Seasonal characteristics, formation mechanisms and geographical origins of PM_{2.5} in two megacities in Sichuan Basin, China

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Abstract. To investigate the characteristics of PM_{2.5} and its major chemical components, formation 1 2 mechanisms, and geographical origins in the two biggest cities, Chengdu (CD) and Chongqing (CQ), in Sichuan Basin, daily PM_{2.5} samples were collected simultaneously at one urban site in each city for four 3 consecutive seasons from autumn 2014 to summer 2015. Annual mean concentrations of PM2.5 were 4 67.0 ± 43.4 and $70.9 \pm 41.4 \ \mu g \ m^{-3}$ at CD and CQ, respectively. Secondary inorganic aerosols (SNA) 5 and organic matter (OM) accounted for 41.1% and 26.1% of PM2.5 mass at CD, and 37.4% and 29.6% 6 7 at CQ, respectively. Seasonal variations of PM_{2.5} and major chemical components were significant, usually with the highest mass concentration in winter and the lowest in summer. Daily PM_{2.5} 8 9 concentration exceeded the national air quality standard on 30% of the sampling days at both sites, and 10 most of the pollution events were at the regional scale within the basin formed under stagnant meteorological conditions. The concentrations of carbonaceous components were higher at CQ than CD, 11 likely partially caused by emissions from the large amount of motorcycles in CQ. Homogeneous 12 gas-phase reactions probably played an important role in the formation of SO_4^{2-} , while both 13 homogeneous and heterogeneous reactions contributed to the formation of NO₃⁻. Geographical origins 14 of emissions sources contributing to high PM_{2.5} masses at both sites were identified to be mainly 15 distributed within the basin based on potential source contribution function analysis. 16 17

2

18 **1 Introduction**

- Fine particles ($PM_{2.5}$, particulate matter with an aerodynamic diameter smaller than 2.5 μ m) have
- adverse effects on human health (Anderson et al., 2012;Lepeule et al., 2012;Taus et al., 2008),
- deteriorate air quality (Zhang et al., 2008;Paraskevopoulou et al., 2015), reduce atmospheric visibility
- 22 (Fu et al., 2016;Cao et al., 2012;Baumer et al., 2008), impact climate (Ramanathan and Feng,
- 23 2009;Hitzenberger et al., 1999;Mahowald, 2011), and affect ecosystem (Larssen et al., 2006). In the past
- two decades, China has experienced serious PM_{2.5} pollution due to the rapidily increasing energy
- consumption through econmic development, industrialization and urbanization (Tie and Cao, 2009; Tao

et al., 2017). The National Ambient Air Quality Standards (NAAQS) for PM_{2.5} was promulgated by the

- 27 Chinese government in 2012, and strict strategies have been implemented nationwide, e.g. controling
- 28 SO₂ emissions by installing desulphurization system in coal-fired power plants and conversion of fuel to
- natural gas (Lu et al., 2011), mitigating NO_x emissions through traffic restrictions, and reducing
- 30 biomass burning through straw shredding. Despite these efforts, there are still many cities that have not
- yet met the current NAAQS (Tao et al., 2017). According to the '2013-2015 Reports on the State of
- Environment of China', annual mean concentration of $PM_{2.5}$ in all the 74 major cities over China was
- $72, 64, and 50 \ \mu g \ m^{-3}$ in 2013, 2014 and 2015, respectively, and only 4.1%, 12.2% and 22.5% of the
- monitored cities met the NAAQS ($35 \mu \text{g m}^{-3}$).

Previous studies showed that Beijing-Tianjin-Hebei area (BTH), Yangtze River Delta (YRD), Pearl 35 River Delta (PRD), and Sichuan Basin were the four main regions in China with severe aerosol 36 pollution (Tao et al., 2017). While many studies have been conducted in BTH, PRD and YRD regions 37 to understand the general characteristics of PM_{2.5} and its chemical components, formation mechanism, 38 and sources (Ji et al., 2016;Li et al., 2015;Quan et al., 2015;Tan et al., 2016;Yang et al., 2015;Zhang et 39 al., 2013;Zhao et al., 2015;Zhao et al., 2013a;Cheng et al., 2015;Zheng et al., 2015a;Yang et al., 2011a), 40 only a few studies have focused on Sichuan Basin (Tao et al., 2014; Tian et al., 2013; Yang et al., 2011b). 41 Covering an area of 260,000 km² and with a population of around 100 million, the Sichuan Basin is the 42 most populated basin in China. It is a subtropical expanse of low hills and plains and is completely 43 encircled by high mountains and plateaus. It is also characterized by persistently high relative humidity 44 and extremely low wind speeds all the year-round (Guo et al., 2016;Chen and Xie, 2013). The 45 characteristics of PM_{2.5} in Sichuan Basin are supposed to be very different from those in eastern coastal 46 China (i.e. PRD and YRD) and North China Plain (i.e. BTH) due to the special topography and 47

meteorological conditions, besides emission sources, in the basin. Furthermore, the terrain in the two
megacities is also distinct from each other significantly, i.e., Chongqing is a mountainous city lying on
the eastern margin of the basin while Chengdu is a flat city on the western margin of the basin.
Therefore, there is a great interest in comparing the chemical components of PM_{2.5} and characterizing

52 pollution episodes in the two cities.

The present study aims to fill this gap by measuring chemically-resolved PM_{2.5} in Chengdu and 53 Chongqing in four consecutive seasons during 2014-2015. The main objectives are to: (1) characterize 54 PM_{2.5} mass and major chemical components in urban environemntss of Chengdu and Chongqing; (2) 55 compare PM_{2.5} chemical compositions under different pollution levels and identify major chemical 56 57 components responsible for long-lasting PM_{2.5} pollution episodes in winter; (3) explore the possible formation mechanism of the secondary aerosols; and (4) reveal the geographical source regions 58 contibuting to the high PM_{2.5} levels through potential source contribution function (PSCF) analysis. 59 Knowledge gained in this study provides scientific basis for making future emision control plocies 60 aiming to allivating heavy PM_{2.5} pollution in this unique basin. 61

62 **2 Methodology**

63 2.1 Sampling sites

PM_{2.5} samples were collected at two urban sites, one in Chengdu and another in Chongqing, the two 64 largest cities in Sichuan Basin, southwest China. The two sampling sites are located 260 km apart (Fig. 65 1). The sampling site in Chengdu (CD) is located on the roof of a sixth floor building in the Sichuan 66 Academy of Environmental Science (104°4' E, 30°37' N) with no large surrounding industries but heavy 67 traffic. The closest main road (Renmin South road of Chengdu) is about 20 m east of the samling site. 68 The sampling site in Chongqing (CQ) is located on the rooftop of Chongqing Monitoring Center 69 (106°30' E, 29°37' N). The highway G50 is 250 m away from this sampling site. The two selected 70 sampling sites are considered to represent typical urban environment in their respective cities (Tao et al., 71 72 2014;Chen et al., 2017).

