Dear Editor:

We have carefully revised the manuscript and addressed all of the comments provided by the two reviewers. The details can be found in our enclosed responses to the reviewers' comments. For your and the reviewers' 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 #2

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:".

General Comments:

This manuscript elucidates the seasonal variations, the formation mechanism, and the sources of $PM_{2.5}$ in two megacities in Sichuan Basin. The concentrations of major chemical components of $PM_{2.5}$ in different seasons are investigated. The chemical characteristics of clean days and polluted days are presented to study the formation of key chemical species as well as transportation pathway of secondary aerosols. In general, the research results provide meaningful information on both formation mechanism and environmental control strategies of $PM_{2.5}$. However, there are still some key issues which need to be addressed before possible publication.

R: We have carefully studied the several key issues raised by this and another reviewer and revised the paper accordingly. We hope the reviewer will find that the quality of the paper has been improved significantly.

1. The factors contributing to the different temporal patterns of sulfate and nitrate should be further discussed. Specific heterogeneous reaction which may play important roles in polluted days and its major contributing components can be clearly pointed out.

R: We have added information of the gaseous precursors and meteorological parameters to facilitate the more in-depth discussion on the temporal patterns of $SO_4^{2^-}$ and NO_3^- in the revised manuscript. We agree with the reviewer that heterogeneous reactions likely contributed to the formation of secondary aerosols considering the high relative humidity (RH) (60-88%) conditions during the study campaign. In the revised paper, the formation of secondary aerosols through heterogeneous reactions was discussed in detail based on the relationships between SOR, NOR and SOC/OC and RH. Note that RH exhibited no significant difference between clean and polluted periods in our study, suggesting RH was not the driving force for the polluted episodes in Sichuan Basin. This phenomenon was different from what was found in eastern coastal China and North China Plain, where sharp RH increase was observed during polluted episodes.

2. The discussion on $PM_{2.5}$ formation process can be combined with the analysis on the variation of gaseous precursors, including SO_2 and NO_2 .

R: As mentioned above, information of gaseous precursors has been added in the revised paper. Temporal variations of $PM_{2.5}$ and major gaseous precursors were then

discussed together. For example, gaseous precursors (SO₂ and NO₂) and secondary inorganic aerosols (SO₄²⁻ and NO₃⁻) increased by a factor of 1.5-3.7 during the polluted periods than clean periods. To exclude the influence of atmospheric physical processes on these variations, CO-scaled variations were also provided. The CO-scaled SO₄²⁻ was 40-70% higher and that of NO₃⁻ was 80-120% higher during the polluted periods, while their respective gaseous precursors were no more than 30% higher. These numbers suggested stronger chemical transformation from gaseous precursors to PM_{2.5} during the polluted periods, as well as the significant contribution of meteorological condition to the high PM_{2.5} levels.

3. More discussion on geographical sources of different chemical components of $PM_{2.5}$ is recommended. I also suggest the analysis on the different topography of these two megacities, which will help to better explain the impact of local emission and regional transportation.

R: We have plotted several PSCF maps to illustrate the geographical sources of the different chemical components in $PM_{2.5}$ and their gaseous precursors. Generally, similar spatial distributions of potential sources for $PM_{2.5}$ and its chemical components were observed. At the CD site, high concentrations of the pollutants were mostly associated with sources broadly located in the southeast of the basin, covering Neijiang, Zigong, Yibin, Luzhou and east part of Chongqing. At the CQ site, the northeast area of Chongqing was identified as the major sources.

The impact of the special topography and meteorological conditions on $PM_{2.5}$ levels at the two sampling sites were also discussed in detail. Firstly, CD and CQ sampling sites are both located in the Sichuan Basin, which is surrounded by high mountains. Such topography often forms a barrier for the dispersion of pollutants and causes air stagnation within the basin, therefor facilitates regional-scale pollution episodes inside the Basin. Back trajectory analysis showed that air masses reaching CD and CQ only traveled for short distances, primarily within the Sichuan Basin. This highlighted the impact of the special topography on $PM_{2.5}$ pollution at the two sites. Secondly, Chongqing is a famous mountain city with the majority of population using motorcycle instead of bicycle as the main daily travel tools. This contributed more VOCs emissions and high OC concentrations at CQ than CD.

Besides, I have some specific comments on the manuscript as follows: 1. Section 2.5: I'd like to recommend adding detailed equations of PSCF analysis for better understanding.

R: Information added.

2. Line 170-171: Citation format error: "Tao et al. (2013, 2014)" should be corrected into "(Tao et al., 2013, 2014)".

R: Corrected.

3. Line 244: The authors claimed the concentration of NO_3^- decreased on the polluted days in the warm season of CQ. But in Figure 6(d), the concentration of NO_3^- is higher in the polluted days. There seems to be contradictory.

R: Thanks for pointing out this negligence, which has been corrected in the revised paper.

4. Section 3.4.2: The authors applied CO-scaled $PM_{2.5}$ and major components to isolate the impact of meteorological conditions. Specific scaling approach or related references should be provided.

R: The CO-scaled pollutant concentration was calcualetd as the ratio of concentrations between a pollutant of interest and CO (e.g. $PM_{2.5}/CO$, SO_4^{2-}/CO , OC/CO). We have added explanaiton and related references (Zheng et al., 2015, Zhang et al., 2014) in the revised paper.

5. Section 3.4.3: I'd like to recommend adding a graph containing RH levels and NO₃⁻ concentration between the two sites. Also, a correlation between $[NO_3^-]/[SO_4^{2-}]$ and $[NH_4^+]/[SO_4^{2-}]$ is suggested to investigate the difference of NO₃⁻ formation between CQ and CD.

R: NO₃⁻ concentrations at CD and CQ were compared for all the seasons. NO₃⁻ was 58% lower at CQ than CD in summer, but was at similar levels in the other seasons. NO₂ and most meteorological parameters (except RH) were comparable at both sites in summer. Thus, the lower NO₃⁻ at CQ in summer was likely mainly caused by the lower RH, which inhibited the formation of NH₄NO₃. We have added a figure in the supplemental information document showing the temporal variations of ambient RH and deliquescence relative humidity (DRH), which was used to explain the different NO₃⁻ concentrations between CD and CQ in summer.

We have also added correlation analysis between $[NO_3^-]/[SO_4^{2^-}]$ and $[NH_4^+]/[SO_4^{2^-}]$ and related in-depth discussion on the formation mechanism of NO_3^- in winter in the revised paper.

6. Figure 3: The black dots which indicate the average values should be stated in the figure caption.

R: We have added the description of the legend in this figure.

Reference cited above:

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, 2015.

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.

Response to Referee #3

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:".

The manuscript is based on the observation conducted in four selected months in two cities in the Sichuan Basin, China. It represents the results of $PM_{2.5}$ and the chemical components. The seasonal variations are shown and the difference in terms of the formation mechanisms and geographical influence between the two cities is discussed.

The content of this manuscript fits the scope of ACP and the data is interesting to be studied. However, I found this manuscript is only a report of the results in a rarely investigated region in China but without in-depth analysis. No novel point has been raised and discussed in this manuscript. I would not recommend it to be published in ACP in the current stage.

R: Based on this and another reviewer's critical comments, we have added many in-depth analyses in the revised manuscript. These include: (1) providing gaseous precursors and meteorological parameters data to explain the seasonal variation trends of $PM_{2.5}$ and its chemical components; (2) conducting air mass back trajectory analyses to illustrate the influence of topography on $PM_{2.5}$ pollution in Sichuan Basin; (3) adding deliquescence relative humidity (DRH) analysis for the summer season to explain the different NO3- concentrations at the two sites, and (4) comparing the characteristics of $PM_{2.5}$ pollution episodes in Sichuan Basin with those in the other regions of China.

The quality of the paper has been substantially improved, as demonstrated by the many novel findings. A few major ones are detailed below.

(1) The study identified different driving mechanisms for the polluted PM2.5 episodes in the Sichuan Basin than in the other regions of China. For example, sharply increased relative humidity (RH) was thought to be one of the main factors causing high inorganic aerosol concentrations during the polluted periods in eastern coastal China and North China Plain where mostly with flat terrain (Li et al., 2017; Zhao et al., 2013; Zheng et al., 2015a; Zheng et al., 2015b, Gao et al., 2015; Hua et al., 2015; Wang et al., 2015). In contrast, RH did not differ much between polluted and clear periods in Sichuan Basin. Instead, the special topography and meteorological conditions in this region resulted in the polluted PM2.5 levels, and different local topography between CD and CQ further added different pollution characteristics between the two sites. Note that Sichuan Basin is completely surrounded by high mountains and constantly characterized by low wind speeds. RH in the region is high throughout the year, which is conducive for heterogeneous reactions forming

inorganic aerosols.

