

Dear Editor:

We have carefully revised the manuscript and addressed all of the comments provided by the reviewer. The details can be found in our enclosed responses to the reviewer's comments. For your and the reviewer's convenience in reviewing the changes, a copy of the paper with track-changes is also attached below.

Thank you for taking care of the review process for this paper.

Sincerely,

Huanbo Wang and co-authors

Response to Referee #4

We greatly appreciate the helpful comments from the reviewer, which have helped us improve the paper. We have addressed all of the comments carefully, as detailed below. Our responses start with “R:”.

Sichuan Basin is one of the regions in China with severe aerosol pollution, while the chemical component analysis is still rare. This study fills the gap in this area. Under this condition, the short-term (four selected months) and low time resolution sampling is still acceptable. Thus, I suggest it published after major revision.

In general, the manuscript is not well organized. Authors should put related results together to support one conclusion. The results now are presented with several short paragraphs which are not carefully ordered, e.g., section 3.1.2. From line 197 to line 234, it shows the results of SNA, SNA, carbonaceous aerosols, and SNA again. The readers can hardly find the sufficient information to know and understand the results. Presentation should be modified by native speaker before publication.

R: We have better organized sections 3.1.1, 3.1.2, 3.1.3, and 3.2.1 following this comment. Several short paragraphs in sections 3.1.1 and 3.1.2 were combined based on their contents. Six short paragraphs in section 3.1.3 were reorganized into four paragraphs following the order of similarity, difference (SNA and carbonaceous component) and correlation analysis between CD and CQ sampling site. Section 3.2.1 was also integrated according to the pollution episodes during the one-year sampling periods and key chemical compositions caused PM_{2.5} pollution in winter.

We have rewritten section 3.1.2 following this order: we first summarized the seasonal variations of PM_{2.5} concentrations and the impacts of the meteorological parameters on the seasonal trends. We then explored the seasonal trends of major components of PM_{2.5} with discussions for the same chemical components grouped into one place, as recommended by the reviewer.

In addition, our discussion basically kept the same sequence for the major chemical components groups: we first discussed the fine soil due to their different seasonal trends and spatial variations at CD and CQ, then SNA and individual SO₄²⁻, NO₃⁻, NH₄⁺; and finally, carbonaceous components including organic carbon and elemental carbon.

We have also carefully proofread the revised paper to minimize any grammar errors, and have asked a native speaker to have a final check of the paper.

There are many qualitative speculations in the article. Without robust evidence, to do such speculations is unreliable and may even mislead readers. Many conclusions are not based on strict logic.

Line 203: “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.” I think it will be more appropriate to show precipitation to support this statement.

R: We have added quantitative discussion wherever possible. For example, we have added seasonal precipitation amount in Table 1 and related discussions. The precipitation amount was the highest in summer at both CD and CQ, which supported our conclusion. We admit that there are still places with qualitative discussions due to the nature of the study, the lack of data or the limitation for the current knowledge on this topic.

Line 208 and 217. The statement could not only be supported by other references. Other mechanisms can also lead to similar or opposite results. More observed results are needed.

R: We have added the observed results such as gaseous precursors to explain the seasonal trends of major chemical components in PM_{2.5}. Detailed discussions are included in section 3.1.2 in the revised manuscript.

Line 237: “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 regional-scale characteristics of urban-environment pollution while the differences between the two sites should reflect the sub-regional characteristics of urban pollution.” As the authors response to previous suggestions, “The two monitoring sites selected in this study should represent the typical urban environment in their respective cities”. Thus, many similarities reflect the characteristics of urban region instead of the whole region.

R: Yes, the selected sampling sites at CD and CQ represent the typical urban environment. We have changed the sentence “a moderate similarity was observed in autumn, winter and spring on the basis of low COD values (0.15-0.18), indicating the regional-scale PM_{2.5} pollution pattern in Sichuan Basin” to “a moderate similarity was observed in autumn, winter and spring on the basis of low COD values (0.15-0.18), indicating limited differences between the two urban environments in the Sichuan Basin”.

Line 403, the interaction between aerosol and ozone are quite complicated. Aerosols can provide an interface for the heterogeneous reaction of ozone products. Previous study shows that this mechanism usually contributes more than the impact through photochemical process. Fig S5 also could not support that “the formation of SO₄²⁻ during the polluted periods was dominated by heterogeneous aqueous processes rather than photochemical reactions”.

R: Yes, we agree with the reviewer’s comments and added the explanation on why high PM_{2.5} concentrations associated with lower O₃ concentrations: On the one hand, aerosols are generally considered as a constraining factor to O₃ production due to their absorption and scattering of UV radiation, which reduce solar radiation and

consequently decrease photochemical activity. On the other hand, aerosols can provide an interface for the heterogeneous reaction, in accordance with O₃ consumption and secondary aerosol formation, which would result in decreasing O₃ concentrations and increasing PM_{2.5} concentrations.

Fig. S5 could not give a solid evidence for the formation mechanism of SO₄²⁻. However, it can be found that the ambient RH remained high at low O₃ concentrations, which was beneficial to form SO₄²⁻ through heterogeneous aqueous processes, resulting high SOR value at high RH accompanied with low O₃ concentrations.

Line 365, “Similar diurnal variations were also found between clean and polluted periods for CO (Fig. S4), suggesting no significant extra CO emission during polluted periods.” Is that possible to give a quantitative value to support that the variations are similar? Also, I don’t consider this can support no extra CO emission directly.

R: The diurnal variations of CO between clean and pollution periods were significant correlation with Pearson coefficient of 0.83 and 0.50 at both CD and CQ (p<0.05) based on statistical analysis. As suggested by the reviewer, it also could not support the statement that no extra CO emission occurred only according to the diurnal variations of CO. Thus, we deleted those explanations in the revised manuscript. Nevertheless, in practice scaling the concentrations of other pollutants to that of CO (or BC) was also an effective method to reduce the impact of atmospheric physical processes on other pollutants, which has been used widely in the previous study (Zhang et al., 2015; Zheng et al., 2015; Liggio et al., 2016; Hu et al., 2013), and we added those citations in the revised manuscript.

Zhang, Q., Quan, J. N., Tie, X. X., Li, X., Liu, Q., Gao, Y., and Zhao, D. L.: Effects of meteorology and secondary particle formation on visibility during heavy haze events in Beijing, China, *Sci Total Environ*, 502, 578-584, 10.1016/j.scitotenv.2014.09.079, 2015.

Zheng, G. J., Duan, F. K., Su, H., Ma, Y. L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T., Chang, D., Poschl, U., Cheng, Y. F., and He, K. B.: Exploring the severe winter haze in Beijing: the impact of synoptic weather, regional transport and heterogeneous reactions, *Atmos Chem Phys*, 15, 2969-2983, 10.5194/acp-15-2969-2015, 2015b.

Liggio, J., Li, S.M., Hayden, K., Taha, Y.M., Stroud, C., Darlington, A., Drollette, B.D., Gordon, M., Lee, P., Liu, P., Leithead, A., Moussa, S.G., Wang, D., O'Brien, J., Mittermeier, R.L., Brook, J.R., Lu, G., Staebler, R.M., Han, Y.M., Tokarek, T.W., Osthoff, H.D., Makar, P.A., Zhang, J.H., Plata, D.L., Gentner, D.R., 2016. Oil sands operations as a large source of secondary organic aerosols. *Nature* 534, 91-94.

Hu, W.W., Hu, M., Yuan, B., Jimenez, J.L., Tang, Q., Peng, J.F., Hu, W., Shao, M., Wang, M., Zeng, L.M., Wu, Y.S., Gong, Z.H., Huang, X.F., He, L.Y., 2013. Insights on organic aerosol aging and the influence of coal combustion at a regional receptor site of central eastern China. *Atmospheric Chemistry and Physics* 13, 10095-10112.

Some speculations are even self-contradictory. Line 208: “It is also noted that the seasonal variations of NO_3 were much larger than those of SO_4 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.” And Line 348: “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.” Also, it is not convinced to claim RH might not be the driving force supported by this. Many factors including meteorological conditions and emission are combined together to form polluted episodes.

R: Line 208 and line 348 is not self-contradictory. As shown in Table 1, the average ambient RH in winter was 12% higher than that in summer. Therefore, compared with that in summer, the increased ambient RH in winter would enhance the formation of NO_3^- through the heterogeneous aqueous processes.

However, the average ambient RH during clean period and pollution period in winter was 81.9% and 80.2% at CD, and 70.2% and 68.0% at CQ, respectively (Table S1). No significant variations of ambient RH between clean period and pollution period were observed (less than 3%). Thus, the high ambient RH during the whole sampling period in winter was beneficial to the NO_3^- formation, but it might not be the primary cause of the dramatic increase of $\text{PM}_{2.5}$ concentrations during the pollution period.

The conclusions part are all qualitative even without a number.

R: We feel that Conclusion should be rewritten differently from the Abstract. In the Abstract quantitative statement summarizing major results should be presented while in the Conclusion section, results not covered in the abstract, uncertainty discussion, future research recommendations should be presented. However, we have added some quantitative statement following this comment.

Besides, I have some specific comments on the manuscript as follows:

1. Line 238, “regional” instead of “reginal”.

R: Corrected.

2. Line 453, It is better for understanding if “Neijiang, Zigong, Yibin and Luzhou” could be marked in Fig 1.

R: We have added the mentioned cities in Fig 1.

3. The period should be stated in caption of Fig 6 and Fig 7.

R: We have added the clean period (CP) and pollution period (PP) in the caption of Fig 6 and Fig 7. At CD: CP, 6 January and 27 January-2 February 2015; PP, 7-26

January 2015. At CQ: CP, 6-7 January and 27 January-2 February 2015; PP, 8-26 January 2015.