73 2.2 Sample collection

74 Daily (23-h) integrated PM_{2.5} samples were collected in four months, each in a different season: autumn

- 75 (23 October to 18 November, 2014), winter (6 January to 2 February, 2015), spring (2 to 29 April, 2015),
- and summer (2 to 30 July, 2015). At both sites, $PM_{2.5}$ samples were collected in parallel on Teflon filters
- (Whatman Corp., 47 mm) and quartz filters (Whatman Corp., 47 mm). At CD site, PM_{2.5} sampling was

78 carried out using a versatile air pollutant sampler (Wang et al., 2017). One channel was used to load 79 PM_{2.5} sample on Teflon filter for mass and trace elements anlysis and the other one was equipped with quatz filter for water-soluble inorganic ions and carbonaceous components analysis. The sampler was 80 running at 15 L min⁻¹ for each channel. At CQ site, a low-volume aerosol sampler (BGI Corp., frmOmni, 81 USA) operating at a flow rate of 5 L min⁻¹ was used to collect PM_{2.5} samples on Teflon filter, and 82 another sampler (Thermo Scientific Corp. Partisol 2000i, USA) with a flow rate of 16.7 L min⁻¹ was 83 used to collect PM_{2.5} samples on quartz filter. A total of 112 samples and 8 field blanks, nearly equally 84 distributed in the four seasons, were collected at each site during the campaign. In addition, three lab 85 blank filters in each campaign were stored in a clean Petri slides in the dark and analysed in the same 86 ways as the collected samples to evaluate the background contamination. 87

Before sampling, all the quartz filters were preheated at 450°C for 4 h to remove the organic 88 compounds. All sampled filters were stored in clean Petri slides in the dark and at -18°C until analysis 89 to prevent the evaporation of volatile compounds. Before and after sample collection, all the Teflon 90 filters were weighted at least three times using an microbalance (Sartorius, ME 5-F, Germany) after 91 their stabilization for 48 h under controlled conditions (temperature: 20~23°C, relative humidity: 92 45~50%). Differences among replicate weights were mostly less than 15 µg for each sample. 93

2.3 Chemical analysis 94

For the analysis of water-soluble inorganic ions, a quarter of each quartz filter was first extracted using 95 ultrapure water in an ultrasonic bath for 30 min, and then filtered through a 0.45 µm pore syringe filter. 96 Anions (SO₄²⁻, NO₃⁻ and Cl⁻) and cations (Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺) were determined using ion 97 chromatograph (Dionex Corp., Dionex 600, USA). Anions were separated using AS11-HC column with 98 30 mM KOH as an eluent at a flow rate of 1.0 ml min⁻¹. Cations were determined using CS12A column 99 with 20 mM MSA (methanesulfonic acid) at a flow rate of 1.0 ml min⁻¹. Individual standard solutions of 100 all investigated anions and cations (1000 mg L⁻¹, o2si, USA) were diluted to construct the calibration 101 curves. The correlation coefficients of the linear regression of the standard curves were all above 0.999. 102 Field blanks were prepared and analyzed together with the samples and then subtracted from the 103 samples. The concentrations of the water-soluble inorganic ions in the field blanks were in the range of 104 0.008-0.13 µg m⁻³. The relative standard deviation of each ion was better than 8% for the reproducibility 105 test. 106

107

Organic carbon (OC) and elemental carbon (EC) were measured by thermal-optical reflectance

108 (TOR) method using a DRI OC/EC analyzer (Atmoslytic Inc., USA). The methodology for OC/EC

analysis was based on TOR method as described in (Chow et al., 2007). For calibration and quality

110 control, measurement with filter blank, standard sucrose solution and replicate analysis were performed.

111 Blank corrections were performed by subtracting the blank values from the sampled ones. The

112 concentration of EC in field blanks was zero while OC was below $0.7 \ \mu g \ C \ cm^{-2}$. The repeatability was

113 better than 15%.

114 The elements including Al, Si, Ca, Fe, and Ti were analyzed on Teflon filter using X-ray

115 fluorescence analyzer (Epsilon 5ED-XRF, PAN'alytical Corp., Netherlands), the QA/QC procedures of

the XRF analysis have been described in (Cao et al., 2012). The gaseous species were continuously

- measured by a set of online gas analyzers, including EC9850 SO₂ analyzer, 9841 NO/NO₂/NO_x analyzer,
- 118 9830 CO analyzer, and 9810 O₃ analyzer (Ecotech Corp., Australia) at CD, and Thermo 42i
- 119 NO/NO₂/NO_x analyzer, 43i SO₂ analyzer, 48i CO analyzer, and 49i O₃ analyzer (Thermo Scientific

120 Corp., USA) at CQ. The mass concentration of PM_{2.5} was automatically measured by online particulate

- 121 monitor instruments (BAM1020, Met one Corp., USA, at CD and 5030 SHARP, Thermo Scientific
- 122 Corp, USA, at CQ). Hourly meteorological parameters, including ambient temperature (T), relative
- humidity (RH), wind speed (WS) and direction, barometric pressure (P), and solar radiation (SR) were
- 124 obtained from an automatic weather station (Lufft Corp. WS501, Germany) at each site. Planetary
- boundary layer height (PBLH) was obtained from HYSPLIT model
- 126 (http://ready.arl.noaa.gov/HYSPLIT.php).

127 **2.4 Data analysis**

- 128 The EC-tracer method has been widely used to estimate SOC (Turpin and Lim, 2001;Castro et al.,
- 129 1999), which can be expressed as
- 130 $POC=(OC/EC)_{prim} \times EC$ (1)
- 131 SOC=OC-POC (2)

Where POC, SOC and OC represent estimated primary OC, secondary OC and measured total OC, respectively. $(OC/EC)_{min}$ was simplified as the $(OC/EC)_{prim}$ to estimate SOC in this study. $(OC/EC)_{min}$ was 2.4, 2.6, 1.6 and 2.2 in autumn, winter, spring and summer at CD, respectively, and 1.9, 2.8, 1.1 and 1.5 at CQ. The estimated SOC was only an approximation with uncertainties, e.g., from influence of biomass burning (Ding et al., 2012).

