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 (WSIIs), 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 $56.2 \pm 31.0 \mu\text{g m}^{-3}$, 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 $\leq 2.5 \mu\text{m}$) 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 $70.9 \pm 41.4 \mu\text{g m}^{-3}$ 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

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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 (firmOMNI 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-NO_x Analyzer; Thermo Scientific) for NO/NO₂/NO_x. 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 (Lufft 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 (ME5-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 by 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⁺, Mg²⁺ and Ca²⁺) and four anions (F⁻, Cl⁻, SO₄²⁻ and NO₃⁻) 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 Al₂O₃, SiO₂, CaO, FeO, Fe₂O₃, and TiO₂ (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 (HYSPPLIT) 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:

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \quad (1)$$

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).

$$w_{ij} = \begin{cases} 1.00 & n_{ij} > 3n_{ave} \\ 0.70 & 1.5n_{ave} < n_{ij} \leq 3n_{ave} \\ 0.42 & n_{ave} < n_{ij} \leq 1.5n_{ave} \\ 0.20 & n_{ij} \leq n_{ave} \end{cases} \quad (2)$$

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 $0.5^\circ \times 0.5^\circ$. 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 $162.5 \mu\text{g m}^{-3}$, with an annual average of $56.2 \pm 31.0 \mu\text{g m}^{-3}$, which was 1.6 times of the Chinese NAAQS ($35 \mu\text{g m}^{-3}$). $PM_{2.5}$ 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 ($80.4 \pm 39.5 \mu\text{g m}^{-3}$), 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 ($52.1 \pm 9.4 \mu\text{g m}^{-3}$) than in spring ($43.9 \pm 18.0 \mu\text{g m}^{-3}$) and autumn ($39.0 \pm 17.5 \mu\text{g m}^{-3}$) 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 $\pm$ standard deviation) of PM_{2.5}, its major chemical components, and gaseous pollutants at JY.

	Autumn	Winter	Spring	Summer	Annual
Sample number	23	30	21	18	92
PM _{2.5} ($\mu\text{g m}^{-3}$)	39.0 ± 17.5	80.4 ± 39.5	43.9 ± 18.0	52.1 ± 9.4	56.2 ± 31.0
OC ($\mu\text{gC m}^{-3}$)	7.3 ± 3.3	17.1 ± 10.0	8.8 ± 3.4	5.6 ± 2.6	10.5 ± 7.8
EC ($\mu\text{gC m}^{-3}$)	1.7 ± 0.6	3.5 ± 2.2	1.9 ± 0.7	1.1 ± 0.7	2.2 ± 1.6
OC/EC	4.4 ± 0.8	4.9 ± 0.7	4.8 ± 1.2	5.7 ± 1.2	4.9 ± 1.0
SOC ($\mu\text{gC m}^{-3}$)	1.8 ± 1.7	4.5 ± 2.8	4.4 ± 2.1	1.5 ± 0.8	3.2 ± 2.5
SOC/OC (%)	21.8 ± 12.7	25.8 ± 10.4	47.7 ± 14.7	30.1 ± 15.3	30.6 ± 16.1
NH ₄ ⁺ ($\mu\text{g m}^{-3}$)	4.2 ± 2.4	7.5 ± 4.3	4.7 ± 3.5	4.5 ± 2.2	5.5 ± 3.6
K ⁺ ($\mu\text{g m}^{-3}$)	0.26 ± 0.21	0.65 ± 0.45	0.58 ± 0.39	0.36 ± 0.29	0.48 ± 0.39
SO ₄ ²⁻ ($\mu\text{g m}^{-3}$)	9.7 ± 5.7	14.4 ± 6.6	10.7 ± 6.6	13.5 ± 5.6	12.2 ± 6.4
NO ₃ ⁻ ($\mu\text{g m}^{-3}$)	5.3 ± 2.5	9.0 ± 6.7	4.1 ± 2.4	2.0 ± 1.2	5.6 ± 4.9
SNA ($\mu\text{g m}^{-3}$)	19.3 ± 10.1	30.9 ± 17.3	19.5 ± 11.7	20.0 ± 8.5	23.3 ± 13.9
SNA/PM _{2.5} (%)	48.0 ± 5.8	36.4 ± 7.0	42.8 ± 11.4	37.8 ± 12.8	41.0 ± 10.3
Σions ($\mu\text{g m}^{-3}$)	20.4 ± 10.8	32.6 ± 18.0	21.9 ± 12.2	21.1 ± 8.7	24.8 ± 14.4
$\Sigma\text{ions}/\text{PM}_{2.5}$ (%)	50.6 ± 6.8	38.8 ± 6.3	48.2 ± 9.8	39.9 ± 12.7	44.1 ± 10.1
FS ($\mu\text{g m}^{-3}$)	0.82 ± 0.45	0.98 ± 0.53	1.72 ± 1.23	1.62 ± 0.90	1.23 ± 0.88

