in summer, which might be due to low contribution of primary organic compounds from coal combustion and strong biogenic oxidation in summer at the rural background area with dense vegetation (Hallquist et al., 2009; Zhang et al., 2017).

**Water-soluble Inorganic Ions (WSII)**

The annual average of total WSII concentration was 24.8 ± 14.4 µg m\(^{-3}\), accounting for 44.1 ± 10.2% of PM\(_{2.5}\). As shown in Table 1, the annual mean of SO\(_2^2\), NO\(_3^-\), and NH\(_4^+\) were 12.2 ± 6.4, 5.6 ± 4.9, and 5.5 ± 3.6 µg m\(^{-3}\), respectively, the sum of which accounted for 93.0% of WSII. This indicated that the secondary inorganic ions (SNA, including SO\(_2^2\), NO\(_3^-\), and NH\(_4^+\)) were predominant components in WSII at JY. The annual average contribution of SNA to PM\(_{2.5}\) was 41.0% in JY, slightly higher than the typical value observed in urban Chongqing (37.4%; Wang et al., 2018b). This result might be related to the aging process for aerosols during transportation from source regions to the background area (Liu et al., 2018; Wang et al., 2018b). The PM\(_{2.5}\) pollution in JY was mainly from regional or long-range transport. During the transportation, particles would undergo aging process and consequently resulted in the increase of the proportion of secondary component such as SNA.

The seasonal variations of the total SNA were the same as those of PM\(_{2.5}\), i.e., winter (30.9 ± 17.3 µg m\(^{-3}\)) > summer (20.0 ± 8.5 µg m\(^{-3}\)) > spring (19.5 ± 11.7 µg m\(^{-3}\)) > autumn (19.3 ± 10.1 µg m\(^{-3}\)). The seasonal trend of SO\(_2^2\) and NH\(_4^+\) concentrations were both highest in winter and lowest in summer. However, NO\(_3^-\) concentration had a different trend with the lowest in summer. Besides, the scale of the seasonal variations was much larger for NO\(_3^-\) (up to 4.5 times) than for SO\(_2^2\) and NH\(_4^+\) (up to 1.5 times).

One main reason for the above-mentioned differences was the dissociation of NH\(_4\)NO\(_3\) in summer under high temperature condition, as was found in urban areas (Wang et al., 2018b).

Sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) have been used to investigate the conversion efficiencies of SO\(_2\) to SO\(_2^2\) and NO\(_2\) to NO\(_3^-\), respectively. They are calculated as (Lin, 2002):

\[
\text{SOR} = \frac{[\text{SO}_2^2]}{[\text{SO}_2^2] + [\text{SO}_2]} \tag{5}
\]

\[
\text{NOR} = \frac{[\text{NO}_3^-]}{[\text{NO}_3^-] + [\text{NO}_2]} \tag{6}
\]

where [SO\(_2^2\)], [SO\(_2\)], [NO\(_3^-\)], and [NO\(_2\)] are molar concentrations.

The seasonal variations of SO\(_2\), NO\(_2\), O\(_3\), SOR and NOR during the sampling campaign are illustrated in Fig. S3. When SOR was higher than 0.1, the secondary transformation of SO\(_2\) to SO\(_2^2\) would have occurred (Ohta and Okita, 1990). As shown in Fig. S3, the seasonal average of SOR was higher in summer than in other three seasons, which might be due to the following reasons: 1) Oxidation of SO\(_2\) could be enhanced under high O\(_3\) concentration and strong solar irradiation condition (Meng et al., 2016), which was supported by the significant correlation between SOR and O\(_3\) in summer (R = 0.74, p < 0.01) (Fig. S4); 2) ammonium-rich condition at JY was favorable for the formation of secondary sulfate (Fig. 6), especially during summer, when SOR was strongly related to NH\(_4^+\) concentration (R = 0.93, p < 0.01) (Fig. S4) (Zhang et al., 2011; Wang et al., 2016); 3) transportation of aged SO\(_2^2\) aerosol from urban area (YB) might lead to high SOR value at JY in summer (Fig. 2) (Liu et al., 2018).