137 The coefficient of divergence (COD) has been used to evaluate the spatial similarity of chemical

compositions at different sites (Wongphatarakul et al., 1998;Qu et al., 2015), which is defined as

139
$$COD_{jk} = \sqrt{\frac{1}{p} \sum_{i}^{p} (\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}})^2}$$
 (3)

Where *x_{ij}* and *x_{ik}* represent the average concentration for a chemical component *i* at site *j* and *k*,
respectively, *p* is the number of chemical components. Generally, a COD value lower than 0.2 indicates
a relatively similarity of spatial distribution.

143 **2.5 Geographical origins of PM**_{2.5}

144 72-h air mass back trajectories were generated based on the Hybrid Single Particle Lagrangian

145 Integrated Trajectory (HYSPLIT) model using 0.5°×0.5° meteorological data for PM_{2.5} measurements

from October 2014 to July 2015 at both sites. Four trajectories at 04:00, 10:00, 16:00, and 22:00 UTC

every day with the starting height of 300 m above ground level were calculated (Squizzato and Masiol,2015).

PSCF is substantially a conditional probability that trajectories with pollutant concentrations larger than a given criterion passed through a grid cell (i,j) (Ashbaugh et al., 1985;Polissar et al., 1999), that means a grill cell (i,j) with high PSCF values are mostly potential source locations of pollutants. PSCF is defined as follows,

153
$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}}$$
(4)

Where n_{ij} is the total number of endpoints falling in the grid cell (i,j) and m_{ij} denotes the number of endpoints that are associated with samples exceeding the threshold criterion in the same cell. To reduce the PSCF uncertainties associated with small n_{ij} values, weighting function was adopted as follows,

$$157 \quad W_{ij} = \begin{cases} 1.0 & 3n_{ave} < n_{ij} \\ 0.7 & 1.5n_{ave} < n_{ij} \le 3n_{ave} \\ 0.42 & n_{ave} < n_{ij} \le 1.5n_{ave} \\ 0.2 & n_{ij} \le n_{ave} \end{cases}$$
(5)

158 Where n_{ave} is the average number of endpoints in each grid cell.

159 The trajectories coupled with daily pollutants concentrations were used for PSCF analysis, with the

threshold criterion in PSCF analysis being set at the upper 50% of $PM_{2.5}$ and other pollutants. The

trajectory covered area was in the range of 20-45° N and 90-120° E and divided into $0.5^{\circ} \times 0.5^{\circ}$ grid cells.

162 **3 Results and discussion**

163 **3.1 PM_{2.5} mass concentration and chemical composition**

164 **3.1.1 Overview**

165 Table 1 presents seasonal and annual mean concentrations of PM2.5 and its major chemical components at CD and CQ during the sampling periods. Daily $PM_{2.5}$ ranged from 11.6 to 224.7 µg m⁻³ with annual 166 average being $67.0 \pm 43.4 \ \mu g \ m^{-3}$ at CD and $70.9 \pm 41.4 \ \mu g \ m^{-3}$ at CQ, which were about two times the 167 NAAQS annual limit. Secondary inorganic aerosol (SNA, the sum of SO_4^{2-} , NO_3^{-} and NH_4^{+}) and 168 carbonaceous species together represented more than 70% of PM_{2.5} mass at both sites (Fig. 2). The 169 annual mean concentrations of SNA were 27.6 µg m⁻³ at CD and 26.5 µg m⁻³ at CQ, contributing 41.1% 170 and 37.4% to PM_{2.5} mass, respectively. $SO_4^{2^-}$, NO₃⁻ and NH₄⁺ accounted for 16.8%, 13.6% and 10.8%, 171 respectively, of PM_{2.5} mass at CD, and 17.2%, 10.9% and 9.2%, respectively, at CQ. Organic matters 172 (OM), estimated from OC using a conversion factor of 1.6 to account for other elements presented in 173 organic compounds (Turpin and Lim, 2001; Tao et al., 2017), were the most abundant species in PM_{2.5}, 174 accounting for 26.1% and 29.6% of PM_{2.5} mass at CD and CQ, respectively. In contrast, EC only 175 comprised of around 6% at both sites. The annual mean concentrations of OC and EC were 20% and 176 25%, respectively, higher at CQ than CD. 177

The annual mean concentration of fine soil (FS), calculated by summing the oxides of major crustal elements, i.e., Al₂O₃, SiO₂, CaO, FeO, Fe₂O₃, and TiO₂ (Huang et al., 2014), was 6.7 μ g m⁻³ (9.5% of PM_{2.5} mass) at CQ. It is noted that this was about two times that at CD (3.8 μ g m⁻³, 5.7% of PM_{2.5} mass). The minor components such as K⁺ and Cl⁻ constituted less than 5% of PM_{2.5}. The unaccounted portions of PM_{2.5} reached 18.3% at CD and 15.3% at CQ, which were likely related to the uncertainties in the multiplication factor used for estimating OM and FS, other unidentified species, and measurement uncertainties.

185 **3.1.2 Seasonal variations**

Figure 3 shows the seasonal variations in mass concentrations of PM_{2.5} and its major chemical 186 components at CD and CQ. Seasonal variations of any pollutants should be influenced by the seasonal 187 variations in source emission intensities, atmospheric processes and meteorological conditions. Unlike 188 in northern China, there were no extensive coal combustion or wood burning for domestic heating in 189 winter due to the warm temperature (around 10°C on average) in Sichuan Basin, hence atmospheric 190 processes and meteorological conditions played a vital role in the seasonal variations of PM_{2.5}. On a 191 seasonal basis, PM2.5 mass was highest in winter at both CD and CQ, which was 1.8-2.5 times of those 192 in the other seasons. In contrast, its seasonal differences among the other three seasons were generally 193 small, i.e., less than 40%. Stagnant air condition with frequent calm winds and low planetary boundary 194

layer height was the major cause of the highest $PM_{2.5}$ mass in winter (Table 1) (Liao et al., 2017;Chen and Xie, 2013).

All the major $PM_{2.5}$ components except FS followed the seasonal pattern of $PM_{2.5}$ mass with subtle differences. The highest FS concentrations were observed in spring at both sites. The relatively high wind speed and lower RH in spring were conducive for re-suspension of crustal dust and resulted in higher FS concentrations. In addition, frequent spring dust storms originated in the northwestern China was able to reach Sichuan Basin via long-rang transport, and cause the elevated FS concentrations (Chen et al., 2015;Tao et al., 2013).

The majority of $PM_{2.5}$ components showed a summer minimum, which was caused by high planetary boundary layer height favoring pollutants dispersion and abundant precipitation favoring wet scavenging. In contrast, the lowest seasonal average concentrations did not appear in summer for SO_4^{2-} likely due to the enhanced photochemical reactions associated with high temperature and strong solar radiation. High O₃ concentrations in summer also supported this seasonal trend.