(2) The study identified the sub-regional characteristics of emission sources. An additional VOCs emission source was identified for CQ than CD based on higher OC concentrations at CQ. This additional source was attributed to motorcycle traffic in CQ since it is a famous mountain city where most people use motorcycle as daily traffic tools. According to the Chongqing Statistical Yearbook 2015, the number of motorcycles was 2.0 million (among the total of 2.3 million motor vehicles) in 2014, which was much higher than those (0.7 million) in Chengdu (Chengdu Statistical Yearbook 2015).

(3) The study identified sub-regional characteristics of inorganic aerosols. Although the whole Sichuan Basin (as the regional scale) was characterized by special topography (surrounded by mountains) and hot and humid air, there were sub-regional differences within the basin, as contrasted between the two largest cities (CD and CQ) in this region. Thus, different aerosol characteristics were found at the two sites. For example, the lower NO3- at CQ than at CD was identified to be caused by the lower RH based on the deliquescence relative humidity (DRH) of NH₄NO₃ (Mozurkewich, 1993).

With these additoanl in-depth analyses and inovative results, we hope the reviewer will find ithe paper meets the standard of the jorunal.

General comments:

1. The sampling campaign in four selected months may not be enough to provide sufficient data to answer the questions (objectives) which are supposed to be studied in this work. The two sampling sites seems not ideal to understand the characteristics of $PM_{2.5}$ in two basined cities with typical geographical features. Regional sites without direct emissions are better in my opinion. In order to discover and reveal the formation mechanisms of secondary aerosols, more data and analysis are necessary.

R: Based on existing literature, the four month data observed in four typical seasons should be enough for exploring the seasonal and annual patterns of aerosol pollution levels and for exploring potential formation mechanisms, as has been demonstrated in studies for other regions of China as well as for other countries (Paraskevopoulou et al., 2015; Pietrogrande et al., 2016; Squizzato and Masiol, 2015; Ming et al., 2017; Tao et al., 2014; Wang et al., 2016; Wang et al., 2015; Zhao et al., 2013).

We agree with the reviewer that a traditional regional background site would choose a rural site far away from urban areas/local emissions in order to study the background pollution levels. However, this is not the focus of our study. Emission control policies aim to reduce PM2.5 pollution for populated regions for human health concerns. In this sense, urban areas, especially in megacities, are the major concerns. Chengdu and

Chongqing are the two biggest cities in Sichuan Basin. Thus, emission sources, transportation and chemical transformation of atmospheric aerosols observed in these cities should be investigated thoroughly. The two monitoring sites selected in this study should represent the typical urban environment in their respective cities (Chen et al., 2017; Tao et al., 2014). Although none of the two sites alone would represent the whole region of the Sichuan basin, the similarities 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. This reviewer seemed to have a different view of the regional-scale phenomenon than what we had in mind, which we understand, was due to the different considerations. The selection of our sites perfectly served the goals of our study.

Although the current data set is not very big, it is enough to provide many in-depth analyses, as we have done in the revised paper after incorporating both reviewers' recommendations (with more details in our responses to the specific comments below).

2. The data are not well presented in this manuscript. The readers can hardly find the sufficient information to know and understand the results. For example, how many samplers were collected in the campaign? How many samples were taken and how about the variations of data in clear days, moderate polluted days and heavy polluted days? Were there some different pollution episodes?

R: We have added more details about the sampling information in the revised manuscript. A total of 112 samples were collected on daily basis at each site, which were 27, 28, 28 and 29 days in autumn, winter, spring and summer, respectively. To view the pollution episodes clearly, we have added a figure describing the temporal variations of daily $PM_{2.5}$ concentrations, gaseous precursors and meteorological parameters during the entire study periods. The number of polluted days was 8, 21, 4 and 1 in autumn, winter, spring and summer (total 34 days), respectively, at CD, and was 4, 19, 6 and 2 (total 31 days) at CQ.

3. The analysis and discussion are superficial and full of speculation. No solid evidence can be provided to support the conclusions, which makes the significance and implication ungrounded. For example, to support their hypothesis, the diurnal variations of monitored gases are presented and discussed. However, the data of $PM_{2.5}$ and their chemical components are on daily basis, which weaken the analysis and leads to vague conclusions.

R: We agree that it is ideal to have hourly aerosol data for more detailed analyses, which unfortunately could not be obtained in this study due to instruments limitations. However, in-depth analyses can be done using daily data as demonstrated in earlier studies as well as in our revised version of this manuscript (more details below in our

responses to specific comments).

More specific comments are shown as follows:

1. As I suggested above, are the two sampling sites and the data representative for this investigation on the characteristics of aerosol in the two basined cities? Obviously they are both highly affected by the traffic emissions which may bias the analysis. The topography of the two sites and the influence should be discussed.

R: See our responses to point 1 of general comments above regarding regional representative of the sites. We have added discussion on topography related impacts in the revised paper. Briefly, CD is located in the west while CQ on the eastern margin of Sichuan Basin. The basin is surrounded by mountains in all directions, which forms a barrier for pollutants dispersion and thus causes frequent stagnant air in the basin. This results in regional-scale pollution episodes in Sichuan Basin. Air mass back trajectory analysis showed that air masses reaching CD and CQ only traveled for short distances and primarily within the basin. Such a phenomenon highlighted the impacts of the special topography on $PM_{2.5}$ pollution.

2. Line 78: Please provide the details of the sampler. Three samplers were used in this campaign. The comparison of the three samplers should be provided to show the accuracy and consistency of the data.

R: The samplers used in this study are described in the manuscript. At CD site, $PM_{2.5}$ sampling was carried out using a versatile air pollutant sampler (URG Corp., URG-3000K, North Carolina, USA), which has three channels. One channel was used to load $PM_{2.5}$ 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. At the CQ site, a low-volume aerosol sampler (BGI Corp., frmOmni, 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 two parallel channel at CD site and the simultaneous sampling on two instruments at CQ site allowed the contemporary chemical determination of the loading $PM_{2.5}$.

The three samplers used in this study were commercial instruments and widely used in $PM_{2.5}$ sampling. We examined the flow rate of each sampler before and after sampling carfully to ensure the quality of sampling.

3. How many samples were collected? How the blank filters (lab blank and field blank) were collected?

R: See our responses to point 2 of general comments. Field blanks were collected

every two weeks in each season, resulting 8 filed blanks at each site. In order to check the background contamination from the laboratory, three lab blank filters in each campaign were stored in a clean Petri slides in the dark and were analyzed the same ways as the sampling filters. The detailed information has been added in the revised manuscript.

4. Line 111-113: There were only 5 elements detected by XRF. Normally I would expect more elements could be measured by the XRF technique. Why?

R: Besides the 5 crustal elements (Al, Si, Ca, Fe and Ti) used in the study, another 16 elements including Na, Mg, S, Cl, K, V, Cr, Mn, Co, Ni, Cu, Zn, Rb, Sb, Ba and Pb were also determined by the XRF method. Among those elements, Na, Mg, Cl, S and K were discussed in the form of ions, and other metal elements accounted for less than 1% of the $PM_{2.5}$. Thus, the above 16 elements were not considered in identifying the major chemical components that were responsible for the $PM_{2.5}$ pollution.

5. Line 121: Please provide the details of the weather station.

R: We have added some details of the weather station in the revised manuscript.

6. Line 178-179: The authors pointed out that higher sulfate concentrations were found in summer. In Table 1, I found that lower sulfate average was in summer than that in winter. Please check the data.

R: We have clarified the explanation. SO_4^{2-} was the highest in winter, but not the lowest in summer. In contrast, many other pollutants had the lowest in summer.

7. Line 178-185: The discussion on sulfate, nitrate, chloride and potassium seems superficial and arbitrary. The analysis should be based on the data from this campaign and be made with in-depth study instead of guesses.

R: We have rewritten this section completely with additional data of meteorological parameters and gaseous precursors. See our summary responses at the top of this file.

8. Line 188-190: The high SOC content was observed in winter. In this work, the estimation of SOC mainly depends on the seasonal minimum of OC/EC. However, it should not be surprise to see high OC in winter because organic aerosols may not necessarily be only formed by secondary reaction but also by direct emissions (e.g. biomass burning).