The lowest seasonal average of NOR in summer is largely caused by the higher temperature as mentioned above (Deng et al., 2016b). NOR showed high values in winter and positively correlated with NH\(_4^+\) (R\(^2\) = 0.80) (Figs. S3 and 4), implying the association between NH\(_4^+\) and NO\(_3^-\) under low temperature condition (Squizzato et al., 2012). The formation of NO\(_3^-\) may be dominated by heterogeneous process under ammonium-poor condition and by homogeneous gas-phase reaction under ammonium-rich condition (Pathak et al., 2009). The molar ratio of [NH\(_4^+\)]/[SO\(_2^2\)] > 1.5 was generally regarded as ammonium-rich condition (Huang et al., 2011). A threshold value of 1.5 was used to calculate the excess NH\(_4^+\) concentration in this study. The concentration of excess NH\(_4^+\) as a function of NO\(_3^-\) showed significant positive correlations (R\(^2\) = 0.84) (Fig. 5), indicating evident gas-phase reaction between NH\(_4^+\) and HNO\(_3\) (Wang et al., 2018b). Thus, reducing NH\(_4^+\) emissions may reduce NO\(_3^-\) formation.

Strong correlation (R\(^2\) = 0.95) was found between anion equivalents (AE) and cation equivalents (CE) (Fig. S5) with a slope of the linear regression being 1.06, indicating neutralized aerosols at JY. NH\(_4^+\) is the most abundant cation and mainly associates with SO\(_2^2\) and NO\(_3^-\) (Zhang et al., 2008; Zhou et al., 2016). When NH\(_4^+\) exists as (NH\(_4\))\(_2\)SO\(_4\) and NH\(_4\)NO\(_3\), the concentration of NH\(_4^+\) can be calculated according to:

\[
C_{\text{AE}} = 0.29C_{\text{SO}_4^{2-}} + 0.192C_{\text{NH}_4^+} \tag{7}
\]

When NH\(_4^+\) is in the form of NH\(_4\)HSO\(_4\) and NH\(_4\)NO\(_3\), it is calculated as (Lai et al., 2007):

\[
C_{\text{AE}} = 0.29C_{\text{NO}_3^-} + 0.38C_{\text{SO}_4^{2-}} \tag{8}
\]
Fig. 4. Correlation between nitrogen oxidation ratio (NOR) and NH$_4^+$ concentration.

Fig. 5. (a) Molar ratio of NO$_3^-$/SO$_4^{2-}$ as a function of NH$_4^+$/SO$_4^{2-}$, and (b) NO$_3^-$ molar concentration as a function of NH$_4^+$ excess.

The slope of the linear regression was 0.96 between the measured and the Eq. (7)-calculated NH$_4^+$ concentrations, and was only 0.65 if using the Eq. (8)-calculated values (Fig. 6(a)). In addition, the equivalent ratio of NH$_4^+$ to the sum of SO$_4^{2-}$ and NO$_3^-$ was close to 1 (Fig. 6(b)), implying that most of sulfate and nitrate were neutralized by ammonium in the form of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ (Huang et al., 2011).

**Identification of Potential Source Regions**

Forty-eight hour air mass backward trajectories were classified into five clusters as shown in Fig. S6. PSCF results for PM$_{2.5}$ and its major components are illustrated in Fig. 7. Air masses in Clusters 1 and 2, occurring in all the seasons, were all originated from inside Chongqing with Cluster 1 (42.4% of the total trajectories) being short-distance trajectories from the north direction and Cluster 2 (30.4%) being relatively long distance from the northeast direction. Among the five clusters, Cluster 1 had the highest SO$_4^{2-}$ and the second highest PM$_{2.5}$ concentrations while Cluster 2 had the highest EC (Table S2). There are some important industries located in the northern part of
Fig. 6. Correlation (a) between the measured and calculated NH$_4^+$ concentrations, and (b) between NH$_4^+$ equivalents and NO$_3^-$ + SO$_4^{2-}$ equivalents.