Carbonaceous Components

The annual mean concentrations of OC and EC were 10.5 ± 7.8 and $2.2 \pm 1.6 \mu\text{gC m}^{-3}$ 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 $3.5 \pm 2.2 \mu\text{gC m}^{-3}$, 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):

$$OC = EC \times (OC/EC)_{min} \quad (3)$$

$$SOC = OC - EC \times (OC/EC)_{min} \quad (4)$$

where POC represented the estimated primary OC and $(OC/EC)_{min}$ 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 (WSIIs)

The annual average of total WSII concentration was $24.8 \pm 14.4 \mu\text{g m}^{-3}$, accounting for $44.1 \pm 10.2\%$ of $\text{PM}_{2.5}$. As shown in Table 1, the annual mean of SO_4^{2-} , NO_3^- and NH_4^+ were 12.2 ± 6.4 , 5.6 ± 4.9 and $5.5 \pm 3.6 \mu\text{g m}^{-3}$, respectively, the sum of which accounted for 93.0% of WSIs. This indicated that the secondary inorganic ions (SNA, including SO_4^{2-} , NO_3^- and NH_4^+) were predominant components in WSIs at JY. The annual average contribution of SNA to $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$, i.e., winter ($30.9 \pm 17.3 \mu\text{g m}^{-3}$) > summer ($20.0 \pm 8.5 \mu\text{g m}^{-3}$) > spring ($19.5 \pm 11.7 \mu\text{g m}^{-3}$) > autumn ($19.3 \pm 10.1 \mu\text{g m}^{-3}$). The seasonal trend of SO_4^{2-} and NH_4^+ concentrations were both highest in winter and lowest in autumn. 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_4^{2-} and NH_4^+ (up to 1.5 times). One main reason for the above-mentioned differences was the dissociation of NH_4NO_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_4^{2-} and NO_2 to NO_3^- , respectively. They are calculated as (Lin, 2002):

$$\text{SOR} = [\text{SO}_4^{2-}] / ([\text{SO}_4^{2-}] + [\text{SO}_2]) \quad (5)$$

$$\text{NOR} = [\text{NO}_3^-] / ([\text{NO}_3^-] + [\text{NO}_2]) \quad (6)$$

where $[\text{SO}_4^{2-}]$, $[\text{SO}_2]$, $[\text{NO}_3^-]$ and $[\text{NO}_2]$ 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_4^{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_4^{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 $[\text{NH}_4^+]/[\text{SO}_4^{2-}] > 1.5$ 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_3 and HNO_3 (Wang *et al.*, 2018b). Thus, reducing NH_3 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_4^{2-} and NO_3^- (Zhang *et al.*, 2008; Zhou *et al.*, 2016). When NH_4^+ exists as $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 , the concentration of NH_4^+ can be calculated according to:

$$C_{cal(1)} = 0.29C_{\text{NO}_3^-} + 0.192C_{\text{SO}_4^{2-}} \quad (7)$$

When NH_4^+ is in the form of NH_4HSO_4 and NH_4NO_3 , it is calculated as (Lai *et al.*, 2007):

$$C_{cal(2)} = 0.29C_{\text{NO}_3^-} + 0.38C_{\text{SO}_4^{2-}} \quad (8)$$

Fig. 4. Correlation between nitrogen oxidation ratio (NOR) and NH_4^+ concentration.