R: We are aware of the limitations of approach, but think it is a practical method for estimating SOC, as has frequently been used in literature. We noted that there was no extensive coal combustion or wood burning for domestic heating in winter due to the warm climate in this region. Therefore, biomass burning should have small effects on

OC concentrations.

9. Section. 3.3 discusses the difference of data between the two sites. As it known to all, the difference can be due to many possible factors (emissions, atmospheric reactivity, meteorological conditions, the surrounding terrains). It is really hard to synthesize significant information from the comparison. Therefore, more in-depth studies are necessary.

R: We have identified major factors causing the differences between the two sites through the following in-depth analyses, such as back trajectory analyses and deliquescence relative humidity analyses (see some details in our summary responses at the top of this file).

10. Line 227-238: More information should be provided for the pollution episodes. For example, how many polluted days and in which seasons were captured? How many pollution episodes were observed?

R: We have added a figure and related information in the revised paper (also see response to point 2 of general comments above).

11. Line 254-256: The distinct characteristics in the urban area in the Sichuan Basin should be further investigated and discussed. How may the topography and meteorological conditions influence on the characteristics?

R: See our summary responses at the top of this file.

12. Line 271-272: "Both CO and EC concentrations increased on polluted days, suggesting the important role the meteorological condition played on $PM_{2.5}$ accumulation." Why? I cannot see any link. The occurrence of CO and EC in the troposphere should be influenced by the emissions, removal mechanisms and other factors (including meteorological conditions but not exclusively).

R: Such a conclusion was based on this hypothesis: the variations of CO were mainly controlled by meteorological factors (Zheng et al., 2015b; Zhang et al., 2015) while those of the other pollutants were by both meteorology and chemical transformation. In this study, PM2.5 and gaseous precursors increased by a factor of 1.8-3.3 during polluted periods than clean periods while CO only increased by a factor of 1.8 at CD and 1.5 at CQ during the same periods. Furthermore, similar diurnal variations were found for CO during polluted and clean periods. Thus, comparing the different enhancing factors between CO and other pollutants of interest can shed some light on the impact of non-meteorological factors on pollutants accumulation, as was done by using the CO-scaled pollutant concentrations.

13. Line 274-275: "CO can be considered as a reference pollutant species whose

temporal variations were mainly from the impact of meteorological conditions." Why? See the comment 11. Also, I think the CO-scaling method should be further explained with more details and with references.

R: See our response to the previous comment. The CO-scaled pollutant concentration means the ratio of the pollutant concentration to CO concentration (e.g. $PM_{2.5}/CO$, SO_4^{2-}/CO , OC/CO, etc.). We have added the related reference (Zheng et al., 2015b, Zhang et al., 2015) in the revised manuscript.

14. Section 3.4.2: The diurnal trends of monitored gases could not give any solid evidence to support their hypothesis. In this case, especially when the formation mechanisms of secondary aerosols are discussed, high resolution data are necessary. We should not rely on the unsolid speculation.

R: We agree that high-resolution data would provide more and better information on the formation mechanisms of secondary aerosols. Unfortunately, such data cannot be obtained during the sampling campaign due to the lack of expensive on-line instruments. As explained n our response to general comment 3 above, even with daily data in-depth analyses can be conducted. In this study, Sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) were defined to evaluate the degree of secondary transformation. Considering the low-resolution data, SOR and NOR were grouped according to temperature, RH and O₃ concentration bins to explore the variation trends of SOR, NOR and SOC/OC. Such an analysis revealed that SO_4^{2-} was predominantly formed through heterogeneous aqueous process while NO3- was formed by both homogeneous and heterogeneous reactions at both sites. The proposed formation mechanism of NO_3^- in the present study agreed with those found in an earlier study using high-resolution inorganic ions data (Tian et al., 2017).

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Seasonal characteristics, formation mechanisms and geographical 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, Chengdu (CD) and Chongqing (CQ), in
3	Sichuan Basin, daily PM _{2.5} samples were collected simultaneously at one urban site in each city for four
4	consecutive seasons from October autumn 2014 to July summer 2015. Annual mean concentrations of
5	$PM_{2.5}$ were 67.0 ± 43.4 and $70.9 \pm 41.4 \ \mu g \ m^{-3}$ at CD and CQ, respectively. Secondary inorganic
6	aerosols (SNA) and organic matter (OM) accounted for 41.1% and 26.1%, respectively, of PM _{2.5} mass
7	at CD, and 37.4% and 29.6% at CQ, respectively. Seasonal variations of PM _{2.5} and its-major chemical
8	components were significant, usually with the highest mass concentration values in winter and the
9	lowest in summer. Daily PM _{2.5} concentration exceeded the national air quality standard on 30% of the
10	sampling days at both sites, and most of the pollution events were at the regional scale within the basin
11	formed by stagnant meteorological conditions. The concentrations of carbonaceous components were
12	higher at CQ than CD, likely partially caused by emissions from the large amount of motorcycles in CQ.
13	SNA and OM concentrations on polluted days were 12.7-3.4 3 times higher those on polluted days than-
14	on clean days at both sites, whereas their percentage contributions to PM _{2.5} -mass varied differently-
15	among the components and between the two sitescities. Homogeneous Gasgas-phase oxidation-
16	<u>reactions</u> probably played an important role <u>on-in</u> the formation of <u>SO₄²⁻</u> , while both homogeneous and
17	heterogeneous reactions contributed to the formation of NO3 ⁻ .secondary aerosols when PM2.5-mass-
18	varied in the range of 75-150 µg m ⁻³ , while heterogeneous transformation was likely the major-
19	mechanism on the heavy polluted days. Geographical origins of emissions sourcesregions causing-
20	<u>contributing to high PM_{2.5} masses at both sites were identified to be mainly distributed</u> within the basin
21	at both sites based on potential source contribution function (PSCF) analysis.
22	

24 **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
- 28 (Fu et al., 2016;Cao et al., 2012;Baumer et al., 2008), impact climate (Ramanathan and Feng,
- 29 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
- 31 consumption through econmic development, industrialization and urbanization (Tie and Cao, 2009; Tao

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

- Chinese government in 2012, and strict strategies have been implemented nationwide, e.g. controling
- 34 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
- 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 µg 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 µg m⁻³).

41 Previous studies showed that Beijing-Tianjin-Hebei area (BTH), Yangtze River Delta (YRD), Pearl River Delta (PRD), and Sichuan Basin were the four main regions in China with severe aerosol 42 pollution (Tao et al., 2017). While many studies have been conducted in BTH, PRD and YRD regions 43 to understand the general characteristics of PM_{2.5} and its chemical components, formation mechanism, 44 45 and sources (Ji et al., 2016;Li et al., 2015;Quan et al., 2015;Tan et al., 2016;Yang et al., 2015;Zhang et al., 2013;Zhao et al., 2015;Zhao et al., 2013a;Cheng et al., 2015;Zheng et al., 2015a;Yang et al., 2011a), 46 only a few studies have focused on Sichuan Basin (Tao et al., 2014; Tian et al., 2013; Yang et al., 2011b). 47 Covering an area of 260,000 km² and with a population of around 100 million in southwest China, the 48 Sichuan Basin is a subtropical expanse of low hills and plains and the most populated basin in China. It 49 is a subtropical expanse of low hills and plains and is completely encircled by high mountains and 50 plateaus, and It is also characterized by persistently high relative humidity, and extremely low wind 51 speeds all the year-round (Guo et al., 2016; Chen and Xie, 2013). It is supposed that tThe characteristics 52 of PM_{2.5} in Sichuan Basin are supposed toshould be very different from those in eastern coastal China 53

(i.e. PRD and YRD) and North China Plain (i.e. BTH) due to its-the special topography and 54 meteorological conditions, besides emission sources, in the basin. More specificallyFurthermore, the 55 terrain inof the two megacities in the basin are is also distinct from each other significantly, i.e., 56 Chongqing is a mountainous citymunicipality lying on the eastern margin of the basin while Chengdu is 57 located in a completely a flat city on the western margin of the basin. Therefore, there is a great interest 58 59 in comparing the chemical components of PM_{2.5} and characterizing pollution episodes between in 60 Chengdu and Chongqingthe two cities. The present study aims to fill this gap by measuring chemically-resolved PM_{2.5} in Chengdu and 61 Chongqing in four consecutive seasons during 2014-2015. The main objectives are to: (1) characterize 62 the seasonal and site differences of PM_{2.5} mass and its major chemical components at between the two-63 urban sites in Sichuan Basinin urban environemntss of Chengdu and urban-Chongqing; (2) compare the 64 PM_{2.5} chemical components compositions under different PM_{2.5} pollution levels and identify the major 65 chemical components that are responsible for long-lasting PM_{2.5} pollution episodes in winter; (3) 66 explore the possible formation mechanism of the secondary organic and inorganic aerosols; and (4) 67 reveal the geographical source regions causing contibuting to the high PM_{2.5} levels through potential 68 source contribution function (PSCF) analysis. The comparison of the differences of PM_{2.5} in this paper-69

provides insights regarding the extent to which fine particulatePM_{2.5} pollution can vary in terms of in-

chemical composition, formation mechanisims, and geographical origins between the two megacities in-

a great basin. This information has implications for better understanding the reasonsKnowledge gained

in this study provides scientific basis for making future emision control plocies aiming to allivating –

75 **2 Methodology**

for heavy haze PM_{2.5} pollution in this unique basin.