4. Line 415, the ref should not be in brackets.

R: Corrected.

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

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1 **Abstract.** To investigate the characteristics of PM_{2.5} and its major chemical components, formation
2 mechanisms, and geographical origins in the two ~~biggest cities~~megacities, Chengdu (CD) and
3 Chongqing (CQ), in Sichuan Basin of southwest China, daily PM_{2.5} samples were collected
4 simultaneously at one urban site in each city for four consecutive seasons from autumn 2014 to summer
5 2015. Annual mean concentrations of PM_{2.5} were 67.0 ± 43.4 and $70.9 \pm 41.4 \mu\text{g m}^{-3}$ at CD and CQ,
6 respectively. Secondary inorganic aerosols (SNA) and organic matter (OM) accounted for 41.1% and
7 26.1% of PM_{2.5} mass at CD, and 37.4% and 29.6% at CQ, respectively. Seasonal variations of PM_{2.5} and
8 major chemical components were significant, usually with the highest mass concentration in winter and
9 the lowest in summer. Daily PM_{2.5} concentration exceeded the national air quality standard on 30% of
10 the sampling days at both sites, and most of the pollution events were at the regional scale within the
11 basin formed under stagnant meteorological conditions. The concentrations of carbonaceous
12 components were higher at CQ than CD, likely partially caused by emissions from the large amount of
13 motorcycles and spraying process during automobile production in CQ. ~~Heterogeneous~~Homogeneous
14 ~~gas-phase~~ reactions probably played an important role in the formation of SO₄²⁻, while both
15 homogeneous and heterogeneous reactions contributed to the formation of NO₃⁻. Geographical origins
16 of emissions sources contributing to high PM_{2.5} masses at both sites were identified to be mainly
17 distributed within the basin based on potential source contribution function (PSCF) analysis.

19 **1 Introduction**

20 Fine particles (PM_{2.5}, particulate matter with an aerodynamic diameter smaller than 2.5 µm) have
21 adverse effects on human health (Anderson et al., 2012; Lepeule et al., 2012; Taus et al., 2008),
22 deteriorate air quality (Zhang et al., 2008; Paraskevopoulou et al., 2015), reduce atmospheric visibility
23 (Fu et al., 2016; Cao et al., 2012; Baumer et al., 2008), impact climate (Ramanathan and Feng,
24 2009; Hitztenberger et al., 1999; Mahowald, 2011), and affect ecosystem (Larssen et al., 2006). In the past
25 two decades, China has experienced serious PM_{2.5} pollution due to the rapidly increasing energy
26 consumption through economic development, industrialization and urbanization (Tie and Cao, 2009).
27 The National Ambient Air Quality Standards (NAAQS) for PM_{2.5} was promulgated by the Chinese
28 government in 2012, and strict strategies have been implemented nationwide, e.g. controlling SO₂
29 emissions by installing desulphurization system in coal-fired power plants and conversion of fuel to
30 natural gas (Lu et al., 2011), mitigating NO_x emissions through traffic restrictions, and reducing
31 biomass burning through straw shredding. Despite these efforts, there are still many cities that have not
32 yet met the current NAAQS (Tao et al., 2017). According to the ‘2013-2015 Reports on the State of
33 Environment of China’, annual mean concentration of PM_{2.5} in ~~all the~~ 74 major cities ~~over~~across China
34 was 72, 64, and 50 µg m⁻³ in 2013, 2014 and 2015, respectively, and only 4.1%, 12.2% and 22.5% of
35 the monitored cities met the NAAQS (35 µg m⁻³).

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

topography and 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 pollution episodes [between](#) the two cities.

The present study aims to fill this gap by measuring chemically-resolved PM_{2.5} in Chengdu and Chongqing in four consecutive seasons during 2014-2015. The main objectives are to: (1) characterize PM_{2.5} mass and major chemical components in urban environments of Chengdu and Chongqing; (2) compare PM_{2.5} chemical compositions under different pollution levels and identify major chemical 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 contributing to the high PM_{2.5} levels through ~~potential source contribution function~~ (PSCF) analysis. Knowledge gained in this study provides scientific basis for making future emission control policies aiming to alleviating heavy PM_{2.5} pollution in this unique basin.

2 Methodology

2.1 Sampling sites

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

2.2 Sample collection

Daily (23-h) integrated PM_{2.5} samples were collected in four months, each in a different season: autumn (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 carried out using a versatile air pollutant sampler (Wang et al., 2017). One channel was used to load PM_{2.5} sample on Teflon filter for mass and trace elements analysis and the other one was equipped with quartz filter for water-soluble inorganic ions and carbonaceous components analysis. The sampler was running at 15 L min⁻¹ for each channel. At CQ site, a low-volume aerosol sampler (BGI Corp., from Omni, USA) operating at a flow rate of 5 L min⁻¹ was used to collect PM_{2.5} samples on Teflon filter, and another sampler (Thermo Scientific Corp. Partisol 2000i, USA) with a flow rate of 16.7 L min⁻¹ was used to collect PM_{2.5} samples on quartz filter. A total of 112 samples and 8 field blanks, nearly equally distributed in the four seasons, were collected at each site during the campaign. In addition, three lab blank filters in each campaign were stored in a clean Petri slides in the dark and analysed in the same ways as the collected samples to evaluate the background contamination.

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

2.3 Chemical analysis

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

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

(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 control, measurement with filter blank, standard sucrose solution and replicate analysis were performed. Blank corrections were performed by subtracting the blank values from the sampled ones. The concentration of EC in field blanks was zero while OC was below $0.7 \mu\text{g C cm}^{-2}$. The repeatability was better than 15%.

The elements including Al, Si, Ca, Fe, and Ti were analyzed on Teflon filter using X-ray 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, 9830 CO analyzer, and 9810 O₃ analyzer (Ecotech Corp., Australia) at CD, and Thermo 42i NO/NO₂/NO_x analyzer, 43i SO₂ analyzer, 48i CO analyzer, and 49i O₃ analyzer (Thermo Scientific Corp., USA) at CQ. The mass concentration_s of PM_{2.5} ~~was~~were automatically measured by online particulate monitor instruments (BAM1020, Met one Corp., USA, at CD and 5030 SHARP, Thermo Scientific 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 obtained from an automatic weather station (Lufft Corp. WS501, Germany) at each site.

Hourly precipitation data were recorded at the nearest weather station operated by China Meteorology Administration (<http://www.weather.com.cn/>). Planetary boundary layer height (PBLH) was obtained from the HYSPLIT model (<http://ready.arl.noaa.gov/HYSPLIT.php>).

2.4 Data analysis

The EC-tracer method has been widely used to estimate SOC (Turpin and Lim, 2001;Castro et al., 1999), which can be expressed as

$$\text{POC}=(\text{OC/EC})_{\text{prim}} \times \text{EC} \quad (1)$$

$$\text{SOC}=\text{OC}-\text{POC} \quad (2)$$

Where POC, SOC and OC represent the 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).

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

$$COD_{jk} = \sqrt{\frac{1}{p} \sum_1^p \left(\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2} \quad (3)$$

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.

2.5 Geographical origins of PM_{2.5}

72-h air mass back trajectories were generated based on the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model using 0.5°×0.5° meteorological data for [the period of PM_{2.5}–measurements from](#) October 2014 to July 2015 [when PM_{2.5} measurements were made](#) 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,

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

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,

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

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

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°×0.5° grid cells.

164 3 Results and discussion

165 3.1 PM_{2.5} mass concentration and chemical composition

166 3.1.1 Overview

167 Table 1 presents seasonal and annual mean concentrations of PM_{2.5} and its major chemical components
168 at CD and CQ during the sampling periods. Daily PM_{2.5} ranged from 11.6 to 224.7 $\mu\text{g m}^{-3}$ with annual
169 average being $67.0 \pm 43.4 \mu\text{g m}^{-3}$ at CD and $70.9 \pm 41.4 \mu\text{g m}^{-3}$ at CQ, which were about two times the
170 NAAQS annual limit. Secondary inorganic aerosol (SNA, the sum of SO_4^{2-} , NO_3^- and NH_4^+) and
171 carbonaceous species together represented more than 70% of PM_{2.5} mass at both sites (Fig. 2). The
172 annual mean concentrations of SNA were $27.6 \mu\text{g m}^{-3}$ at CD and $26.5 \mu\text{g m}^{-3}$ at CQ, contributing 41.1%
173 and 37.4% to PM_{2.5} mass, respectively. SO_4^{2-} , NO_3^- and NH_4^+ accounted for 16.8%, 13.6% and 10.8%,
174 respectively, of PM_{2.5} mass at CD, and 17.2%, 10.9% and 9.2%, respectively, at CQ. Organic matters
175 (OM), estimated from OC using a conversion factor of 1.6 to account for other elements presented in
176 organic compounds (Turpin and Lim, 2001), were the most abundant species in PM_{2.5}, accounting for
177 26.1% and 29.6% of PM_{2.5} mass at CD and CQ, respectively. In contrast, EC only comprised of around
178 6% at both sites. The annual mean concentrations of OC and EC were 20% and 25%, respectively, and
179 were higher at CQ than CD.

180 The annual mean concentration of fine soil (FS), calculated by summing the oxides of major crustal
181 elements, i.e., Al_2O_3 , SiO_2 , CaO , FeO , Fe_2O_3 , and TiO_2 (Huang et al., 2014), was $6.7 \mu\text{g m}^{-3}$ (9.5% of
182 PM_{2.5} mass) at CQ. It is noted that this was about two times that at CD ($3.8 \mu\text{g m}^{-3}$, 5.7% of PM_{2.5}
183 mass). The minor components such as K^+ and Cl^- constituted less than 5% of PM_{2.5}. The unaccounted
184 portions of PM_{2.5} reached 18.3% at CD and 15.3% at CQ, which were likely related to the uncertainties
185 in the multiplication factors used for estimating OM and FS, other unidentified species, and
186 measurement uncertainties.