It is also noted that the seasonal variations of NO_3^- were much larger than those of SO_4^{2-} and NH_4^+ . This can be explained by the enhanced formation of NO_3^- under high RH in winter, and volatility of NH_4NO_3 in summer under high temperature condition (Pathak et al., 2009;Quan et al., 2015;Squizzato et al., 2013). In addition, thermodynamically driven behavior of NH_4NO_3 was another factor for the lower NO_3^- concentrations in summer (Wang et al., 2016;Kuprov et al., 2014).

Both OC and EC exhibited the highest concentrations in winter at CD and CQ, whereas seasonal 213 differences of those carbonaceous components were less distinct in other seasons, e.g. the variations of 214 OC and EC among the other three seasons were less than 30%. Seasonal average SOC was 215 unexpectedly highest in winter at both sites, different from the anticipated high value in summer in 216 consideration of strong photochemical reaction. Condensation of semi-volatile organic aerosols in 217 winter seemed to play a larger role than photochemical reaction in summer, knowing that low 218 temperature favors condensation process (Sahu et al., 2011;Cesari et al., 2016). Although high O₃ and 219 strong solar radiation condition in summer was conducive to strong photochemical reactions, high 220 temperature favored gas-particle partitioning in the gas phase and thus limited the increase of SOC 221 (Strader et al., 1999). 222

Seasonal average relative contributions of major chemical components to PM_{2.5} are depicted in Fig.
2. The seasonal average contributions of SNA to PM_{2.5} only varied within a small range from 39.5% to

- 43.2% at CD, whereas in a relatively larger range from 31.0% in summer to 37.1-41.5% in other
- seasons at CQ. The smaller contribution in summer at CQ was mainly due to the lower NO_3^{-1}
- 227 concentrations. At both CD and CQ, NO_3^- and NH_4^+ showed the highest contributions in winter and the
- lowest ones in summer, whereas an opposite trend was found for SO_4^{2-} . The contributions of
- 229 carbonaceous components (the sum of OC and EC) generally followed the seasonal patterns of SNA,
- accounting for 26.7-38.8% of $PM_{2.5}$ mass. Among these, OM showed the lowest fractions in $PM_{2.5}$ in
- spring (21.1%) at CD and highest value in winter (33.6%) at CQ, while the percentages of OM in other
- seasons were similar at both sites, around 27%. The seasonal variations of EC fractions were not
- obvious, with a slightly higher value in spring. The highest contributions from FS was more than 10%,
- appeared in spring at both sites.

235 **3.1.3 Similarities and differences between the two sites**

Although none of the two sites alone can represent the whole region of the Sichuan basin, the similarities in the characteristics of the major pollutants between the two sites should represent the reginal-scale characteristics of urban-environment pollution while the differences between the two sites should reflect the sub-regional characteristics of urban pollution. A comparison between the two sites in terms of seasonal-average concentrations of major chemical components is shown in Fig. 4 and discussed in detail below.

Despite the 260 km distance between the two sampling sites, a moderate similarity was observed in 242 autumn, winter and spring on the basis of low COD values (0.15-0.18), indicating the regional-scale 243 PM_{2.5} pollution pattern in Sichuan Basin and the similarities in major emission sources for both sites. 244 The regional pollution was related to the special topography of the basin, which is a closed lowland 245 surrounded by high mountains on all sides (Fig. 1). The mean elevation in the basin is about 200-700 m, 246 while the surrounded mountains are around a scope of 1000-3000 m elevation. The Tibetan Plateau lies 247 close to the western Sichuan Basin, with an elevation above 4000 m. Such a Plateau-Basin topography 248 forms a barrier for the dispersion of pollutants and causes air stagnation within the basin, thereby 249 facilitating regional scale pollution events in the Basin. 250

72-h air masses back trajectories analysis (18:00 local time) showed that air masses reaching at CD and CQ mainly originated from local areas in the basin (Fig. S1), confirming the influence of the high mountainous surrounding the basin. These results were consistent with those found in earlier studies in Chengdu and Chongqing (Tian et al., 2017;Liao et al., 2017), which suggested that air masses had short-range trajectories and primarily originated from inside the Sichuan Basin, highlighting the impacts of the special topography on $PM_{2.5}$ pollution. A similar case has also been found elsewhere, such as in Po Valley, Italy (Ricciardelli et al., 2017). Po Valley is bordered by the Alps in the north and Apennines in the south, which caused a strong homogeneity in $PM_{2.5}$ pollution at the regional sacle.

It is worth to note that the COD values used to identify the similarities or differences of two sites 259 were calculated based on seasonal-average concentrations of all components in PM2.5. However, if 260 focusing on individual components, several chemical species in PM2.5 differed by up to a factor of 2.5 in 261 their season-average concentrations between CD and CQ, e.g. OC and EC in winter and spring, and 262 Cl and FS in all the four seasons. In summer, the differences for several major chemical components 263 (FS, OC, SO₄²⁻, NO₃⁻, EC) between the two sites were larger than in other seasons, causing a high COD 264 value (0.33). These discrepancies were partly caused by the different atmospheric chemical processes, 265 local sources and meteorological parameters between the two sites. 266

Specifically, FS mostly deviated from the 1:1 straight line in all seasons, with substantially higher 267 concentrations at CQ than CD (Fig. 4). The main cause of this difference was the higher wind speeds 268 and lower RH at CQ than CD. There was no significant difference in NH₄⁺ concentrations between CD 269 and CQ, but considerable differences in SO_4^{2-} and NO_3^{-} in spring and summer. SO_2 concentration was 270 271 around 25% higher at CQ than CD in spring and summer, which partially explained the site-differences in SO_4^2 . In contrast, NO₂ concentration was comparable at both sites in summer, but NO₃⁻ concentration 272 was 58% lower in CQ than CD. The site-differences in NO₃⁻ concentration was caused by NH₄NO₃ 273 thermodynamic equilibrium controlled by ambient temperature and RH, instead of by its gaseous 274 precursors. The equilibrium would be shifted toward the particulate phase when ambient RH was above 275 the deliquescence relative humidity (DRH) of NH₄NO₃, and the dissociation constant decreased by 276 about one order of magnitude when RH was above 75% (Kuprov et al., 2014). DRH was calculated 277 from ambient RH following Mozurkewich (1993). As shown in Table 1, the average temperature was 278 279 comparable at CD and CQ during the summer period, hence leading to similar DRH values of NH₄NO₃, ranging from 59% to 64% with an average value of 60.7%. However, the ambient RH was substantially 280 lower at CQ (61%) than CD (72%), causing lower NO₃⁻ concentration at CQ. As shown in Fig. S2, 53% 281 of the hourly data in summer having ambient RH lower than DRH at CQ, while only 19% such data at 282 CD, which explained the different NO₃⁻ concentrations between CD and CQ.Fig.4 shows higher 283 concentrations of carbonaceous component (OC and EC) at CQ than CD in all seasons except OC in 284