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76 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

samling site. The sampling site in Chongqing (CQ) is located on the rooftop of Chongqing Monitoring

83 Center (106°30' E, 29°37' N). The highway G50 is 250 m away from this sampling site. The two

84 selected sampling sites are considered to represent typical urban environment in their respective cities-

85 without the influence of local point sources from industry activities (Tao et al., 2014; Chen et al., 2017).

86 2.2 Sample collection

Daily (23-h) integrated PM_{2.5} samples were collected in four months, each in a different season: autumn 87 (23 October to 18 November, 2014), winter (6 January to 2 February, 2015), spring (2 to 29 April, 2015), 88 and summer (2 to 30 July, 2015). At both sites, PM_{2.5} samples were collected in parallel on Teflon filters 89 90 (Whatman Corp., 47 mm) and quartz filters (Whatman Corp., 47 mm) and used for different chemicalanalyses. At the CD site, PM_{2.5} sampling was carried out using an versatile air pollutant sampler (Wang 91 et al., 2017). One channel was used to load PM_{2.5} sample on Teflon filter for mass and trace elements 92 anlysis and the other one was equipped with quatz filter for water-soluble inorganic ions and 93 carbonaceous components analysis. The sampler was running at 15 L min⁻¹ for each channel. At the CQ 94 site, a low-volume aerosol sampler (BGI Corp., frmOmni, USA) operating at a flow rate of 5 L min⁻¹ 95 was used to collect PM_{2.5} samples on Teflon filter, and another sampler (Thermo Scientific Corp. 96 Partisol 2000i, USA) with a flow rate of 16.7 L min⁻¹ was used to collect PM_{2.5} samples on quartz filter. 97 A total of 112 samples and 8 field blanks, nearly equally distributed in the four seasons, were collected 98 at each site during the campaign. In addition, three lab blank filters in each campaign were stored in a 99 clean Petri slides in the dark and analysed in the same ways as the sampling filters collected samples to 100 evaluate the background contamination. 101

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.

108 **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 111 chromatograph (Dionex Corp., Dionex 600, USA). Anions were separated using AS11-HC column with 112 30 mM KOH as an eluent at a flow rate of 1.0 ml min⁻¹. Cations were determined using CS12A column 113 with 20 mM MSA (methanesulfonic acid) at a flow rate of 1.0 ml min⁻¹. Individual standard solutions of 114 all investigated anions and cations (1000 mg L^{-1} , o2si, USA) were diluted to construct the calibration 115 curves. The correlation coefficients of the linear regression of the standard curves were all above 0.999. 116 117 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 118 0.008-0.13 µg m⁻³. The relative standard deviation of each ion was better than 8% for the reproducibility 119 test. 120

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 <u>waswere</u> below 0.7 μ 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 131 EC9850 SO₂ analyzer, 9841 NO/NO₂/NO_x analyzer, 9830 CO analyzer, and 9810 O₃ analyzer (Ecotech 132 Corp., Australia) at the CD-site, and Thermo 42i NO/NO₂/NO_x analyzer, 43i SO₂ analyzer, 48i CO 133 analyzer, and 49i O₃ analyzer (Thermo Scientific Corp., USA) at the CQ-site. The mass concentration of 134 PM_{2.5} was automatically measured by online particulate monitor instruments (BAM1020, Met one 135 Corp., USA, at CD and 5030 SHARP, Thermo Scientific Corp, USA, at CQ). Hourly meteorological 136 137 parameters, including ambient temperature (T), relative humidity (RH), wind speed (WS) and direction, 138 barometric pressure (P), and solar radiation (SR), were obtained from an automatic weather station_ (Lufft Corp. WS501, Germany) at each site. Planetary boundary layer height (PBLH) was obtained 139 from HYSPLIT model (http://ready.arl.noaa.gov/HYSPLIT.php). 140

141 **2.4 Data analysis**

142 The EC-tracer method has been widely used to estimate SOC (Turpin and Lim, 2001;Castro et al.,

- 143 1999), which can be expressed as
- 144 POC= $(OC/EC)_{prim} \times EC$ (1)
- 145 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).

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

153
$$COD_{jk} = \sqrt{\frac{1}{p} \sum_{1}^{p} (\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}})^2}$$
 (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.

157 **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°40 km gridded meteorological data-(GDAS 40km) 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,

167 $PSCF_{ij} = \frac{m_{ij}}{n_{ij}}$ (4)

168 Where n_{ij} is the total number of endpoints falling in the grid cell (i,j) and m_{ij} denotes the number of

169 endpoints that are associated with samples exceeding the threshold criterion in the same cell. To reduce

170 the PSCF uncertainties associated with small n_{ij} values, weighting function was adopted as follows,

171
$$W_{ij} = \begin{cases} 1.0 & 3n_{ave} < n_{ij} \\ 0.7 & 1.5n_{ave} < n_{ij} \le 3n_{ave} \\ 0.42 & n_{ave} < n_{ij} \le 1.5n_{ave} \\ 0.2 & n_{ij} \le n_{ave} \end{cases}$$
(5)

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

The trajectories coupled with daily <u>pollutantsPM_{2.5}</u> 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.

177 **3 Results and discussion**

178 **3.1** Overview of PM_{2.5} mass concentrations and major components chemical composition

179 **<u>3.1.1 Overview</u>**

Table 1 presents seasonal and annual mean concentrations of PM2.5 and its major chemical components 180 at CD and CQ during the sampling periods. Daily $PM_{2.5}$ ranged from 11.6 to 224.7 µg m⁻³ with annual 181 average being 67.0 \pm 43.4 µg m⁻³ at CD site and 70.9 \pm 41.4 µg m⁻³ at CO site. The annual average 182 values, which were about two times of the NAAQS annual limit. Secondary inorganic aerosol (SNA, 183 the sum of SO_4^{2-} , NO_3^{-} and NH_4^{+}) and carbonaceous species together represented more than 70% of 184 $PM_{2.5}$ mass at both sites (Fig. 2). The annual mean concentrations of the total SNA were 27.6 μ g m⁻³ at 185 <u>CD</u> and 26.5 μ g m⁻³ at CD and CQ, respectively, contributing 41.1% and 37.4% of to PM_{2.5} mass, 186 respectively. Among these At CD, SO₄²⁻, NO₃⁻ and NH₄⁺ were 11.2, 9.1, and 7.2 µg m⁻³, respectively, 187 oraccounteding for 16.8%, 13.6% and 10.8%, respectively, of PM_{2.5} mass at CD, and 12.2, 7.7 and 6.6 188 µg m⁻³ or<u>while at CQ the corresponding percentages were</u>-17.2%, 10.9% and 9.2%, respectively, of-189 PM_{2.5}-mass at CQ. Organic matters (OM), estimated from OC by-using a conversion factor of 1.6 to 190 account for other elements presented in organic compounds (Turpin and Lim, 2001; Tao et al., 2017), 191 were the most abundant species in PM2.5, accounting for 26.1% and 29.6% of PM2.5 mass at CD and 192 CQ, respectively. In contrast, EC only comprised of around 6% at both sites. The annual mean 193 concentrations of OC and EC at CQ were 20% and 25%, respectively, higher at CQ than those at CD. 194

195 The annual mean concentration of Fine fine soil (FS), can be estimated calculated by summing the oxides of the major crustal elements mainly associated with soil, i.e., Al₂O₃, SiO₂, CaO, FeO, Fe₂O₃, 196 and TiO₂ (Huang et al., 2014), The annual mean concentration of FS at CQ was 6.7 µg m⁻³ (or 9.5% of 197 $PM_{2.5}$ mass) at CQ, which. It is noted that this was about two times of that at CD (3.8 µg m⁻³ or, 5.7% of 198 $PM_{2.5}$ mass). The minor components such as K⁺ and Cl⁻ constituted less than 5% of $PM_{2.5}$. The 199 200 unaccounted portions of PM_{2.5} reached 18.3% at CD and 15.3% at CQ, which wereas likely related to 201 the uncertainties in the multiplication factor used for estimatingon of OM and FS, other unidentified 202 species, and measurement uncertainties.