187 3.1.2 Seasonal variations

188 Figure 3 shows the seasonal variations in mass concentrations of PM_{2.5} and its major chemical
189 components at CD and CQ. Seasonal variations of any pollutants ~~should be~~were influenced by the
190 seasonal variations in source emission intensities, atmospheric processes and meteorological conditions.
191 Unlike in northern China, there were no extensive coal combustion or wood burning for domestic heating
192 in winter due to the warm temperature (around 10°C on average) in the Sichuan Basin, hence atmospheric
193 processes and meteorological conditions played ~~a~~-vital roles in the seasonal variations of PM_{2.5}. On a

194 seasonal basis, PM_{2.5} mass was the highest in winter at both CD and CQ, which was 1.8-2.5 times of those
195 in the other seasons. In contrast, its seasonal differences among the other three seasons were generally
196 small, i.e., less than 40%. Stagnant air conditions with frequent calm winds and low planetary boundary
197 layer heights were—~~was~~ the major causes of the highest PM_{2.5} mass in winter (Table 1) (Liao et al.,
198 2017;Chen and Xie, 2013;Li et al., 2017b).

199 All the major PM_{2.5} components except FS followed the seasonal pattern of PM_{2.5} mass with subtle
200 differences. The highest FS concentrations were observed in spring at both sites. The relatively high
201 wind speed and lower RH in spring were conducive for re-suspension of crustal dust and resulted in
202 higher FS concentrations. In addition, frequent spring dust storms originated in the northwestern China
203 was able to reach Sichuan Basin via long-rang transport, and caused d the elevated FS concentrations
204 (Chen et al., 2015;Tao et al., 2013). The highest contributions from FS to PM_{2.5} mass was more than
205 10%, appeared in spring at both sites.

206 The majority of PM_{2.5} components showed a summer minimum, which was caused by high
207 planetary boundary layer height favoring pollutants dispersion and abundant precipitation favoring wet
208 scavenging (Table 1). ~~In contrast~~However, the lowest seasonal average concentrations did not appear in
209 summer forOne exception was SO₄²⁻, which had a minimum in spring at CD and in autumn at CQ,
210 likely due to the enhanced photochemical reactions associated with high temperature and strong solar
211 radiation in summer. High O₃ concentrations in summer also supported this seasonal trend. It is also
212 noted that the seasonal variations of NO₃⁻ were much larger than those of SO₄²⁻ and NH₄⁺. SO₄²⁻ and
213 SO₂ showed similar seasonal trends, with their concentrations 1.4-2.0 times higher in winter than in the
214 other seasons (Table 1). In contrast, the seasonal variations of NO₃⁻ were much larger than that of NO₂,
215 e.g., while the concentrations of NO₂ were 1.2-1.6 times higher in winter than in the other seasons,
216 those of NO₃⁻ were 9.6 times higher in winter than in summer at CQ. Thus, seasonal variations of SO₂
217 and NO_x emissions were comparable, but the atmospheric chemical processes caused the much larger
218 seasonal variations in NO₃⁻. The concentration of NO₃⁻ could be enhanced in winter under high RH
219 through heterogeneous aqueous processes and decreased in summer due to volatility of NH₄NO₃ under
220 high temperature, which increased the seasonal differences in NO₃⁻ concentrations between winter and
221 summer (Pathak et al., 2009;Quan et al., 2015;Squizzato et al., 2013). In addition, thermodynamically
222 driven behavior of NH₄NO₃ was another factor for the lower NO₃⁻ concentrations in summer (Wang et
223 al., 2016;Kuprov et al., 2014). As shown in Fig. 2, ~~T~~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 the other seasons at CQ. The smaller contribution in summer at CQ was mainly due to the lower NO_3^- 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-} .

Both OC and EC exhibited the highest concentrations in winter at CD and CQ, around 1.9-3.1 times of those in the other seasons whereas seasonal differences of these carbonaceous components were less distinct in other seasons, e.g. the variations of OC and EC among the other three seasons were less than 30%. Seasonal average SOC was unexpectedly also the highest in winter at both sites, similarly to what observed for OC, which. This seasonal trends were can be partly explained by the enhanced condensation process forming SOC under low temperature, that different from the anticipated high value in summer in consideration of strong photochemical reaction. Condensation of semi-volatile organic aerosols in winter seemed to play a larger role than photochemical reaction in summer, knowing that low temperature in winter favors favored condensation process and was beneficial to form SOC (Sahu et al., 2011; Cesari et al., 2016). Although high O_3 and strong solar radiation condition in summer was conducive to strong photochemical reactions, In contrast, high temperature in summer favored gas-particle partitioning in the gas phase and thus limited the formation/increase of SOC (Strader et al., 1999). Seasonal average relative contributions of major chemical components to $\text{PM}_{2.5}$ are depicted in Fig. 2. The seasonal average contributions of SNA to $\text{PM}_{2.5}$ 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^- 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 carbonaceous components (the sum of OC and EC) generally followed the seasonal patterns of SNA, accounting for 26.7-38.8% of $\text{PM}_{2.5}$ mass. Among these, OM showed the lowest fractions in $\text{PM}_{2.5}$ in spring (21.1%) at CD and the 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.

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~~Basin, the similarities in the characteristics of the major pollutants between the two sites should represent the regional-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 autumn, winter and spring on the basis of low COD values (0.15-0.18), indicating ~~the regional-scale PM_{2.5} pollution pattern~~ ~~there was no limited significant regional differences between the two urban environments~~ in ~~the~~ Sichuan Basin and the similarities in major emission sources for both sites. The ~~regional-similar~~ pollution ~~patterns observed at both CD and CQ~~ ~~was/were likely to be~~ related to the ~~similar meteorological parameters and~~ special topography of the basin, which is a closed lowland surrounded by high mountains on all sides (Fig. 1). The mean elevation in the basin is about 200-700 m, while the surrounded mountains are around a scope of 1000-3000 m elevation. The Tibetan Plateau lies close to the western Sichuan Basin, with an elevation above 4000 m. Such a Plateau-Basin topography forms a barrier for the dispersion of pollutants and causes air stagnation within the basin, thereby facilitating regional scale pollution events in the ~~Basin~~basin. 72-h air masses ~~back trajectory~~ies 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 scale.~~

It is worth to note that the COD values used to identify the similarities or differences of ~~the~~ two sites were calculated based on seasonal-average concentrations of all ~~the~~ components in PM_{2.5}. However, if focusing on individual components, several chemical species in PM_{2.5} differed by up to a factor of 2.5 in their season-average concentrations between CD and CQ, e.g. OC and EC in winter and spring, and Cl⁻ and FS in all the four seasons. In summer, the differences for several major chemical

283 components (FS, OC, SO_4^{2-} , NO_3^- , ~~and~~ EC) between the two sites were larger than in [the](#) other seasons,
 284 causing a high COD value (0.33). These discrepancies were partly caused by the different atmospheric
 285 chemical processes, local sources and meteorological parameters between the two sites. Specifically, FS
 286 mostly deviated from the 1:1 straight line in all [the](#) seasons, with substantially higher concentrations at
 287 CQ than CD (Fig. 4). ~~The main cause of this difference was the higher wind speeds and lower RH at CQ~~
 288 ~~than CD.~~ There was no significant difference in NH_4^+ concentrations between CD and CQ, but
 289 considerable differences in SO_4^{2-} and NO_3^- in spring and summer. SO_2 concentration was around 25%
 290 higher at CQ than CD in spring and summer, which partially explained the site-differences in SO_4^{2-} . In
 291 contrast, NO_2 concentration was comparable at both sites in summer, but NO_3^- concentration was 58%
 292 lower in CQ than CD. The site-differences in NO_3^- concentration was caused by NH_4NO_3
 293 thermodynamic equilibrium controlled by ambient temperature and RH, instead of by its gaseous
 294 precursors. The equilibrium would be shifted toward the particulate phase when ambient RH was above
 295 the deliquescence relative humidity (DRH) of NH_4NO_3 , and the dissociation constant decreased by
 296 about one order of magnitude when RH was above 75% (Kuprov et al., 2014). DRH was calculated
 297 from ~~ambient RH~~[temperature](#) following Mozurkewich (1993). As shown in Table 1, the average
 298 temperature was comparable at CD and CQ during the summer period, hence leading to similar DRH
 299 values of NH_4NO_3 , ranging from 59% to 64% with an average value of 60.7%. However, the ambient
 300 RH was substantially lower at CQ (61%) than CD (72%), causing lower NO_3^- concentration at CQ. As
 301 shown in Fig. S2, 53% of the hourly data in summer having ambient RH lower than DRH at CQ, while
 302 only 19% such data at CD, which explained the different NO_3^- concentrations between CD and CQ.

303 Fig.4 shows higher concentrations of carbonaceous component (OC and EC) at CQ than CD in all
 304 [the](#) seasons except OC in autumn and EC in winter. OC and EC mainly originate from fossil fuel
 305 combustion and biomass burning. K^+ is usually regarded as a tracer of biomass burning (Tao et al.,
 306 2016). During the sampling campaign, no significant differences in K^+ levels were observed between
 307 CD and CQ (Table 1), suggesting that biomass burning was not be the major cause of the higher
 308 concentrations of carbonaceous component at CQ. Motorcycle traffic was likely a major source of
 309 volatile organic compounds (VOCs) in CQ since it is a famous mountain city where most people use
 310 motorcycle as daily traffic tools. ~~According to the Chongqing Statistical Yearbook 2015, the The~~
 311 ~~number of motorcycles was 2.0 million (among the total of 2.3 million motor vehicles) in Chongqing in~~
 312 2014, which was much higher than those (0.7 million) in Chengdu ([Chongqing and](#) Chengdu Statistical

Yearbook 2015). Moreover, Chongqing has become 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 via photochemical reaction under high temperature or vapor condensation under low temperature. This hypothesis is supported by the large differences in OC concentrations in winter between the two sites.