285 autumn and EC in winter. OC and EC mainly originate from fossil fuel combustion and biomass burning. K^+ is usually regarded as a tracer of biomass burning (Tao et al., 2016). During the sampling 286 campaign, no significant differences in K⁺ levels were observed between CD and CQ (Table 1), 287 suggesting that biomass burning was not be the major cause of the higher concentrations of 288 carbonaceous component at CQ. Motorcycle traffic was likely a major source of volatile organic 289 compounds (VOCs) in CQ since it is a famous mountain city where most people use motorcycle as 290 daily traffic tools. According to the Chongqing Statistical Yearbook 2015, the number of motorcycles 291 was 2.0 million (among the total of 2.3 million motor vehicles) in 2014, which was much higher than 292 those (0.7 million) in Chengdu (Chengdu Statistical Yearbook 2015). Moreover, Chongqing has become 293 294 China's largest automobile production base, which likely also emit VOCs from the spraying process. Higher concentrations of VOCs in CQ would cause higher concentrations of secondary organic carbon 295 via photochemical reaction under high temperature or vapor condensation under low temperature. This 296 hypothesis is supported by the large differences in OC concentrations in winter between the two sites. 297

Correlation analysis may also provide an insight into the similarities/differences between the two sites over an intensive sampling period. Good correlations between the two sites were found for daily SNA, OC, EC and K^+ concentrations in autumn, winter and spring (Table 2). However, for NO₃⁻, a significant correlation was identified only in autumn, likely due to the strong impact of local vehicle emissions and the subsequent atmospheric processes forming NO₃⁻. Similarly, a moderate correlation was observed just in winter for both Cl⁻ and FS. In summer, weak or no correlations were identified between the two sites for almost all chemical components.

305 **3.2 PM_{2.5} formation mechanisms and geographical origins**

306 3.2.1 Pollution episodes and key chemical components

307 Pollution episodes during the campaign are highlighted with shaded areas in Fig. 5. These pollution

periods (PP) were defined as daily $PM_{2.5}$ concentration being above the NAAQS guideline value of 75

 μ g m⁻³. Similarly, the days with PM_{2.5} concentration below 75 μ g m⁻³ were characterized to be clean

310 periods (CP). A total of seven pollution episodes were identified during the campaign at each site. There

- 311 were three long-lasting pollution episodes occurred simultaneously at the two sites on 23-27 October
- 312 2014, 7(8)-26 January, and 26-28 (29) April 2015. A total of 34 and 31 polluted days were counted at
- CD and CQ site, respectively, accounting for 30.4% and 28.6% of the entire sampling days (112 days).
- The number of polluted days at CD was 8, 21, 4 and 1 in autumn, winter, spring and summer,

- accounting for 29.6%, 75%, 14.3% and 3.4% of the total sampling days in each season, respectively,
- and at CQ they were 4, 19, 6 and 2, accounting for 14.8%, 67.9%, 21.4% and 6.9%.

Stagnant atmosphere and high relative humidity were important factors causing PM_{2.5} pollution 317 events, as was found in this and earlier studies (Zheng et al., 2015b;Chen et al., 2017;Liao et al., 2017). 318 Compared with the clean periods, the pollution periods were usually characterized by low planetary 319 boundary layer height and weak wind speed (Table S1), which suppress pollutants dispersion vertically 320 and horizontally. Temperature increased during the long-lasting pollution episodes, which promoted 321 gas-to-particle transformation, forming secondary aerosols. RH remained high (68-88%) during 322 pollution episodes (except in spring at CQ), although not much different from clean periods, which was 323 also conducive for aqueous-phase reactions converting gaseous pollutants into aerosols (Chen et al., 324 2017;Tian et al., 2017). 325

Looking more closely at a regional-scale long-lasting pollution episode in winter, from 8 January to 326 26 January 2015, the concentrations of PM_{2.5} and major chemical components increased dramatically 327 compared with clean periods (Fig. 6). PM_{2.5} concentrations were more than three times higher at both 328 sites, with the two dominant groups of components, SNA and OC, being 2.5-2.8 times higher at CD and 329 1.7-2.7 times higher at CQ. The enhancement of SNA and OC during pollution periods were similar at 330 CD, but OC increased much more than SNA at CQ, indicating some different contributing factors to the 331 high PM_{2.5} pollution at the two sites. Pollutants accumulation under stagnant meteorological conditions 332 might be a main factor at CD based on the similar magnitudes of the enhancements of PM_{2.5} and its 333 dominant components, while additional processes should have increased OC more than other 334 components at CQ. 335

The percentage contributions of SNA to PM_{2.5} were similar during clean and polluted periods, 336 38-41% at CD and CQ (Fig. S3). However, the percentage contribution of OM to PM_{2.5} decreased from 337 30.1% on clean days to 27.5% on polluted days at CD, and increased from 26.9% to 34.9% at CQ. 338 Concentrations of the individual SNA species ($SO_4^{2^-}$, NO_3^{-} and NH_4^{+}) increased by a factor of 2.5-3.3 339 on polluted days compared with clean days in all the cases (Fig. 6). But the percentage contributions 340 differed among the species as NO_3^{-1} increased and SO_4^{2-1} decreased on polluted days. The percentage 341 contributions of SNA and OM to PM2.5 discussed above were different from those found in eastern 342 coastal China and North China Plain, where considerable increases were found for SNA and decreases 343 for OM on polluted days than clean days (Tan et al., 2009; Wang et al., 2015a; Quan et al., 2014; Zhang 344

et al., 2015;Zhang et al., 2016;Cheng et al., 2015). The polluted periods in eastern coastal China and

North China Plain were accompanied with sharp increases of RH, which would promote aqueous-phase

formation of secondary inorganic aerosols and resulted in rapid elevation of SO_4^{2-} and NO_3^{-}

concentrations (Zheng et al., 2015b;Zheng et al., 2015a;Zhao et al., 2013b;Li et al., 2017). In contrast,

RH remained high during clean or polluted periods in the present study, suggesting that high RH might

not be the driving force for the pollution episodes in Sichuan Basin. Another point that need to be

351 mentioned is that, local sources were the main contributors to the pollution episodes in Sichuan basin

while sources outside local regions frequently contributed to pollution episodes in eastern coastal China

and North China Plain through long/medium range transport (Gao et al., 2015; Hua et al., 2015; Wang et

al., 2015b).