203 **3.1.2 Seasonal variations**

Figure 3 shows the seasonal variations of PM_{2.5} and its major chemical 204 components at CD and CQ-sites. Seasonal variations of any pollutants should be influenced by the 205 seasonal variations of n source emission intensities, atmospheric processes and meteorological 206 conditionsparameters. Unlike in northern China, Tthere wereas no significant extensive coal combustion 207 or wood burning utilization for domestic heating in winter due to the warmhigher temperature (around 208 209 10°C on average) in Sichuan Basin, hence atmospheric processes and meteorological conditions played 210 a vital role in the seasonal variations of PM_{2.5}. On a Seasonal basis, average PM_{2.5} mass was the 211 highest in winter at both sites CD and CQ, which was 1.8-2.5 times of those in the other seasons. In 212 contrast, Sits seasonal differences among the other three seasons were generally small, i.e.g., less than <u>40%.</u> Besides the high emissions of SO_2 and NO_* in winter, stagnant Stagnant air condition with 213 frequent calm winds and low boundary planetary boundary layer height layer height was the another 214 major cause of the highest PM_{2.5} mass in this seasonwinter (Table 1) (Liao et al., 2017; Chen and Xie, 215 216 2013). Seasonal differences among the other three seasons were generally small, e.g., less than 40%. All the major PM_{2.5} components but except FS followed the seasonal pattern of PM_{2.5} mass with-217 the highest concentrations in winter, but with subtle differences. The highest FS concentrations were 218 219 observed in spring at both sites. The relatively higher wind speeds and lower RH in spring were 220 conducive for re-suspension of crustal dust and resulted in higher FS concentrations. In addition, thefrequent spring dust storms originated in the northwestern China was able to reach Sichuan Basin via 221 long-rang transport, and would cause the elevated FS concentrations (Chen et al., 2015;Tao et al., 2013). 222 The majority of the PM_{2.5} components showed a summer minimum, but not SO_4^2 . The minimum-223 224 of OC at CD and FS at CQ appeared in spring and autumn, respectively. The which was caused by high

225 <u>temperature and planetary boundary layer height favoringed the pollutants dispersion in summer. In-</u>

226 addition, and abundant precipitation favoring wet scavengingin summer could scavenge the air

227 pollutants through wet deposition and in turn decreased the pollutant levels in the air. HigherIn contrast,

228 the lowest seasonal average concentrations did not appear in summer for SO_4^{2-} concentrations in-

summer were-likely due to the enhanced photochemical reactions associated with higher temperature
 and stronger solar radiation in summer. High O₃ concentrations in summer also supported this seasonal
 trend.

It is also noted that the seasonal variations inof NO_3^- were much larger than those in of $SO_4^{2^-}$ and NH₄⁺, which. This can be explained by the enhanced formation of NO₃⁻ under high <u>RH</u>relativehumidity in winter, and volatility of NH₄NO₃ in summer <u>under high temperature condition</u> (Pathak et al., 2009;Quan et al., 2015;Squizzato et al., 2013). In addition, thermodynamically driven behavior of NH₄NO₃ was another factor for the lower NO₃⁻ concentrations in summer (Wang et al., 2016;Kuprov et al., 2014). High levels of CI⁻ and K⁺ in winter and of FS in spring should be caused by biomass burningor spring dust storms (Tao et al. 2013, 2014).

239 Both OC and EC showed exhibited the highest concentrations in winter at CD and CQ, whereas seasonal differences of those carbonaceous components were less distinct in other seasons, e.g. the 240 241 variations of OC and EC among the other three seasons were less than 30%. Seasonal average SOC was unexpectedly the highest in winter at both sites, different from the anticipated high value in summer in 242 243 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 244 temperature favors condensation process (Sahu et al., 2011;Cesari et al., 2016). Although high O₃ and 245 strong solar radiation condition in summer was conducive to strong photochemical reactions, high 246 247 temperature favoreds gas-particle partitioning in the gaseous phase and thus limited the increase of SOC (Strader et al., 1999). 248

The sS easonal average relative contributions of major chemical components to $PM_{2.5}$ are showndepicted 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 $NO_3^$ 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 $PM_{2.5}$ 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.

261 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 <u>isare</u> shown in Fig. 4 and <u>discussed in detail below</u>.

Despite the 260 km distance between the two sampling sites, a moderate similarity was observed in 268 autumn, winter and spring on the basis of low COD values (0.15-0.18), indicating the regional-scale 269 270 PM_{2.5} pollution pattern in Sichuan Basin and the similaritiesy in major emission sources for both sites. 271 The regional pollution was related to the special topography of the basin, which is a closed lowland 272 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 273 close to the western Sichuan Basin, with an elevation above 4000 m. Those uniqueSuch a Plateau-Basin 274 topography feature often forms a barrier for the dispersion of pollutants and causes air stagnation within 275 the basin, thereby obviously facilitating a regional scale pollution events in the Sichuan Basin. 276

277 72-h air masses back trajectories analysis (18:00 local time) showed that air masses reaching at CD 278 and CQ mainly originated from the local areas in the basin (Fig. S1), confirming the influence of the 279 high mountainous surroundingaround the basin and the possibility of forming regional pollution. 280 TheseOur results were consistent with those foundconducted in earlier studiesby in Chengdu and Chongqing (Tian et al., 2017; Liao et al., 2017) in Chengdu and Chongqing, which suggested that air 281 282 masses had short-range trajectoriesy 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 283 found elsewhere, such as The regional pollution of PM_{2.5} were also observed in Po Valley, Italy 284

285	described by (Ricciardelli et al., 2017). The topography of Po Valley is bordered by the Alps in the north
286	and Apennines to north and in the south, which caused a strong homogeneity in is similar to the Sichuan
287	Basin. It indicated that the major components of PM2.5 pollution in Po Valley showed a strong
288	homogeneity at the regional sacle level.
289	It is worth to note that the COD values used to identify the similarities or differences of two sites
290	were calculated based on seasonal-average concentrations of all componentssitions in PM _{2.5} . However,
291	if focusing on individual componentssitions, several components chemical species compositions in
292	<u>PM_{2.5}</u> differed by up to a factor of 2.5 in their season-average concentrations between at CD and CQ,
293	e.g. OC and EC in winter and spring, and Cl ⁻ and FS in all the four seasons. <u>In summer, the differences</u>
294	for several major chemical components (FS, OC, SO_4^{2-} , NO_3^{-} , EC) between the two sites were larger
295	than in other seasons, causing a high COD value (0.33). These discrepancies were partly caused by the
296	different atmospheric chemical processes and, local sources and meteorological parameters between the
297	two sites.
298	Specifically, FS mostly deviated from the 1:1 straight line in all seasons, with substantially higher
299	concentrations at CQ than CD (Fig. 4). The mainly cause of this difference iwas the higher wind speeds
300	and lower RH at CQ than compared with CD. There was no significant difference in for NH_4^{\pm}
301	concentrations between at CD and CQ, but considerable differences in SO_4^{2-} and NO_3^{-} in spring and
302	summer. SO ₂ concentration was around 25% higher at CQ than CD in spring and summer, which
303	partially explained the site-differences in SO_4^2 . <u>In contrast, NO₂ concentrations wasere comparable at</u>
304	both sites in summer, but NO3 ⁼ concentration was 58% lower in CQ than CD. The site-differences in
305	<u>NO₃⁻ concentration was caused by NH₄NO₃ thermodynamic equilibrium controlled by ambient</u>
306	temperature and RH, instead of by its gaseous precursors. Another consideration is the thermodynamic-
307	equilibrium between particulate $NH_{4}NO_{3}$ and gaseous HNO ₃ , which depends on temperature and RH.
308	Kuprov et al. (2014) (Kuprov et al., 2014) found that tThe equilibrium would be shifted toward the
309	<u>particulate phase when ambient RH was above the deliquescence relative humidity (DRH) of NH_4NO_3.</u>
310	and the dissociation constant decreased byto about onean order of magnitude when RH was above 75%
311	(Kuprov et al., 2014) As shown in Fig. S4, on polluted days, RH was lower than DRH most of the
312	time in the warm season at CQwas_estimated from ambient RH following .Mozurkewich (1993), which
313	explains the lower NO3 ² concentrations. In contrast, RH was above the DRH most of the time at CD.
314	<u>Thus, despite similar concentrations of SO₄² and NH₄[±] between CD and CQ in summer, NO₃ was 50%</u>