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 [2S1](#)). However, for NO_3^- , a significant correlation was identified only in autumn, likely due to the strong impact of local vehicle emissions and the subsequent atmospheric processes forming NO_3^- . 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.

3.2 $PM_{2.5}$ formation mechanisms and geographical origins

3.2.1 Pollution episodes and key chemical components

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 $75 \mu g m^{-3}$. Similarly, the days with $PM_{2.5}$ concentration below $75 \mu g m^{-3}$ were characterized to be clean periods (CP). A total of seven pollution episodes were identified during the campaign at each site. There were three long-lasting pollution episodes occurred simultaneously at the two sites on 23-27 October 2014, 7(8)-26 January, and 26-28 (29) April 2015. A total of 34 and 31 ~~polluted-pollution~~ 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-pollution~~ 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~~RH were important factors causing $PM_{2.5}$ pollution events, as was found in this and earlier studies (Zheng et al., 2015b; Chen et al., 2017; Liao et al., 2017). Compared with the clean periods, the pollution periods were usually characterized by low planetary boundary layer height and weak wind speed (Table [S1](#)S2), which suppressed ~~pollutants~~ dispersion vertically and horizontally. Temperature increased during the long-lasting pollution episodes, which promoted gas-to-particle transformation, forming secondary aerosols. RH remained high (68-88%)

343 during pollution episodes (except in spring at CQ), although not much different from clean periods,
344 which was also conducive for aqueous-phase reactions converting gaseous pollutants into aerosols
345 (Chen et al., 2017; Tian et al., 2017).

346 Looking more closely at a regional-scale long-lasting pollution episode in winter, from 8 January to
347 26 January 2015, the concentrations of PM_{2.5} and major chemical components increased dramatically
348 compared with clean periods (Fig. 6). PM_{2.5} concentrations were more than three times higher at both
349 sites, with the two dominant groups of components, SNA and OC, being 2.5-2.8 times higher at CD and
350 1.7-2.7 times higher at CQ. The enhancement of SNA and OC during pollution periods were similar at
351 CD, but OC increased much more than SNA at CQ, indicating some different contributing factors to the
352 high PM_{2.5} pollution at the two sites. Pollutants accumulation under stagnant meteorological conditions
353 might be a main factor at CD based on the similar magnitudes of the enhancements of PM_{2.5} and its
354 dominant components, while additional processes should have increased OC more than other
355 components at CQ. The percentage contributions of SNA to PM_{2.5} were similar during clean and
356 ~~polluted-pollution~~ periods, 38-41% at CD and CQ (Fig. S3). However, the percentage contributions of
357 OM to PM_{2.5} decreased from 30.1% on clean days to 27.5% on ~~polluted-pollution~~ days at CD, and
358 increased from 26.9% to 34.9% at CQ. Concentrations of the individual SNA species (SO₄²⁻, NO₃⁻ and
359 NH₄⁺) increased by a factor of 2.5-3.3 on ~~polluted-pollution~~ days compared with clean days in all the
360 cases (Fig. 6). But the percentage contributions differed among the species as NO₃⁻ increased and SO₄²⁻
361 decreased on ~~polluted-pollution~~ days. The percentage contributions of SNA and OM to PM_{2.5} discussed
362 above were different from those found in eastern coastal China and North China Plain, where
363 considerable increases were found for SNA and decreases for OM on ~~polluted-pollution~~ days than clean
364 days (Tan et al., 2009; Wang et al., 2015a; Quan et al., 2014; Zhang et al., 2015; Zhang et al., 2016; Cheng
365 et al., 2015). The ~~polluted-pollution~~ periods in eastern coastal China and North China Plain were
366 accompanied with sharp increases of RH, which would promote aqueous-phase formation of secondary
367 inorganic aerosols and resulted in rapid elevation of SO₄²⁻ and NO₃⁻ concentrations (Zheng et al.,
368 2015b; Zheng et al., 2015a; Zhao et al., 2013b; Li et al., 2017a). In contrast, RH remained high during
369 ~~both~~ clean or ~~polluted-pollution~~ periods in the present study, suggesting that high RH might not be ~~the~~
370 ~~primary cause of the dramatic increase in~~ PM_{2.5} concentrations during the pollution period ~~the driving~~
371 ~~force for the pollution episodes~~ in ~~the~~ Sichuan Basin. Another point that need to be mentioned is that, ~~as~~
372 ~~shown in Fig. S1,~~ local sources were the main contributors to the pollution episodes in ~~the~~ Sichuan

basin-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).

3.2.2 Transformation mechanisms of secondary aerosols

In most cases, meteorological conditions, atmospheric chemical processes and long-range transport are all responsible for PM_{2.5} accumulation (Zheng et al., 2015b). CO and EC are directly emitted from combustion processes and are not very reactive, thus, their concentrations in the air are strongly controlled by meteorological parameters within a relatively short period, which make them a good tracer that can be used for separating different dominant factors contributing to pollutants accumulation (Zheng et al., 2015b; Zhang et al., 2015; Hu et al., 2013; Ligio et al., 2016). ~~CO concentration increased by a factor of 1.8 at CD and 1.5 at CQ during polluted periods than clean periods. In comparison, other chemical species (except NO₂) increased by a factor of 1.8-3.3. A similar contrast between CO and other pollutants was also seen in. Similar diurnal variations were also found between clean and polluted periods for CO (Fig. S4), suggesting no significant extra CO emission during polluted periods. Thus, the increased concentrations of CO during polluted periods were primarily driven by meteorological conditions. Therefore,~~ The impact of atmospheric physical processes on other pollutants can be revealed 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, 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 of PM_{2.5} to CO concentration) only showed an enhancement of a factor of 1.6-1.8 (Fig. 7), and the latter values were likely from the enhanced secondary aerosol formation.

As shown in Fig. 7, the CO-scaled SNA was 60-90% higher on polluted days with individual species 40-120% higher, even though their gaseous precursor (SO₂ and NO₂, no data for NH₃) were only less than 30% higher. This suggests stronger chemical transformation from gaseous precursors to particle formation on polluted days. Sulfur oxidation ratio (SOR = $n\text{-SO}_4^{2-}/(n\text{-SO}_4^{2-}+n\text{-SO}_2)$) and nitrogen oxidation ratio (NOR = $n\text{-NO}_3^-/(n\text{-NO}_3^-+n\text{-NO}_2)$) were defined to evaluate the degree of secondary transformation (n refers to as the molar concentration) (Hu et al., 2014). NOR increased from 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 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 2.6 on polluted days at CQ, but no significant change was found

at CD (Fig. 7). The different patterns in SOC (or SOC/OC) than SNA (or SOR and NOR) suggested that secondary organic aerosols (SOA) production was of less important than SNA production at CD.

SO_4^{2-} is predominantly formed via homogeneous gas-phase oxidation. In this pathway, SO_2 is firstly oxidized by OH radical to SO_3 , and then to H_2SO_4 (Stockwell and Calvert, 1983; Blitz et al., 2003). Apart from homogeneous reaction, particulate SO_4^{2-} can also be formed through heterogeneous reactions with dissolved O_3 or H_2O_2 under the catalysis of transition metal and in-cloud process (Ianniello et al., 2011). HNO_3 is primarily produced from the reactions between NO_2 and OH radical during the daytime and later combines with NH_3 to produce particulate NO_3^- (Calvert and Stockwell, 1983). Particulate NO_3^- can also be formed through heterogeneous hydrolysis of N_2O_5 on moist and acidic aerosols during nighttime (Ravishankara, 1997; Brown and Stutz, 2012). Similarly, SOA is mainly formed through photochemical oxidation of primary VOCs followed by condensation of SVOC onto particles as well as through aqueous-phase reactions (Ervens et al., 2011). While photochemical reactions are mostly influenced by temperature and oxidants amount, heterogeneous reactions always depends on ambient RH. To further explore the formation mechanisms of secondary aerosols, SOR, NOR and SOC/OC data were grouped with temperature (at 2°C interval), RH (at 5% interval) and daytime O_3 concentration (at $5 \mu\text{g m}^{-3}$ interval) bins (Fig. 8). An obvious increase of SOR with increasing RH was found at both sites, but this was not the case for temperature and O_3 concentration, suggesting heterogeneous processes played important roles in the formation of SO_4^{2-} , as was suggested in many previous studies (Quan et al., 2015; Zheng et al., 2015a; Zhao et al., 2013b). Interestingly, SOR exhibited a decreasing trend with increasing O_3 concentration at O_3 concentrations lower than $15 \mu\text{g m}^{-3}$ and an opposite trend was found at O_3 concentrations above $20 \mu\text{g m}^{-3}$ (Fig. 8). Additionally, high $\text{PM}_{2.5}$ concentrations were mostly associated with lower O_3 concentrations. This behavior might be explained by the complicated interactions between aerosol and O_3 . On the one hand, Aerosols are generally considered as a constraining factor to O_3 production due to their absorption and scattering of UV radiation, which reduce solar radiation and consequently decrease photochemical activity. On the other hand, aerosols can provide an interface for the heterogeneous reaction, in accordance with O_3 consumption and secondary aerosol formation, which would result in decreased O_3 concentrations and increased secondary aerosols (Zheng et al., 2015b). Apparently, other factors could become dominant in O_3 production and alter such a trend. Low It was further found that the ambient RH remained high at low O_3 concentrations were further found to be associated with high RH (Fig. S5S4),

which was beneficial to SO_4^{2-} formation through indicating that the formation of SO_4^{2-} during the polluted periods was dominated by heterogeneous aqueous processes rather than photochemical reactions at both sites, as suggested in many previous studies (Quan et al., 2015; Zheng et al., 2015a; Zhao et al., 2013b). consistent with the observed results that high SOR value occurred at low O_3 concentrations.