355 3.2.2 Transformation mechanisms of secondary aerosols

In most cases, meteorological conditions, atmospheric chemical processes and long-range transport are 356 all responsible for PM_{2.5} accumulation (Zheng et al., 2015b). CO and EC are directly emitted from 357 combustion processes and are not very reactive, thus, their concentrations in the air are strongly 358 controlled by meteorological parameters within a relatively short period, which make them a good 359 tracer that can be used for separating different dominant factors contributing to pollutants accumulation 360 (Zheng et al., 2015b;Zhang et al., 2015). In the present study, CO was chosen as a reference pollutant 361 species for investigating other pollutants of interest. CO concentration increased by a factor of 1.8 at 362 CD and 1.5 at CQ during polluted periods than clean periods. In comparison, other chemical species 363 (except NO₂) increased by a factor of 1.8-3.3. A similar contrast between CO and other pollutants was 364 also seen in (Li et al., 2017). Similar diurnal variations were also found between clean and polluted 365 periods for CO (Fig. S4), suggesting no significant extra CO emission during polluted periods. Thus, the 366 increased concentrations of CO during polluted periods were primarily driven by meteorological 367 conditions. Therefore, the impact of atmospheric physical processes on other pollutants can be reduced 368 369 by scaling the concentrations of other pollutants to that of CO, meaning that the impact of chemical reactions can then be captured based on the ratio of other pollutants to CO concentrations. For example, 370 PM_{2.5} was enhanced by a factor of 2.7 on polluted days at both sites, but the CO-scaled PM_{2.5} (the ratio 371 of PM_{2.5} to CO concentration) only showed an enhancement of a factor of 1.6-1.8 (Fig. 7), and the latter 372 values were likely from the enhanced secondary aerosol formation. 373

As shown in Fig. 7, the CO-scaled SNA was 60-90% higher on polluted days with individual

375 species 40-120% higher, even though their gaseous precursor (SO₂ and NO₂, no data for NH₃) were 376 only less than 30% higher. This suggests stronger chemical transformation from gaseous precursors to particle formation on polluted days. Sulfur oxidation ratio (SOR = $n-SO_4^{2^-}/(n-SO_4^{2^-}+n-SO_2)$) and 377 nitrogen oxidation ratio (NOR = $n-NO_3^{-1}/(n-NO_3^{-1}+n-NO_2)$) were defined to evaluate the degree of 378 secondary transformation (*n* refers to as the molar concentration) (Hu et al., 2014). NOR increased from 379 0.09 on clean days to 0.16 on polluted days at CD and from 0.07 to 0.14 at CQ. SOR increased only 380 slightly, from 0.31 to 0.35 at CD and 0.28 to 0.35 at CQ. The CO-scaled SOC increased by a factor of 381 2.6 on polluted days at CQ, but no significant change was found at CD (Fig. 7). The different patterns in 382 SOC (or SOC/OC) than SNA (or SOR and NOR) suggest that secondary organic aerosols (SOA) 383 production was of less important than SNA production at CD. 384 SO_4^{2-} is predominantly formed via homogeneous gas-phase oxidation. In this pathway, SO_2 is 385 firstly oxidized by OH radical to SO₃, and then to H₂SO₄ (Stockwell and Calvert, 1983;Blitz et al., 386 2003). Apart from homogeneous reaction, particulate SO_4^{2-} can also be formed through heterogeneous 387 reactions with dissolved O₃ or H₂O₂ under the catalysis of transition metal and in-cloud process 388 (Ianniello et al., 2011). HNO₃ is primarily produced from the reactions between NO₂ and OH radical 389 during the daytime and later combines with NH₃ to produce particulate NO₃⁻ (Calvert and Stockwell, 390 1983). Particulate NO_3^- can also be formed through heterogeneous hydrolysis of N_2O_5 on moist and 391 acidic aerosols during nighttime (Ravishankara, 1997;Brown and Stutz, 2012). Similarly, SOA is 392 mainly formed through photochemical oxidation of primary VOCs followed by condensation of SVOC 393 onto particles as well as through aqueous-phase reactions (Ervens et al., 2011). While photochemical 394 reactions are mostly influenced by temperature and oxidants amount, heterogeneous reactions always 395 depends on RH. To further explore the formation mechanisms of secondary aerosols, SOR, NOR and 396 SOC/OC data were grouped with temperature (at 2°C interval), RH (at 5% interval) and daytime O₃ 397 concentration (at 5 µg m⁻³ interval) bins (Fig. 8). An obvious increase of SOR with increasing RH was 398 found at both sites, but this was no the case for temperature and O₃ concentration, suggesting 399 heterogeneous processes played important roles in the formation of SO_4^{2-} . Interestingly, SOR exhibited 400 a decreasing trend with increasing O_3 concentration at O_3 concentrations lower than 15 µg m⁻³ and an 401 opposite trend was found at O₃ concentrations above 20 μ g m⁻³ (Fig. 8). Additionally, high PM_{2.5} 402 concentrations were mostly associated with lower O₃ concentrations. Aerosols are generally considered 403 as a constraining factor to O₃ production due to their absorption and scattering of UV radiation, which 404

405 reduce solar radiation and consequently decrease photochemical activity. Apparently, other factors could become dominant in O_3 production and alter such a trend. Low O_3 concentrations were further 406 found to be associated with high RH (Fig. S5), indicating that the formation of SO_4^{2-} during the polluted 407 periods was dominated by heterogeneous aqueous processes rather than photochemical reactions at both 408 sites, as suggested in many previous studies (Quan et al., 2015;Zheng et al., 2015a;Zhao et al., 2013b). 409 Unlike SOR, NOR increased with both temperature and RH, suggesting combined the effects from 410 homogeneous and heterogeneous reactions. However, under the very high temperature and RH 411 conditions, NOR exhibited a decreasing trend with increasing temperature and RH. Volatilization of 412 NH₄NO₃ at high temperature should be the major cause of such a phenomenon, but it is not clear 413

about the cause of the decreasing trend of NOR under high RH.