Fig. 7. PSCF distribution for PM$_{2.5}$, OC, EC, SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$.

Chongqing, such as the thermal power plants in Hechuan, which might be important sources of SO$_2$ and PM$_{2.5}$. PSCF distributions also suggested that the northern area of Chongqing played an important role in occurrence of high concentration of PM$_{2.5}$ (Fig. 7). Moderate PSCF values of secondary ions (SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$) and OC were observed in the northeast areas, which might be related to nearby industries, such as Changshou chemical industrial zone (Wang et al., 2018b).

Air masses in Cluster 3 (5.4% of the total trajectories), occurring mainly in the cold season, were long-distance trajectories originated from the southwest direction, passing over some districts with heavy industries such as Neijiang and Zigong in Sichuan, and Yongchuan and Dazu in Chongqing. Relatively high levels of PM$_{2.5}$ and its major components were associated with this cluster. PSCF distribution also illustrated the southwestern area of Chongqing as an important potential source region for PM$_{2.5}$ and its major components (Fig. 7). Air masses in Cluster 4 (18.2% of the total trajectories) were short-distance trajectories originated from the southeast direction. Air masses in this cluster might carry contaminated air masses from urban Chongqing.
and consequently caused relatively high PM$_{2.5}$ pollution. Air masses in Cluster 5 (3.5% of the total trajectories), mainly occurring in spring and summer, were long-distance trajectories originated from the ocean with clean air masses. Therefore, concentrations of PM$_{2.5}$ and its major components were much lower in Cluster 5 than other clusters (Table S2). The above analysis suggested that PM$_{2.5}$ pollution at JY was affected occasionally by regional sources.

**Analysis of Pollution Episode**

The pollution period (PP) was defined as daily PM$_{2.5}$ concentration above 75 µg m$^{-3}$ while other days were referred to as clean period (CP). The temporal variations of T, RH, O$_3$, NOR, SOR and PM$_{2.5}$ in winter are shown in Fig. 8. There was a long-lasting pollution period during 11–26 January 2015, as highlighted by the shaded area in Fig. 8. During this period, the concentrations of PM$_{2.5}$ and its major chemical components were all enhanced by more than 2 times compared to the clean periods (Fig. 9(a)). Among the detected components, the largest contributor to PM$_{2.5}$ in PP was SNA (39.3%), followed by OC (22.1%). Interestingly, the NO$_3^-$ concentration was enhanced by 3.6 times, much
more than other major components, e.g., SO$_4^{2-}$ (2.14) and OC (2.85). That results in the increased contribution of NO$_3^-$ to PM$_{2.5}$ and decreased one for SO$_4^{2-}$ to PM$_{2.5}$ during the pollution period. Thus, NO$_3^-$ played a more important role for the accumulation of PM$_{2.5}$ than other components.

The accumulation of PM$_{2.5}$ and its major chemical components are influenced by both meteorological conditions and atmospheric chemical processes (Zheng et al., 2015), while that of CO, an inactive tracer with long lifetime, is mainly affected by meteorological conditions (Hu et al., 2013; Quan et al., 2015; Wang et al., 2018b). Thus, the CO-scaled concentrations of various pollutants could reveal the impacts of chemical processes on pollutants’ accumulations. The ratios of PM$_{2.5}$/CO, NO$_3^-$/CO and SO$_4^{2-}$/CO were 2.66, 3.94 and 2.35 times higher during the pollution period than the clean period, while the ratios of NO$_2$/CO and SO$_2$/CO were only 1.51 and 1.89 times higher, respectively. These results were consistent with the higher NO$_3^-$ (0.24) and SOR (0.31) during pollution episode than those during clean period (0.11 and 0.26 for NOR and SOR, respectively). This difference between pollution and clean episode was not likely due to the transportation of aerosols which would increase the SOR and NOR values, because according to the cluster results for air mass backward trajectory analysis (Fig. S7), the air masses at JY site during pollution period were mainly from nearby areas while those during clean episode were mostly from regional or long-range transport. Thus, the higher NOR and SOR values during pollution episode than clean episode was possibly resulted from the stronger chemical conversions from gas-phase (NO$_3^-$ and SO$_2$) to particulate-phase (NO$_3^-$ and SO$_4^{2-}$) during the pollution period.