Unlike SOR, NOR increased with both temperature and RH, suggesting the combined effects from homogeneous and heterogeneous reactions. However, under the very high temperature and RH conditions, NOR exhibited a decreasing trend with increasing temperature and RH. Volatilization of NH_4NO_3 at high temperature should be the major cause of such a phenomenon, but it is not clear about the cause of the decreasing trend of NOR under high RH. Pathak et al. (2009) investigated the formation mechanism of NO_3^- in ammonium-rich and ammonium-poor samples, suggesting homogeneous gas-phase reaction became evident to form NO_3^- under the former conditions while heterogeneous process dominated the NO_3^- formation under the latter conditions. As shown in Fig. 9, SO_4^{2-} and NO_3^- were almost completely neutralized by NH_4^+ , indicating an ammonium-rich environment during the sampling campaign. The ammonium-rich environment was also confirmed by the molar ratios of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ and $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$. The molar ratio $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ as a function of $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ is depicted in Fig. 9, which shows significant positive correlations ($R^2=0.82-0.83$ at the two sites). Linear regression equations were obtained as $[\text{NO}_3^-]/[\text{SO}_4^{2-}] = 0.85[\text{NH}_4^+]/[\text{SO}_4^{2-}] - 1.89$ at CD and $[\text{NO}_3^-]/[\text{SO}_4^{2-}] = 0.92[\text{NH}_4^+]/[\text{SO}_4^{2-}] - 1.82$ at CQ. Based on these equations, the molar ratio of $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ was defined as the threshold value separating ammonium-rich and ammonium-poor conditions when the value of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ was zero. In the present study, the threshold value was 2.2 and 2.0 at CD and CQ, respectively. The molar ratio $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ was higher than the threshold value at both sites, suggesting the prevalence of ammonium-rich condition. The near-perfect fitting between the molar ratios of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ and $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ further demonstrated the characteristics of NO_3^- formed through homogenous gas-phase reaction. Moreover, NO_3^- showed a strong correlation with excess NH_4^+ with correlation coefficients of 0.98-0.99 at both sites, providing an insight into the gas-phase reactions of ambient NH_3 and HNO_3 . Using high-resolution inorganic ions data, Tian et al. (2017) demonstrated that NO_3^- was primarily formed via homogeneous reaction when RH below 75% and through heterogeneous processes when RH was above 75%. The increases in NOR with RH at both sites also revealed the possibility of the heterogeneous processes, although this cannot be verified

directly due to the lack of high-resolution data.

The ratio of SOC/OC decreased with increasing temperature at CD but increased ~~with temperature~~ at CQ when ~~T~~temperature 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 SO₄²⁻ and NO₃⁻.

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

4 Conclusions

Chemically-resolved PM_{2.5} data collected during four seasons at two urban sites in Sichuan basin, southwest China were analyzed in the present study. On about 30% of the days, daily PM_{2.5} exceeded the national air quality standard, with annual mean concentrations of 67.0 ± 43.4 and 70.9 ± 41.4 $\mu\text{g m}^{-3}$ at CD and CQ, respectively. SO₄²⁻, NO₃⁻, NH₄⁺, OM, EC and FS were the major chemical components of PM_{2.5}, accounting for 16.8%, 13.6%, 10.8%, 26.1%, 5.4%, and 5.7% of PM_{2.5} at CD, and 17.2%, 10.9%, 9.2%, 29.6%, 6.4%, and 9.5% at CQ, on annual average, respectively. The

493 concurrent occurrences of heavy pollution events at the two sites and similarities in pollutants
494 characteristics between the two sites ~~demonstrated the regional-scale phenomenon of PM_{2.5} episodes~~
495 ~~inside the Basin, which~~ was mainly caused by the surrounding mountainous topography under typical
496 stagnant meteorological conditions. Such a finding was also supported by back trajectory analysis which
497 showed that air masses reaching at both sites were originated within the basin and only traveled for short
498 distances on heavy polluted days. Differences between the two sites with regards to several major
499 chemical components provided evidences of sub-regional characteristics of emission sources and
500 chemical transformation processes under different meteorological conditions. For example, an additional
501 source factor from motorcycle traffic was identified for VOCs emission in Chongqing, which led to higher
502 ~~high~~ OC concentrations, and lower relative humidity in Chongqing caused lower ~~nitrate~~ NO_3^-
503 concentration in this city despite similar levels of its gaseous precursors in the two cities. The present
504 study also identified different driving mechanisms for the ~~polluted~~ $\text{PM}_{2.5}$ pollution episodes in the
505 Sichuan Basin than in the other regions of China. For example, sharply increased relative humidity was
506 thought to be one of the main factors causing high inorganic aerosol concentrations during the ~~polluted~~
507 pollution periods in eastern coastal China and North China Plain, while in the Sichuan Basin the special
508 topography and meteorological conditions are driving forces for such events considering relative humidity
509 was high throughout the year and did not differ much between ~~polluted~~ pollution and ~~clear~~ clean periods.
510 However, on annual basis heterogeneous reactions might be more important in this basin than in the other
511 regions of China due to the consistent high humidity conditions, as revealed in the case of ~~sulfate~~ SO_4^{2-}
512 formation in the present study. Future studies should use high-resolution data to verify the findings related
513 to chemical transformation paths proposed here. More importantly, a detailed emission inventory of
514 aerosol particles and related gaseous precursors in the basin should be developed promptly, which is
515 needed for further investigating $\text{PM}_{2.5}$ formation mechanisms and for making future emission control
516 policies. Source-receptor analysis using monitored chemical-resolved $\text{PM}_{2.5}$ data should be conducted to
517 verify such emission inventories.

518

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

520

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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.

	CD					CQ				
	Autumn	Winter	Spring	Summer	Annual	Autumn	Winter	Spring	Summer	Annual
Meteorological 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
Precipitation (mm)	<u>76.3</u>	<u>18.3</u>	<u>56.6</u>	<u>247.8</u>	<u>na.</u>	<u>73.3</u>	<u>22.0</u>	<u>104.6</u>	<u>206.3</u>	<u>na.</u>
PBLH _{max} (m)	890±305	852±273	1296±491	1422±529	1119±481	821±252	928±260	1310±491	1329±505	1101±453
Concentrations of gaseous pollutants (µg 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
Concentrations of PM _{2.5} and chemical compositions (µg m ⁻³)										

PM _{2.5}	62.1±38.4	113.5±47.8	48.0±25.2	45.1±15.2	67.0±43.4	56.3±23.6	115.1±53.9	58.3±24.6	54.2±16.2	70.9±41.4
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
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

na. means no data.

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.

	SO ₄ ²⁻	NO ₃ ⁻	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

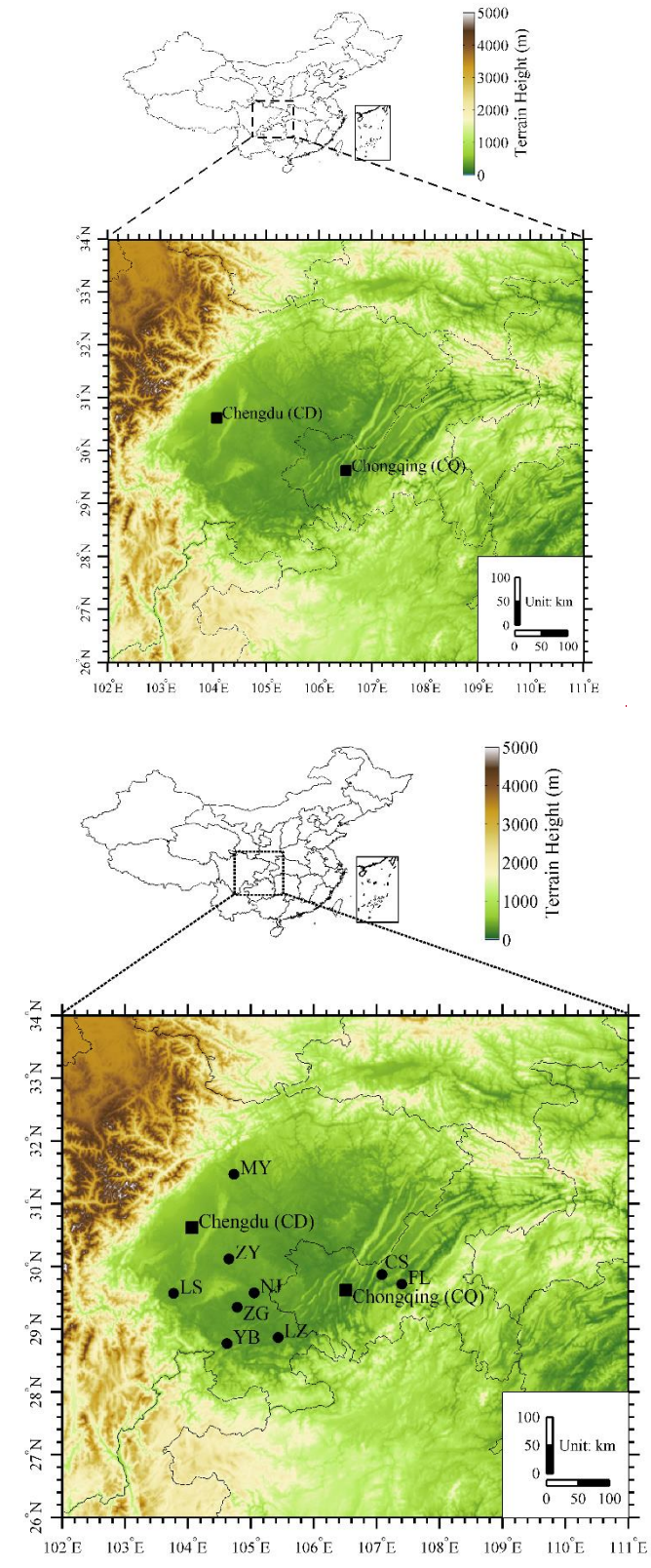


Figure 1. Locations of the sampling sites in Chengdu (CD) and Chongqing (CQ) and major cities in the Sichuan Basin. MY, Mianyang; ZY, Ziyang; LS, Leshan; NJ, Neijiang; ZG, Zigong; YB, Yibin; LZ, Luzhou; CS, Changshou; FL, Fuling.