(Pathak et al., 2004, 2009) investigated the formation mechanism of NO₃⁻ in ammonium-rich and 415 ammonium-poor samples, suggesting homogeneous gas-phase reaction became evident to form NO_3^{-1} 416 under the former conditions while heterogeneous process dominated the NO3⁻ formation under the latter 417 conditions. As shown in Fig. 9, SO_4^{2-} and NO_3^{-} were almost completely neutralized by NH_4^{+} , indicating 418 an ammonium-rich environment during the sampling campaign. The ammonium-rich environment was 419 also confirmed by the molar ratios of $[NO_3^-]/[SO_4^{2-}]$ and $[NH_4^+]/[SO_4^{2-}]$. The molar ratio $[NO_3^-]/[SO_4^{2-}]$ 420 as a function of $[NH_4^+]/[SO_4^{2-}]$ is depicted in Fig. 09, which shows significant positive correlations 421 $(R^2=0.82-0.83 \text{ at the two sites})$. Linear regression equations were obtained as $[NO_3^-]/[SO_4^{2-}] =$ 422 $0.85[NH_4^+]/[SO_4^{2-}]-1.89$ at CD and $[NO_3^-]/[SO_4^{2-}] = 0.92[NH_4^+]/[SO_4^{2-}]-1.82$ at CQ. Based on these 423 equations, the molar ratio of $[NH_4^+]/[SO_4^{2-}]$ was defined as the threshold value separating 424 ammonium-rich and ammonium-poor conditions when the value of $[NO_3^-]/[SO_4^{2-}]$ was zero. In the 425 present study, the threshold value was 2.2 and 2.0 at CD and CQ, respectively. The molar ratio 426 $[NH_4^+]/[SO_4^{2-}]$ was higher than the threshold value at both sites, suggesting the prevalence of 427 ammonium-rich condition. The near-perfect fitting between the molar ratio $[NO_3^-]/[SO_4^{2-}]$ and 428 $[NH_4^+]/[SO_4^{2-}]$ further demonstrated the characteristics of NO₃⁻ formed through homogenous gas-phase 429 reaction. Moreover, NO_3^- showed a strong correlation with excess NH_4^+ with correlation coefficients of 430 0.98-0.99 at both sites, providing an insight into the gas-phase reactions of ambient NH₃ and HNO₃. 431 Using high-resolution inorganic ions data, (Tian et al., 2017) demonstrated that NO₃⁻ was primarily 432 formed via homogeneous reaction when RH below 75% and through heterogeneous processes when RH 433 was above 75%. The increases in NOR with RH at both sites also revealed the possibility of the 434

heterogeneous processes, although this cannot be verified directly due to the lack of high-resolutiondata.

The ratio of SOC/OC decreased with temperature at CD but increased with temperature at CQ when T was lower than 10° C. Although SOC/OC did not correlate well with RH, an opposite trend was also found between CD and CQ at high RH conditions. Heterogeneous reactions seemed to be dominant in the formation of SOA at CD, whereas homogeneous reactions were prevalent at CQ. SOC/OC showed no apparent dependency on O₃ concentrations at either site, indicating more complex formation mechanisms of SOA than SO_4^{2-} and NO_3^{-} .

443 **3.2.3 Geographical origins of high PM_{2.5} pollution**

PSCF analysis was applied to investigate the potential source regions contributing to high PM_{2.5} 444 pollution. As can be seen from the PSCF maps in Fig. 10, all the pollutants including PM_{2.5} and its 445 chemical components as well as gaseous precursors had similar spatial patterns of potential source areas. 446 Basically, all the major source areas for high pollutants concentrations were distributed within the basin. 447 Long-range transports as seen in North Plain and eastern coastal regions were not observed at CD and 448 CQ (Zhao et al., 2015; Zhang et al., 2013). At CD, the major source areas in winter included the areas of 449 the northeastern, southeastern and southern Chengdu and in some areas of eastern Chongqing. A similar 450 spatial distribution of PM2.5 potential sources was also found by (Liao et al., 2017) through PSCF 451 analysis in winter 2013, in which high PM2.5 concentrations were mostly associated with sources 452 broadly located in the southeast of the basin, covering Neijiang, Zigong, Yibin, Luzhou and east part of 453 Chongqing. At CQ, the northeast area of Chongqing was identified as strong sources, where a number 454 of industries were located, such as Changshou chemical industrial ozone. Overall, PM2.5 pollution at CQ 455 was characterized by significant local contribution from major sources located in or nearby Chongqing. 456 In contrast, regional transport in Sichuan Basin from southeast, south and southwest of Chengdu had a 457 major impact on PM_{2.5} pollution at CD. 458

459 **4 Conclusions**

460 Chemically-resolved $PM_{2.5}$ data collected during four seasons at two urban sites in Sichuan basin, 461 southwest China were analyzed in the present study. The concurrent occurrences of heavy pollution 462 events at the two sites and similarities in pollutants characteristics between the two sites demonstrated 463 the regional-scale phenomenon of $PM_{2.5}$ episodes inside the Basin, which was mainly caused by the 464 surrounding mountainous topography under typical stagnant meteorological conditions. Such a finding 465 was also supported by back trajectory analysis which showed that air masses reaching at both sites were originated within the basin and only traveled for short distances on heavy polluted days. Differences 466 between the two sites with regards to several major chemical components provided evidences of 467 sub-regional characteristics of emission sources and chemical transformation processes under different 468 meteorological conditions. For example, an additional source factor from motorcycle traffic was 469 identified for VOCs emission in Chongqing, which led to higher high OC concentrations, and lower 470 relative humidity in Chongqing caused lower nitrate concentration in this city despite similar levels of 471 its gaseous precursors in the two cities. The present study also identified different driving mechanisms 472 for the polluted PM_{2.5} episodes in the Sichuan Basin than in the other regions of China. For example, 473 sharply increased relative humidity was thought to be one of the main factors causing high inorganic 474 aerosol concentrations during the polluted periods in eastern coastal China and North China Plain, while 475 in Sichuan Basin the special topography and meteorological conditions are driving forces for such 476 events considering humidity was high throughout the year and did not differ much between polluted and 477 clear periods. However, on annual basis heterogeneous reactions might be more important in this basin 478 than in other regions of China due to the consistent high humidity conditions, as revealed in the case of 479 sulfate formation in the present study. Future studies should use high-resolution data to verify the 480 findings related to chemical transformation paths proposed here. More importantly, a detailed emission 481 inventory of aerosol particles and related gaseous precursors in the basin should be developed promptly, 482 which is needed for further investigating PM_{2.5} formation mechanisms and for making future emission 483 control policies. Source-receptor analysis using monitored chemical-resolved PM2.5 data should be 484 conducted to verify such emission inventories. 485

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487 *Competing interests*. The authors declare that they have no conflict of interest.