315	lower at CQ than that at CD due to the lower ambient RH at CQ. DRH was calculated from ambient
316	RH following Mozurkewich (1993). As shown in Table 1, the average temperature was comparable at
317	CD and CQ during the summer period, hence leading to similar DRH values of NH ₄ NO ₃ , ranging from
318	59% to 64% with an average value of 60.7%. However, the ambient RH was substantially lower at CQ
319	(61%) than CD (72%), causing lower NO ₃ ⁻ concentrations at CQ. As shown in Fig. S2, 53% of the
320	hourly data in summer having ambient RH lower than DRH at CQ, while only 19% such data at CD,
321	which explained the different NO_3^{-1} concentrations between CD and CQ.
322	Fig.4 shows higher concentrations of carbonaceous component (OC and EC) at CQ than CD in all
323	seasons except OC in autumn and EC in winter. OC and EC mainly originate from fossil fuel
324	combustion and biomass burning. K^{\pm} is usually regarded as a tracer of biomass burning (Tao et al.,
325	2016). During the sampling campaign, no significant differences in K^{\pm} levels were observed between at
326	CD and CQ (Table 1), suggesting that biomass burning was not be the major cause of the higher
327	concentrations of carbonaceous component at CQ. Motorcycle traffic was likely a major source of
328	volatile organic compounds (VOCs) in CQ since it is a famous mountain city where most people use
329	motorcycle as daily traffic tools. According to the Chongqing Statistical Yearbook 2015, the number of
330	motorcycles was 2.0 million (among the total of 2.3 million motor vehicles) in 2014, which was much
331	higher than those (0.7 million) in Chengdu (Chengdu Statistical Yearbook 2015). Moreover, Chongqing
332	has become China's largest automobile production base, which likely also emit VOCs from the spraying
333	process. Higher concentrations of VOCs in CQ would cause higher concentrations of secondary organic
334	carbon via photochemical reaction under high temperature or vapor condensation under low
335	temperature. This hypothesis is supported by the large differences in OC concentrations in winter
336	<u>between the two sites.</u> summer, the differences for several major chemical components (FS, OC, SO_4^2 ,
337	NO_3^{-} , EC) between the two sites were larger than in other seasons, causing the high COD value (0.33)
338	in this season.
339	Correlation analysis may also provide an insight into the similarities/differences between the two
340	sites over an intensive sampling period. Good correlations between the two sites were found for daily
2/11	SNA OC EC and K^+ concentrations in autumn winter and spring (Table 2). However, for NO ₂ ⁻ a

SNA, OC, EC and K⁺ concentrations in autumn, winter and spring (Table 2). 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. Therefore, there existed a fairly uniform

346 distribution of most major components in PM_{2.5} throughout the basin in all the seasons except summer.

- 347 <u>3.2 PM_{2.5} formation mechanisms and geographical origins</u>
- 348 **3.2.1** Pollution episodes and key chemical components
- 349 <u>Pollution episodes during the campaign are highlighted with shaded areas in Fig. 5. Theose pollution</u>
- 350 <u>periods (PP) were defined as daily PM_{2.5} concentration being above the NAAQS guideline value of 75</u>
- 351 $\mu g m^{-3}$. Similarly, the days with PM_{2.5} concentration below 75 $\mu g m^{-3}$ were characterized to be clean
- 352 periods (CP). A total of seven pollution episodes were identified during the campaign at each site. There
- 353 were three long-lasting pollution episodes occurred simultaneously at the two sites on 23-27 October
- 354 <u>2014, 7(8)-26 January, and 26-28 (29) April 2015.</u>, A total of <u>34 and 31 polluted days were counted at</u>
- 355 <u>CD and CQ site, respectively, accounting for 30.4% and 28.6% of the entire sampling days (112 days).</u>
- 356 The number of polluted days at CD was 8, 21, 4 and 1 in autumn, winter, spring and summer,
- 357 accounting for 29.6%, 75%, 14.3% and 3.4% of the total sampling days in each season, respectively,
- 358 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 359 events, as was found in this and earlier studies. (Zheng et al., 2015b; Chen et al., 2017; Liao et al., 2017). 360 Compared with the clean periods, the pollutioned periods were usually characterized by low planetary 361 362 boundary layer height and weak wind speed (Table S1), which suppress pollutants dispersion vertically and horizontally. Temperature increased during the long-lasting pollution episodes, which promoted 363 gas-to-particle transformation, forming secondary aerosols. RH remained high (68-88%) during 364 pollution episodes (except in spring at CQ), although not much different from clean periods, which was 365 also conducive for aqueous-phase reactions converting gaseous pollutants into aerosols (Chen et al., 366
- 367 2017;Tian et al., 2017)<u>.</u>
- 368 To explore the major chemical pollutants responsible for polluted days, daily PM_{2.5} data were-
- 369 categorized into two groups, i.e. clean days and polluted days based on PM_{2.5} concentrations below and
- 370 above the NAAQS guideline value of 75 μ g m⁻³, respectively. 34 and 31 polluted days were counted at-
- 371 CD and CQ site, respectively, accounting for 30.4% and 28.6% of the entire sampling days. The number
- 372 of polluted days at CD was 8, 21, 4 and 1 in autumn, winter, spring and summer, accounting for 29.6%,
- 373 75%, 14.3% and 3.4% of the total sampling days in each season, respectively, and at CQ they were 4, 19,
- 374 6 and 2, accounting for 14.8%, 67.9%, 21.4% and 6.9%. Note that these numbers were only from-

one-month (around 28 days) sampling in each season. Considering the similar meteorological conditions and pollution levels during autumn and spring, these two seasons were combined together and was referred to as the warm season, while winter was referred to as the cold season. Because of the
 very small number of polluted days in summer at both sites, the PM_{2.5} data in this season were not discussed.

380 Looking more closely at a regional-scale long-lasting pollution episode in winter at CD and CQ, 381 from 8 January to 26 January 2015, the concentrations of PM_{2.5} and major chemical componentssitions increased dramatically on during polluted days periods compared to with clean days periods (Fig. 56).-382 For example, PM_{2.5} concentrations were more than doubled three times higher <u>on polluted days</u> 383 periods during the entire sampling periods at both sites,. The with the two dominant groups of 384 385 components-in PM2.5, SNA and OC, werebeing 2.5-2.8 times higher on during polluted days periods inboth cold and warm seasons at CD and 1.7-2.7 times higher at CQ. . However, larger variations were 386 found at CQ with SNA and OC increased by 2.7 and 1.7 times, and OM by 3.4 and 2.1 times in the cold-387 388 and warm season, respectively. Thus, while tThe enhancement of SNA and OC on-during pollutioned 389 days periods were similar at CD, but OC increased much more than SNA at CQ, indicating some different contributing factors to the high PM_{2.5} pollution at the two sites. Pollutants accumulation under 390 stagnant meteorological conditions might be a main factor at CD based on the similar magnitudes of the 391 enhancements of PM_{2.5} and its dominant components, while additional processes should have increased 392 393 OC more than other components at CQ.

In the cold season, the <u>The</u> percentage contributions of SNA to PM_{2.5} were similar <u>on-during</u> clean
 and polluted <u>daysperiods</u>, 38-41% at <u>both sitesCD and CQ</u> (Fig. <u>S1S3</u>). However, the percentage
 contribution of OM to PM_{2.5} decreased from 30.1% on clean days to 27.5% on polluted days at CD, and

397 increased from 26.9% to 34.9% at CQ. A different pattern was seen in the warm season, with no-

398 significant variations of OM fractions in $PM_{2.5}$ between the clean and polluted days at either site, but an

399 increased SNA contribution by around 7% at CD and decreased contribution by 14% at CQ.