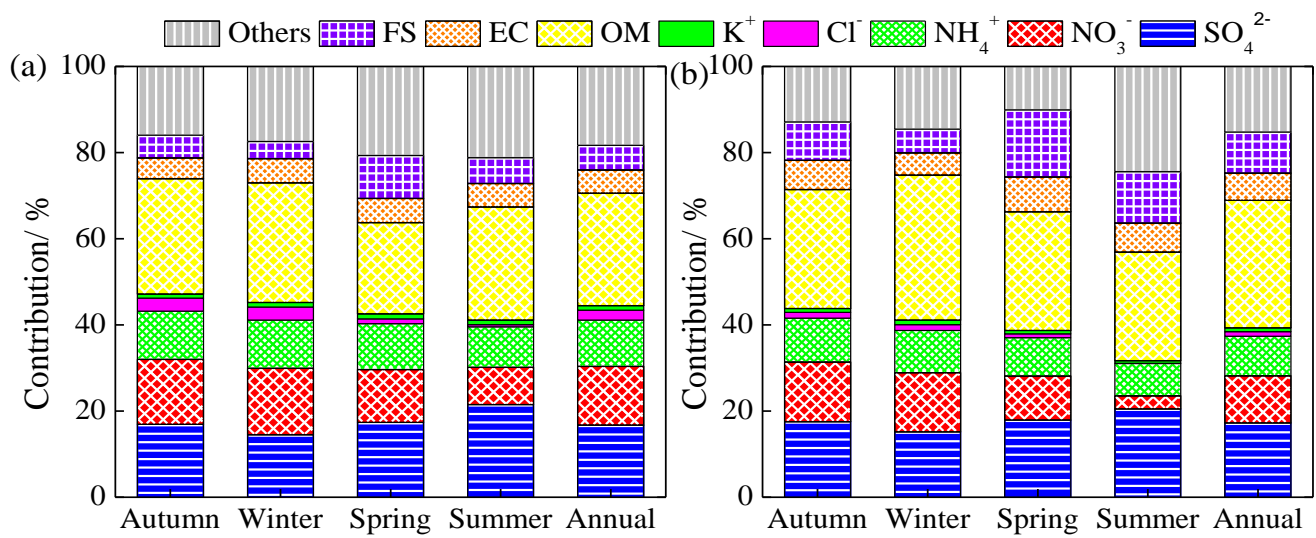


Figure 2. Seasonal and annual contributions of individual chemical components to PM_{2.5} at CD (a) and CQ (b).

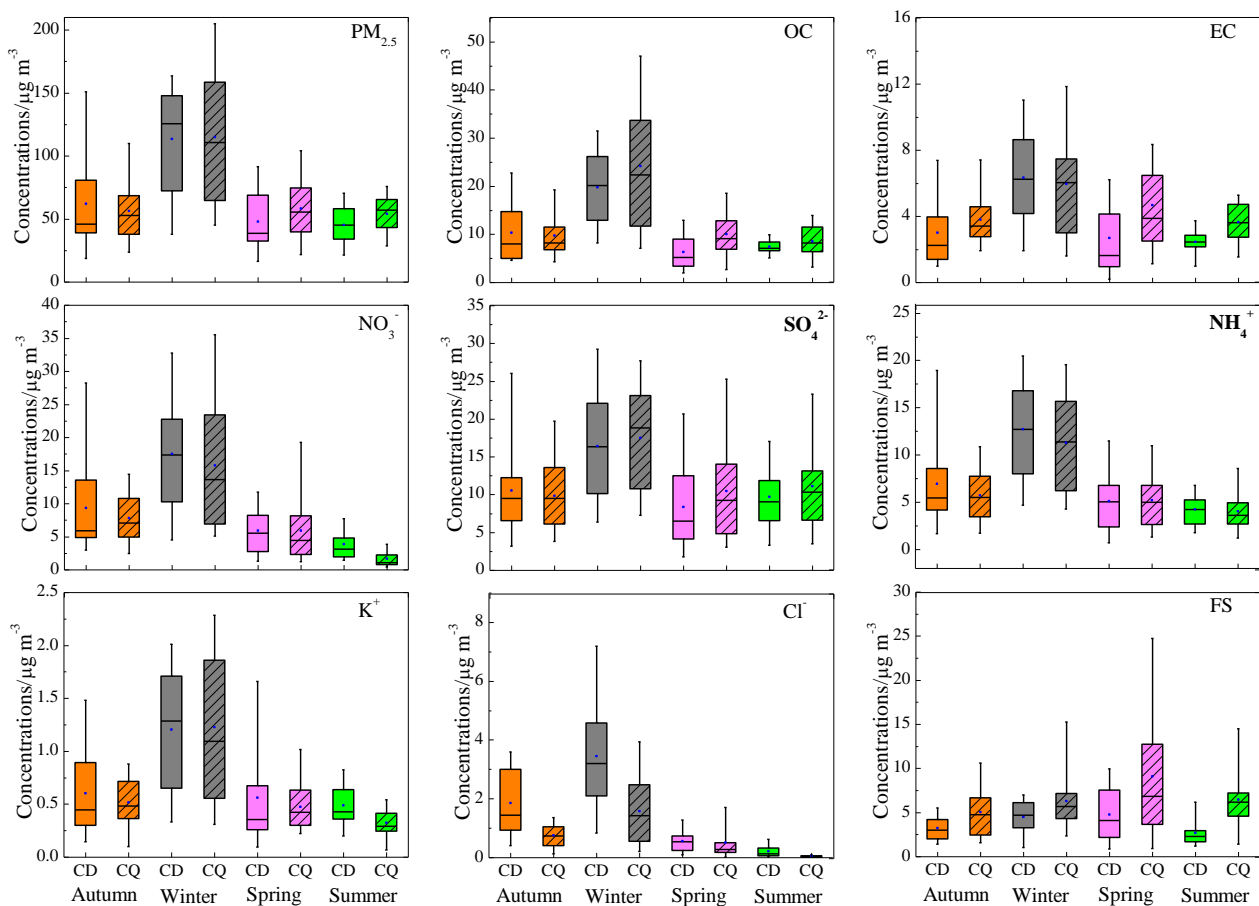


Figure 3. Seasonal distributions of $\text{PM}_{2.5}$ and its major chemical components. Shown in each sub-figure are mean (dot symbol), median (horizontal line), the central 50% data (25th -75th percentiles, box), and the central 90% data (5th-95th percentile, whisker)

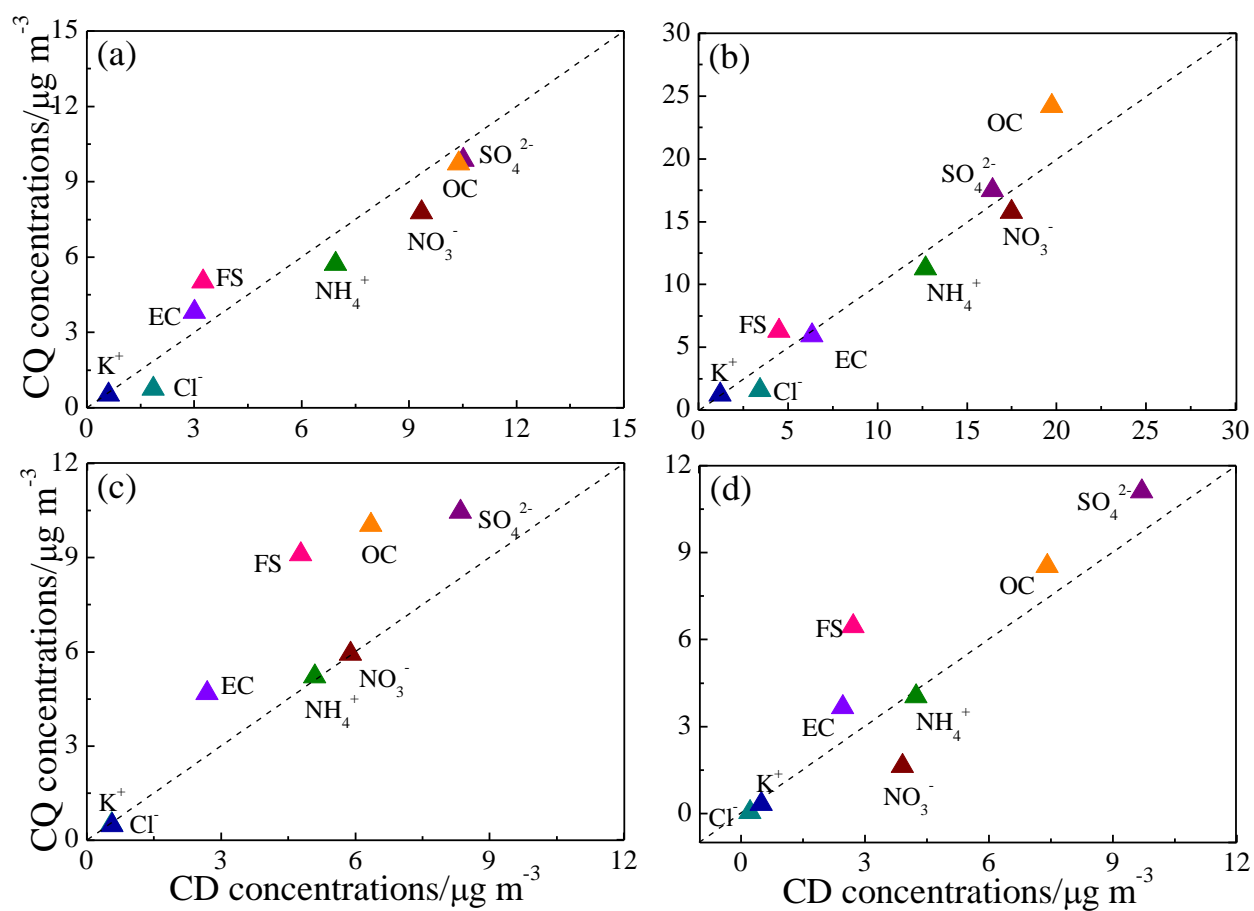


Figure 4. Seasonal mean concentrations of major components in autumn (a), winter (b), spring (c), and summer (d) at CD and CQ sites.