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			CD		_			CQ		_
	Autumn	Winter	Spring	Summer	Annual	Autumn	Winter	Spring	Summer	Annual
Meteorologica	l parameters									
T (°C)	15.8±2.9	9.3±2.5	20.4±4.4	28.3±2.9	18.5±7.7	16.0±3.2	10.0±2.3	20.5±4.5	28.4±3.4	18.8±7.6
P (hPa)	960±3.8	963±4.7	954±7.9	946±2.1	955±8.1	981±4.2	984±5.2	974±8.4	963±2.2	975±7.7
RH (%)	81.9±9.0	80.9±6.8	70.5±8.6	72.2±11.3	76.3±10.3	76.1±5.7	68.7±8.8	60.7±13.6	61.0±13.3	66.5±12.5
$SR (w m^{-2})$	54.9±40.3	37.8±27.2	128.9±65.0	123.6±94.2	67.2±56.7	na.	na.	na.	na.	na.
WS (m s^{-1})	0.5±0.2	0.4±0.3	0.7 ± 0.4	0.5±0.2	0.5±0.3	0.7±0.2	0.7±0.3	1.0±0.4	0.7±0.3	0.8±0.3
$PBLH_{max}(m)$	890±305	852±273	1296±491	1422±529	1119±481	821±252	928±260	1310±491	1329±505	1101±453
Concentrations	s of gaseous	pollutants (µg	$g m^{-3}$)							
O_3	19.3±10.5	11.9±7.6	69.3±22.9	90.5±33.3	48.2±39.6	13.3±8.9	12.5±7.7	56.3±23.5	42.8±17.2	31.5±24.5
SO_2	15.8±7.0	21.5±9.5	11.2±6.3	11.3±4.7	14.9±3.7	16.4±4.6	23.3±9.2	13.9±5.3	14.4±5.4	17.0±7.3
NO ₂	60.2±18.7	75.3±24.5	51.8±26.8	54.2±9.4	60.4±22.5	66.5±15.0	81.3±19.8	50.8±16.7	51.7±20.8	62.4±22.0
<u> </u>		1 1 . 1	(-3						

Table 1 Meteorological parameters, annual and seasonal mean concentrations of $PM_{2.5}$, gaseous pollutants and major chemical components at CD and CQ during 2014-2015.

Concentrations of PM_{2.5} and chemical compositions ($\mu g m^{-3}$)

 $PM_{2.5} \qquad 62.1 \pm 38.4 \qquad 113.5 \pm 47.8 \qquad 48.0 \pm 25.2 \qquad 45.1 \pm 15.2 \qquad 67.0 \pm 43.4 \qquad 56.3 \pm 23.6 \qquad 115.1 \pm 53.9 \qquad 58.3 \pm 24.6 \qquad 54.2 \pm 16.2 \qquad 70.9 \pm 41.4 \qquad 112.5 = 16.2 \qquad 70.9 \pm 16.2 \qquad 112.5 \qquad 112.5 = 16.2 \qquad 112.5 \qquad$

SO_4^{2-}	10.5±6.5	16.4±7.1	8.3±5.9	9.7±4.7	11.2±6.8	9.9±4.7	17.5±7.4	10.4±6.5	11.1±5.7	12.2±6.8
NO ₃ ⁻	9.3±7.4	17.5±8.8	5.9±3.6	3.9±2.2	9.1±8.0	7.8±3.8	15.8±9.5	5.9±5.0	1.6±1.3	7.7±7.6
$\mathrm{NH_4}^+$	6.9±4.8	12.7±5.4	5.1±3.2	4.2±1.9	7.2±5.2	5.7±2.8	11.3±5.2	5.2±3.0	4.0±2.1	6.6±4.4
Cl	1.9±1.2	3.4±1.9	0.6±0.4	0.2±0.2	1.5±1.7	0.8±0.4	1.6±1.2	0.5±0.5	0.04±0.03	0.7±0.9
K^+	0.6±0.4	1.2±0.6	0.6±0.5	0.5±0.2	0.7±0.5	0.5±0.2	1.2±0.7	0.5±0.2	0.3±0.1	0.6±0.5
OC	10.4±6.1	19.7±8.4	6.3±3.7	7.4±1.5	10.9±7.6	9.7±4.7	24.2±13.6	10.0±5.1	8.5±3.4	13.1±10.0
EC	3.0±2.1	6.3±3.0	2.7±2.3	2.5±0.7	3.6±2.7	3.8±1.7	5.9±3.2	4.7 ± 3.0	3.7±1.5	4.5±2.6
FS	3.2±1.6	4.5±2.0	4.8±3.0	2.7±1.5	3.8±2.2	5.0±2.8	6.3±3.3	9.1±7.6	6.5±4.0	6.7±5.0

	SO_4^{2-}	NO ₃ -	$\mathrm{NH_4}^+$	Cl	K^+	OC	EC	FS
Autumn	0.78	0.72	0.75	0.10	0.76	0.87	0.79	0.08
Winter	0.63	0.49	0.60	0.51	0.77	0.83	0.80	0.64
Spring	0.76	0.39	0.59	0.09	0.68	0.78	0.74	0.29
Summer	0. 49	-0.13	0.40	0.37	0.36	0.43	0.23	-0.02
Annual	0.72	0.71	0.76	0.67	0.79	0.80	0.72	0.31

Table 2 Pearson's correlation analysis for daily concentrations of major components in $PM_{2.5}$ between CD and CQ, significant correlation (p<0.01) are bold faced.



Figure 1. Locations of the sampling sites in Chengdu (CD) and Chongqing (CQ).



Figure 2. Seasonal and annual contributions of individual chemical components to $PM_{2.5}$ at CD (a) and CQ (b).



Figure 3. Seasonal distributions of $PM_{2.5}$ and its major chemical components. Shown in each sub-figure are mean (dot symbol), median (horizontal line), the central 50% data (25^{th} - 75^{th} percentiles, box), and the central 90% data (5^{th} - 95^{th} percentile, whisker)



Figure 4. Seasonal mean concentrations of major components in autumn (a), winter (b), spring (c), and summer (d) at CD and CQ sites.



Figure 5 Temporal variations of meteorological parameters, gas-phase pollutants and $PM_{2.5}$ during the campaign at CD (a) and CQ (b). Pollution episodes are highlighted by shaded areas.



Figure 6. PM_{2.5} and major chemical components during clean periods (CP) and polluted periods (PP) in winter at CD (a) and CQ (b).



Figure 7. CO-scaled concentrations of various pollutants and the values of SOR, NOR, and SOC/OC in winter at CD (a) and CQ (b).



Figure 8. Correlations of SOR, NOR and SOC/OC against temperature, RH and O₃ concentration at CD and CQ.



Figure 09. NH_4^+ concentration as a function of the sum of SO_4^{2-} and NO_3^- in equivalent concentrations (left column), molar ratio NO_3^-/SO_4^{-2-} as a function of NH_4^+/SO_4^{-2-} (middle column), and NO_3^- concentration as a function of NH_4^+ (right column) at CD (upper row) and CQ (lower row).



Figure 10. PSCF distribution of $PM_{2.5}$, its chemical components, and gaseous precursors in winter at CD (a) and CQ (b).