400 <u>Concentrations of the individual SNA species (SO₄^{$\frac{2}{2}$}, NO₃^{$\frac{1}{2}$} and NH₄^{$\frac{1}{2}$}) increased by a factor of</u>

401 $\frac{1.22.5-3.3 \text{ on polluted days compared towith clean days in all the cases (Fig. 56). But the percentage}{\frac{1.22.5}{1.2}}$

402 <u>contributions differed among the species as NO_3^{\pm} increased and SO_4^{\pm} decreased on polluted days.</u> The

403 percentage contributions of SNA and OM to $PM_{2.5}$ discussed above were different from those found in

404 eastern coastal China and North China Plain, where considerable increases were found for SNA and

- decreases for OM on polluted days than clean days (Tan et al., 2009;Wang et al., 2015a;Quan et al.,
- 406 2014;Zhang et al., 2015;Zhang et al., 2016;Cheng et al., 2015). The polluted periods in eastern coastal
- 407 <u>China and North China Plain were accompanied with sharp increases of RH, which would promote</u>
- 408 aqueous-phase formation of secondary inorganic aerosols and resulted in rapid elevation of SO_4^{2-} and
- 409 $\underline{NO_3}^{=}$ concentrations (Zheng et al., 2015b;Zheng et al., 2015a;Zhao et al., 2013b;Li et al., 2017). In
- 410 <u>contrast, RH remained high during clean or polluted periods in the present study, suggesting that high</u>
- 411 <u>RH might not be the driving force for the pollution episodes in Sichuan Basin. Another point that need</u>
- 412 <u>to be mentioned is that, local sources were the main contributors to the pollution episodes in Sichuan</u>
- 413 <u>basin while sources outside local regions frequently contributed to pollution episodes in eastern coastal</u>
- 414 China and North China Plain through long/medium range transport (Gao et al., 2015;Hua et al.,
- 415 2015; Wang et al., 2015b). This emphasized again the unique characteristics of PM_{2.5} pollution in-
- 416 Sichuan Basin due to its particular topography and meteorological conditions.
- 417 Concentrations of the individual SNA species (SO_4^2 , NO_3 and NH_4^+) increased by a factor of
- 418 1.2-3.3 on polluted days compared to clean days in all the cases (Fig. 5). But the percentage-
- 419 contributions differed among the species as NO_3^{-} increased and $SO_4^{-2^{-}}$ decreased on polluted days. The
- 420 concentration of FS increased slightly at CD (less than $3 \mu \text{g m}^{-3}$) but significantly (from 5.4 on clean-
- 421 days to 14.7 μg m⁻³ on polluted days) at CQ in warm season. The percentage contribution of FS to-
- 422 PM_{2.5}-reached 15.3% on polluted days at CQ in warm season.

423 **3.2.2 Transformation mechanisms of secondary aerosols**

- 424 In most cases, Mmeteorological conditions, atmospheric chemical processes and long-range transport are all responsible for PM_{2.5} accumulation on polluted days (Zheng et al., 2015b). CO and EC are 425 426 directly emitted from combustion processes and are not very reactive, thus, their concentrations in the 427 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 428 accumulation (Zheng et al., 2015b;Zhang et al., 2015). In the present study, CO was chosen as a 429 reference pollutant species for investigating other pollutants of interest. CO concentration increased by 430 a factor of 1.8 at CD and 1.5 at CQ during polluted periods than clean periods. In comparison, other 431 chemical species (except NO₂) increased by a factor of 1.8-3.3. A similar contrast between CO and 432 other pollutants was also seen in (Li et al., 2017). Similar diurnal variations were also found between 433
- 434 <u>clean and polluted periods for CO (Fig. S4), suggesting no significant extra CO emission during</u>

435 polluted periods. Thus, the increased concentrations of CO during polluted periods were primarily driven by meteorological conditions. Both CO and EC concentrations increased on polluted days (Fig. 5-436 and Fig. S2), suggesting the important role the meteorological condition played on PM_{2.5} accumulation. 437 As expected, very weak winds (less than 0.7 m s⁻¹) were observed on polluted days, which hindered the 438 pollutants horizontal transport. CO can be considered as a reference pollutant species whose temporal-439 440 variations were mainly from the impact of meteorological conditions. Therefore, The the impact of 441 atmospheric physical processes other factors on other pollutants can thus be explored reduced by scaling the concentrations of other pollutants to that of CO, meanings that the impact of chemical reactions can 442 then be captured based on the ratio of other pollutants to CO concentrations. For example, PM_{2.5} was 443 enhanced by a factor of 2.0-2.7 on polluted days than clean days in the two seasons and at the twoboth 444 sites, but the CO-scaled PM_{2.5} (the ratio of PM_{2.5} to CO concentration) only showed an enhancement of 445 a factor of 1.56-1.8 (Fig. 67), and the latter values were likely from the enhanced secondary aerosol 446 formation. 447

448 As shown in Fig. 67, the CO-scaled SNA was 60-90% higher on polluted days with individual 449 species 40-120% higher (except in the warm season at CQ), even though their gaseous precursor (SO₂) and NO₂, no data for NH₃) were only less than 30% higher. This suggests stronger chemical 450 transformation from gaseous precursors to particle formation on polluted days. Sulfur oxidation ratio 451 $(SOR = n-SO_4^{2-}/(n-SO_4^{2-}+n-SO_2))$ and nitrogen oxidation ratio $(NOR = n-NO_3^{-}/(n-NO_3^{-}+n-NO_2))$ were 452 453 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 454 0.14 at CQ. SOR increased only slightly, from 0.31 to 0.35 at CD and 0.28 to 0.35 at CQ. In the warm-455 456 season, NOR and SOR exhibited a similar pattern as those in the cold season with the exception of NOR 457 at CQ, which might be related to the high temperature in the warm season. The CO-scaled SOC 458 increased by a factor of 2.6 and 1.5 on polluted days in the cold and warm season at CQ, but no significant change or decrease was found at CD. Moreover, increased SOC/OC only occurred at CQ in-459 the cold season (Fig. 67). The different patterns in SOC (or SOC/OC) than SNA (or SOR and NOR) 460 461 suggests that secondary organic aerosols (SOA) production iwas of less important than SNA production 462 in most occasions except in the cold season at CQCD.

463 $\underline{SO_4}^{2-}$ is predominantly formed via homogeneous gas-phase oxidation. In this pathway, $\underline{SO_2}$ is 464 <u>firstly oxidized by OH radical to SO_3</u>, and then to H₂SO₄ (Stockwell and Calvert, 1983;Blitz et al.,