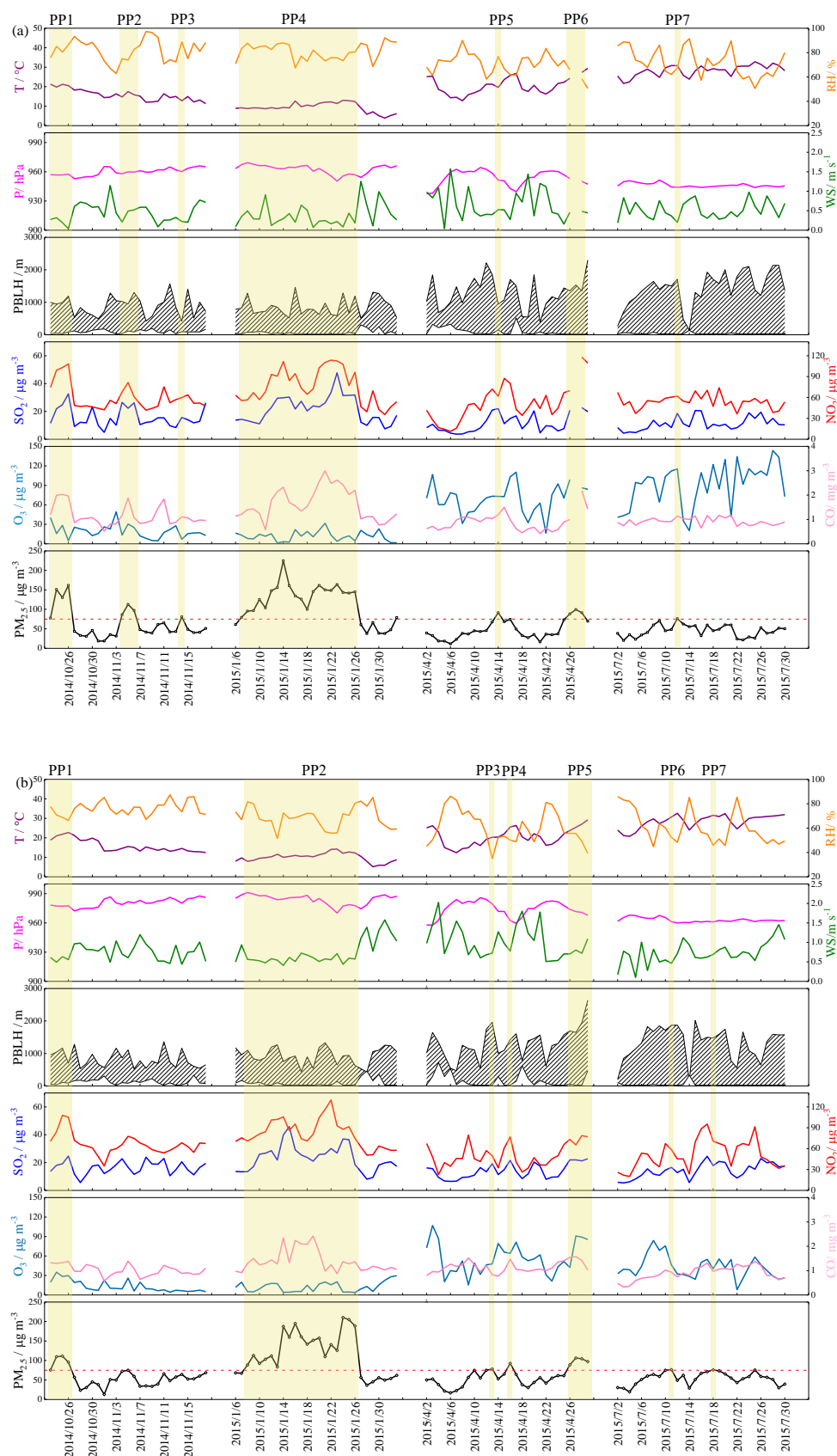


Figure 5 Temporal variations of meteorological parameters, ~~gas-phase~~gaseous pollutants and $PM_{2.5}$ during the campaign at CD (a) and CQ (b). Pollution episodes are highlighted by shaded areas.

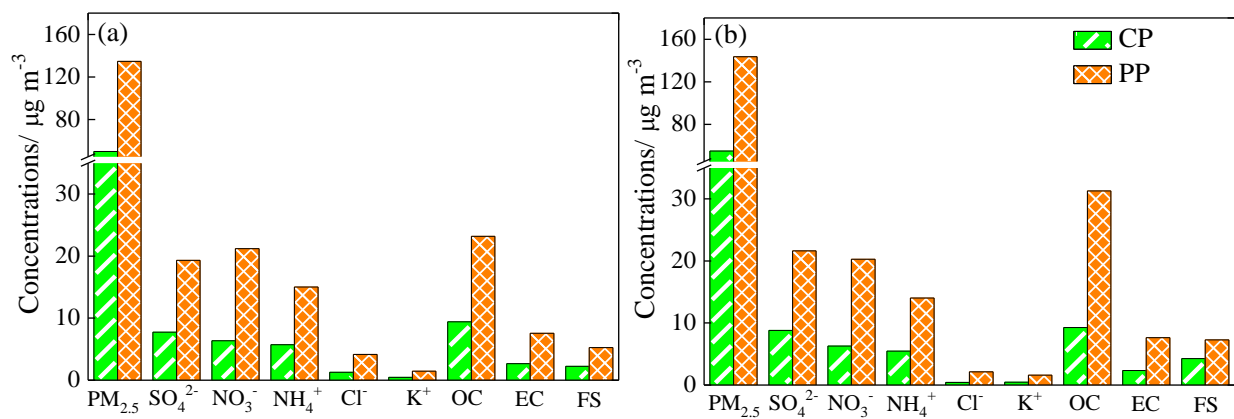


Figure 6. PM_{2.5} and major chemical components during clean periods (CP) and ~~polluted~~ pollution periods (PP) in winter at CD (a) and CQ (b). At CD: CP, 6 January and 27 January-2 February 2015; PP, 7-26 January 2015. At CQ: CP, 6-7 January and 27 January-2 February 2015; PP, 8-26 January 2015.

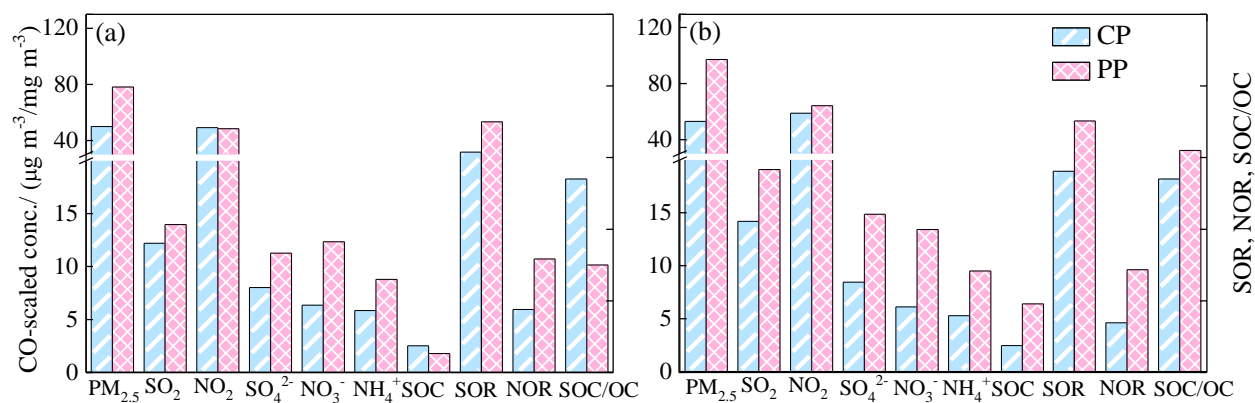


Figure 7. CO-scaled concentrations of various pollutants and the values of SOR, NOR, and SOC/OC in winter at CD (a) and CQ (b). CP and PP is the same period as Figure 6.