Fig. 5. (a) Molar ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ as a function of $\text{NH}_4^+/\text{SO}_4^{2-}$, 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 $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 $\text{NO}_3^- + \text{SO}_4^{2-}$ equivalents.

Fig. 7. PSCF distribution for $\text{PM}_{2.5}$, 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 $\text{PM}_{2.5}$. PSCF distributions also suggested that the northern area of Chongqing played an important role in occurrence of high concentration of $\text{PM}_{2.5}$ (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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ and its major components were much lower in Cluster 5 than other clusters (Table S2). The above analysis suggested that $\text{PM}_{2.5}$ pollution at JY was affected occasionally by regional sources.

Analysis of Pollution Episode

The pollution period (PP) was defined as daily $\text{PM}_{2.5}$

concentration above $75 \mu\text{g m}^{-3}$ while other days were referred to as clean period (CP). The temporal variations of T, RH, O_3 , NOR, SOR and $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ in PP was SNA (39.3%), followed by OC (22.1%). Interestingly, the NO_3^- concentration was enhanced by 3.6 times, much

Fig. 8. Temporal variations of T, RH, O_3 , NOR, SOR and $\text{PM}_{2.5}$ in winter. Long-lasting pollution episode is highlighted by the shaded area.

Fig. 9. The (a) mass concentrations and (b) CO-scaled concentrations of various pollutants, as well as the (c) percentage contributions of major chemical components to $\text{PM}_{2.5}$ and values of SOR and NOR during clean periods (CP) and long-lasting pollution period (PP) in winter at JY. CE: 6–10 January, 27 January–3 February and 5 February 2015; PP: 11–26 January 2015.

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 $\text{PM}_{2.5}$ and decreased one for SO_4^{2-} to $\text{PM}_{2.5}$ during the pollution period. Thus, NO_3^- played a more important role for the accumulation of $\text{PM}_{2.5}$ than other components.

The accumulation of $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}/\text{CO}$, NO_3^-/CO and $\text{SO}_4^{2-}/\text{CO}$ 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 NOR (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 SOR and NOR values during pollution episode than clean episode was possibly resulted from the stronger chemical conversions from gas-phase (NO_2 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 SOR and NOR against RH (at 5% interval), O_3 concentration (at $15 \mu\text{g m}^{-3}$ 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 $\text{PM}_{2.5}$ 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 $70 \mu\text{g m}^{-3}$, NOR and SOR all exhibited obviously decreasing trends with increasing O_3 level. In addition, high $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ were investigated during four consecutive seasons at a rural background site (JY) in Chongqing, Southwest China. The mean annual concentration of the $\text{PM}_{2.5}$ was $56.2 \pm 31.0 \mu\text{g m}^{-3}$ —1.6 times the NAAQS limit. Seasonally, the concentration was 1.6–2.0 times higher in winter ($80.4 \pm 39.5 \mu\text{g m}^{-3}$) than in the other seasons ($52.1 \pm 9.4 \mu\text{g m}^{-3}$, $39.0 \pm 17.5 \mu\text{g m}^{-3}$ and $43.9 \pm 18.0 \mu\text{g m}^{-3}$ 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 $\text{PM}_{2.5}$. Compared to autumn and spring, summer exhibited higher concentrations of SO_4^{2-} , perhaps due to the active homogeneous gas-phase formation ($\text{SOR} = 0.32$) in this season; furthermore, these concentrations were augmented by emissions transported from the urban area of Chongqing. The $\text{PM}_{2.5}$ 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_x 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.aaqr.org>.

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