In order to explore the formation mechanisms of secondary aerosols during the pollution period, the correlations of NOR and SOR against RH (at 5% interval), O$_3$ concentration (at 15 µg m$^{-3}$ interval) and T (at 2°C interval) are illustrated in Fig. S8. Both NOR and SOR obviously increased with increasing RH, but not with O$_3$ concentration and temperature. This suggested that SO$_4^{2-}$ and NO$_3^-$ were mainly formed via aqueous phase processes. Previous studies have also reported the predominant role heterogeneous reactions played for SO$_4^{2-}$ formation (Quan et al., 2015; Xu et al., 2017; Wang et al., 2018b). Moreover, as shown in Fig. S9, SO$_4^{2-}$ and NO$_3^-$ in PM$_{2.5}$ were completely neutralized by NH$_4^+$, indicating neutralized aerosols at JY during the long-lasting pollution period, which could enhance SO$_4^{2-}$ formation via aqueous phase oxidation (Wang et al., 2016). For NO$_3^-$, elevated RH would increase the water content in airborne particles and consequently enhance the uptake of gas-phase HNO$_3$ and NH$_3$ into existing particles (Tian et al., 2017a; Wang et al., 2018b). When O$_3$ concentration was lower than 70 µg m$^{-3}$, NOR and SOR all exhibited obviously decreasing trends with increasing O$_3$ level. In addition, high PM$_{2.5}$ concentrations, RH, NOR and SOR were observed under low O$_3$ concentrations (Fig. 8). These results indicated that photochemical reactions were weak and aqueous-phase reactions were dominant for the increased secondary aerosols during the pollution period (Zheng et al., 2015).

CONCLUSIONS

The chemical characteristics, formation mechanisms, transport pathways and potential source regions of PM$_{2.5}$ were investigated during four consecutive seasons at a rural background site (JY) in Chongqing, Southwest China. The mean annual concentration of the PM$_{2.5}$ was 56.2 ± 31.0 µg m$^{-3}$—1.6 times the NAAQS limit. Seasonally, the concentration was 1.6–2.0 times higher in winter (80.4 ± 39.5 µg m$^{-3}$) than in the other seasons (52.1 ± 9.4 µg m$^{-3}$, 39.0 ± 17.5 µg m$^{-3}$ and 43.9 ± 18.0 µg m$^{-3}$ for summer, autumn and spring, respectively). SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, OC and EC accounted for 22.2%, 9.5%, 9.4%, 18.3% and 3.9%, respectively, of the average annual PM$_{2.5}$. Compared to autumn and spring, summer exhibited higher concentrations of SO$_4^{2-}$, perhaps due to the active homogeneous gas-phase formation (SOR = 0.32) in this season; furthermore, these concentrations were augmented by emissions transported from the urban area of Chongqing. The PM$_{2.5}$ and SNA increased by more than 2.4 times during the pollution period compared to the clean period, and an abundance of ammonium was identified as the condition that promoted NO$_3^-$ formation at lower temperatures. The findings in the present study demonstrate the effects of anthropogenic activities, which are mainly local, on the air quality at this rural background site. Hence, sensitivity studies with chemical transport models should be combined with available measurements to provide quantitative measures for emission controls on the dominant chemical components (e.g., NO$_3^-$ and NH$_3$) in order to effectively reduce fine aerosol pollution in this region.

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SUPPLEMENTARY MATERIAL

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

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