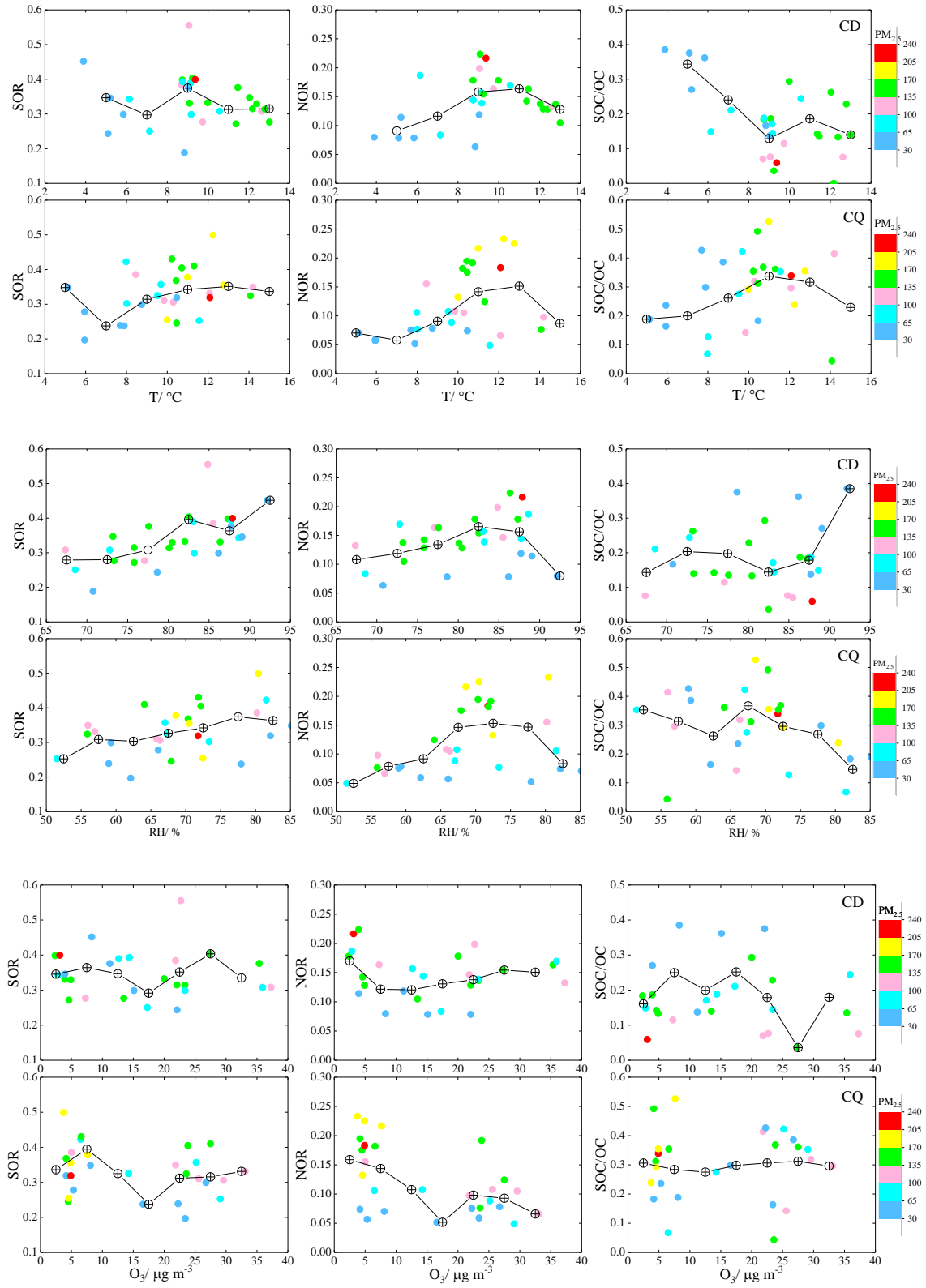


Figure 8. Correlations of SOR, NOR and SOC/OC against temperature (upper), RH (middle) and O₃ concentration (bottom) in winter at CD and CQ.

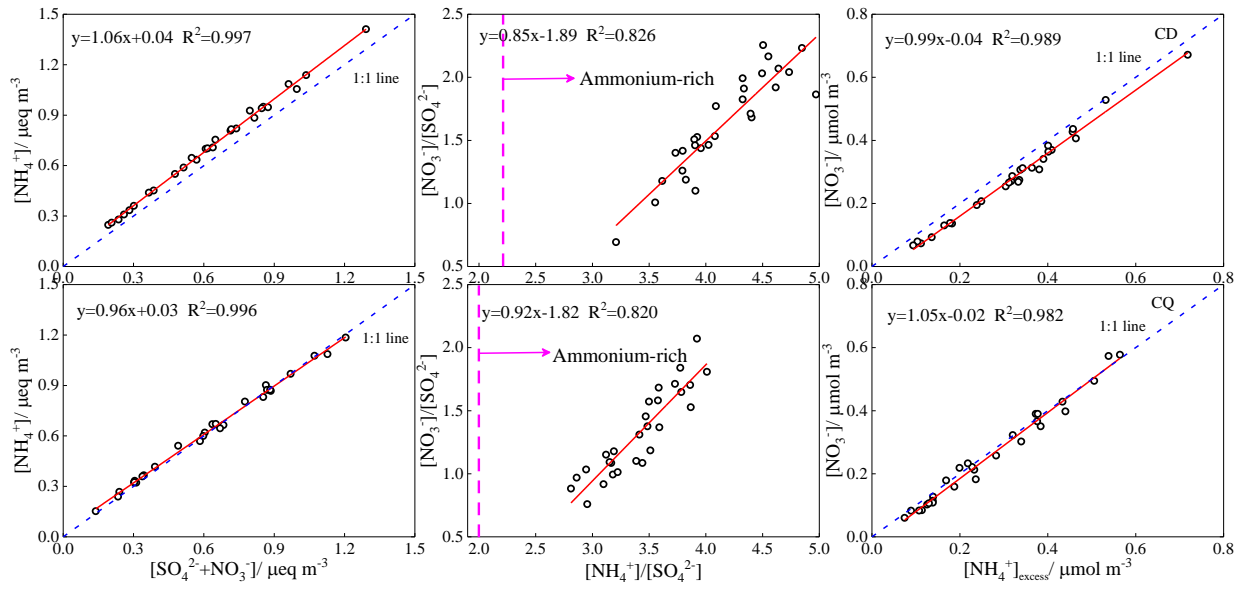


Figure 9. NH_4^+ concentration as a function of the sum of SO_4^{2-} and NO_3^- in equivalent concentrations (left column), molar ratio $\text{NO}_3^-/\text{SO}_4^{2-}$ as a function of $\text{NH}_4^+/\text{SO}_4^{2-}$ (middle column), and NO_3^- concentration as a function of $\text{NH}_4^+_{\text{excess}}$ (right column) at CD (upper row) and CQ (lower row).

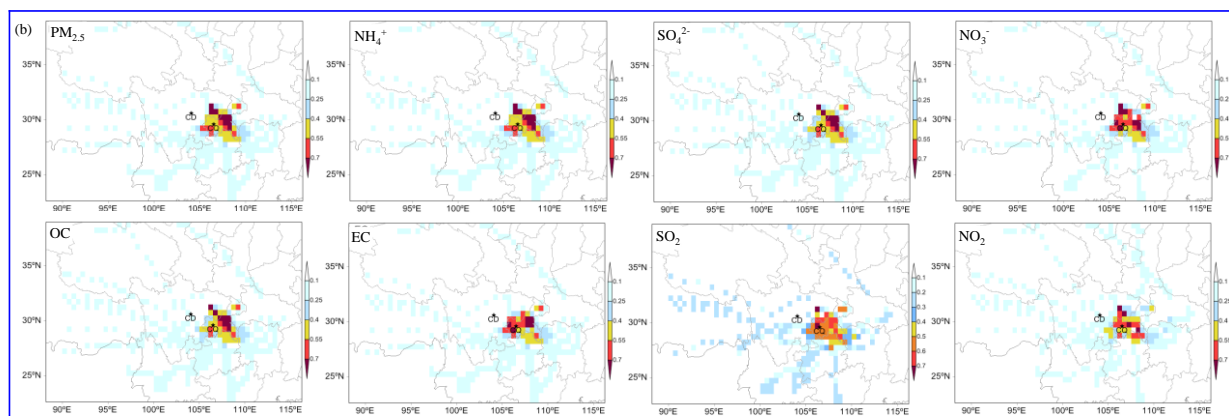
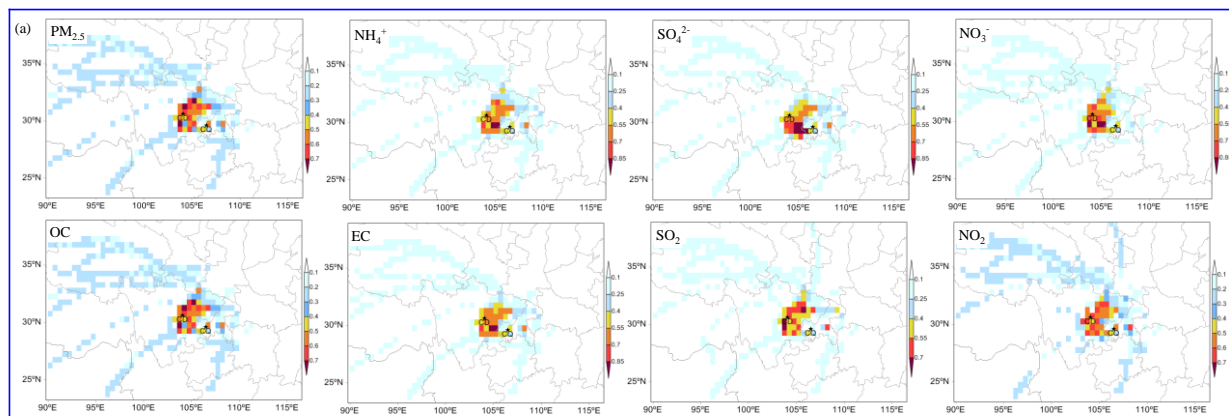


Figure 10. PSCF distribution of $\text{PM}_{2.5}$, its chemical components, and gaseous precursors in winter at CD (a) and CQ (b).