465	2003). Apart from homogeneous reaction, particulate $SO_4^{\frac{2}{2}}$ can also be formed through heterogeneous
466	reactions with dissolved O_3 or H_2O_2 under the catalysis of transition metal and in-cloud process
467	(Ianniello et al., 2011). HNO ₃ is primarily produced from the reactions between NO ₂ and OH radical
468	during the daytime and later combines with NH ₃ to produce particulate NO ₃ ² (Calvert and Stockwell,
469	<u>1983). Particulate NO_3^2 can also be formed through heterogeneous hydrolysis of N_2O_5 on moist and</u>
470	acidic aerosols during nighttime (Ravishankara, 1997;Brown and Stutz, 2012). SO4 ²⁻ and NO3 ⁻ -
471	(Stockwell and Calvert, 1983; Blitz et al., 2003; Calvert and Stockwell, 1983), heterogeneous reactions-
472	might also be important formation mechanisms for these SNA species (Quan et al., 2015; Zheng et al.,
473	2015a; Zhao et al., 2013b). Similarly, SOA is mainly formed through photochemical oxidation of
474	primary VOCs followed by condensation of SVOC onto particles as well as through aqueous-phase
475	reactions (Ervens et al., 2011). While photochemical reactions are mostly influenced by temperature
476	and oxidants amount, heterogeneous reactions always depends on RH. To further explore the formation
477	mechanisms of secondary aerosols, -SOR, NOR and SOC/OC data were grouped with temperature (at
478	2°C interval), RH (at 5% interval) and daytime O ₃ concentration (at 5 μg m ⁻³ interval) bins (Fig. 8). An
479	obvious increase of SOR with increasing RH was found at both sites, but this was no the case for
480	temperature and O ₃ concentration, suggesting heterogeneous processes played an-important roles in the
480 481	<u>temperature and O₃ concentration, suggesting heterogeneous processes played an important roles in the</u> <u>formation of SO₄²⁻. Interestingly, SOR exhibited a decreasinged trend with increasing O₃ concentration</u>
480 481 482	temperature and O_3 concentration, suggesting heterogeneous processes played an-important roles in the formation of $SO_4^{2^-}$. Interestingly, SOR exhibited a decreasinged trend with increasing O_3 concentration at O_3 concentrations lower than 15 µg m ⁻³ and an opposite trend was found at O_3 concentrations above
480 481 482 483	temperature and O_3 concentration, suggesting heterogeneous processes played an-important roles in the formation of $SO_4^{2^-}$. Interestingly, SOR exhibited a decreasinged trend with increasing O_3 concentration at O_3 concentrations lower than 15 µg m ⁻³ and an opposite trend was found at O_3 concentrations above $20 \mu g m^{-3}$ (Fig. 8). Additionally, high PM _{2.5} concentrations were mostly associated with lower O_3 .
480 481 482 483 484	temperature and O ₃ concentration, suggesting heterogeneous processes played an -important roles in the formation of SO ₄ ²⁻ . Interestingly, SOR exhibited a decreasing ed trend with increasing O ₃ concentration at O ₃ concentrations lower than 15 μg m ⁻³ and an opposite trend was found at O ₃ concentrations above 20 μg m ⁻³ (Fig. 8). Additionally, high PM _{2.5} concentrations were mostly associated with lower O ₃ concentrations. Aerosols are generally considered as a constraining factor to O ₃ production due to their.
480 481 482 483 484 485	temperature and O ₃ concentration, suggesting heterogeneous processes played an -important roles in the formation of SO ₄ ²⁻ . Interestingly, SOR exhibited a decreasing ed trend with increasing O ₃ concentration at O ₃ concentrations lower than 15 μg m ⁻³ and an opposite trend was found at O ₃ concentrations above 20 μg m ⁻³ (Fig. 8). Additionally, high PM _{2.5} concentrations were mostly associated with lower O ₃ concentrations. 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
480 481 482 483 484 485 486	temperature and O ₃ concentration, suggesting heterogeneous processes played an -important roles in the formation of SO ₄ ²⁻ . Interestingly, SOR exhibited a decreasing ed trend with increasing O ₃ concentration at O ₃ concentrations lower than 15 μg m ⁻³ and an opposite trend was found at O ₃ concentrations above 20 μg m ⁻³ (Fig. 8). Additionally, high PM _{2.5} concentrations were mostly associated with lower O ₃ concentrations. 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. Apparently, other factors could become dominant in O ₃ production and alter
480 481 482 483 484 485 485 486	temperature and O_3 concentration, suggesting heterogeneous processes played an-important roles in the formation of $SO_4^{2^2}$. Interestingly, SOR exhibited a decreasinged trend with increasing O_3 concentration at O_3 concentrations lower than 15 µg m ⁻³ and an opposite trend was found at O_3 concentrations above $20 µg m^{-3}$ (Fig. 8). Additionally, high PM _{2.5} concentrations were mostly associated with lower O_3 concentrations. 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. Apparently, other factors could become dominant in O_3 production and alter such a trend. Low O_3 concentrations were further found to be associated with high RH (Fig. S5),
480 481 482 483 484 485 485 486 487 488	temperature and O_3 concentration, suggesting heterogeneous processes played an-important roles in theformation of $SO_4^{2^{2}}$. Interestingly, SOR exhibited a decreasinged trend with increasing O_3 concentrationat O_3 concentrations lower than 15 µg m ⁻³ and an opposite trend was found at O_3 concentrations above20 µg m ⁻³ (Fig. 8). Additionally, high PM _{2.5} concentrations were mostly associated with lower O_3 .concentrations. Aerosols are generally considered as a constraining factor to O_3 production due to theirabsorption and scattering of UV radiation, which reduce solar radiation and consequently decreasephotochemical activity. Apparently, other factors could become dominant in O_3 production and altersuch a trend. Low O_3 concentrations were further found to be associated with high RH (Fig. S5),indicating that the formation of $SO_4^{2^{2}}$ during the polluted periods was dominated by heterogeneous
480 481 482 483 484 485 485 486 487 488 489	temperature and O_3 concentration, suggesting heterogeneous processes played an-important roles in theformation of $SO_4^{2^2}$. Interestingly, SOR exhibited a decreasinged trend with increasing O_3 concentrationat O_3 concentrations lower than 15 µg m ⁻³ and an opposite trend was found at O_3 concentrations above $20 µg m^{-3}$ (Fig. 8). Additionally, high PM _{2.5} concentrations were mostly associated with lower O_3 .concentrations. Aerosols are generally considered as a constraining factor to O_3 production due to theirabsorption and scattering of UV radiation, which reduce solar radiation and consequently decreasephotochemical activity. Apparently, other factors could become dominant in O_3 production and altersuch a trend. Low O_3 concentrations were further found to be associated with high RH (Fig. S5),indicating that the formation of $SO_4^{2^2}$ during the polluted periods was dominated by heterogeneousaqueous processes rather than photochemical reactions at both sites, as suggested in many previous.
480 481 482 483 484 485 486 487 488 489 490	temperature and O_3 concentration, suggesting heterogeneous processes played an-important roles in the formation of $SO_4^{2^2}$. Interestingly, SOR exhibited a decreasinged trend with increasing O_3 concentration at O_3 concentrations lower than 15 µg m ⁻³ and an opposite trend was found at O_3 concentrations above $20 µg m^{-3}$ (Fig. 8). Additionally, high PM _{2.5} concentrations were mostly associated with lower O_3 . concentrations. 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. Apparently, other factors could become dominant in O_3 production and alter such a trend. Low O_3 concentrations were further found to be associated with high RH (Fig. S5), indicating that the formation of $SO_4^{2^2}$ 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)
480 481 482 483 484 485 485 486 487 488 489 490 491	temperature and O_3 concentration, suggesting heterogeneous processes played an-important roles in the formation of $SO_4^{2^2}$. Interestingly, SOR exhibited a decreasinged trend with increasing O_3 concentration at O_3 concentrations lower than 15 µg m ⁻³ and an opposite trend was found at O_3 concentrations above $20 µg m^{-3}$ (Fig. 8). Additionally, high PM _{2.5} concentrations were mostly associated with lower O_3 concentrations. 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. Apparently, other factors could become dominant in O_3 production and alter such a trend. Low O_3 concentrations were further found to be associated with high RH (Fig. S5), indicating that the formation of $SO_4^{2^2}$ 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)
480 481 482 483 484 485 485 486 487 488 489 490 491 492	temperature and O_3 concentration, suggesting heterogeneous processes played an-important roles in the formation of $SO_4^{2^2}$. Interestingly, SOR exhibited a decreasinged trend with increasing O_3 concentration. at O_3 concentrations lower than 15 µg m ⁻³ and an opposite trend was found at O_3 concentrations above $20 µg m^{-3}$ (Fig. 8). Additionally, high $PM_{2.5}$ concentrations were mostly associated with lower O_3 concentrations. Acrosols 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. Apparently, other factors could become dominant in O_3 production and alter such a trend. Low O_3 concentrations were further found to be associated with high RH (Fig. S5), indicating that the formation of $SO_4^{2^2}$ 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) Unlike SOR, NOR increased with both temperature and RH, suggesting combined the effects from homogeneous and heterogeneous reactions. However, under the very high temperature and RH.
480 481 482 483 484 485 486 487 488 489 490 491 491 492 493	temperature and O_3 concentration, suggesting heterogeneous processes played an-important roles in the. formation of $SO_4^{2^2}$. Interestingly, SOR exhibited a decreasinged trend with increasing O_3 concentration. at O_3 concentrations lower than 15 µg m ²³ and an opposite trend was found at O_3 concentrations above. 20 µg m ²³ (Fig. 8). Additionally, high PM _{2.5} concentrations were mostly associated with lower O_3 . concentrations. 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. Apparently, other factors could become dominant in O_3 production and alter. such a trend. Low O_3 concentrations were further found to be associated with high RH (Fig. S5), indicating that the formation of $SO_4^{2^2}$ 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) Unlike SOR, NOR increased with both temperature and RH, suggesting combined the 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

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

496	(Pathak et al., 2004, 2009) investigated the formation mechanism of NO ₃ ⁻ in ammonium-rich and
497	ammonium-poor samples, suggesting homogeneous gas-phase reaction became evident to form NO3 ²
498	under the former conditions while heterogeneous process dominated the NO_3^{-1} formation under the latter
499	conditions. As shown in Fig. 9, SO_4^{2-} and NO_3^{-} were almost completely neutralized by NH_4^{\pm} , indicating
500	an ammonium-rich environment during the sampling campaign. The ammonium-rich environment was
501	also confirmed by the molar ratios of $[NO_3^-]/[SO_4^-]$ and $[NH_4^+]/[SO_4^-]$. The molar ratio $[NO_3^-]/[SO_4^-]$
502	as a function of $[NH_4^{\pm}]/[SO_4^{2-}]$ is depicted in Fig. 09, which shows significant positive correlations
503	<u>(R²=0.82-0.83 at the two sites)</u> . Linear regression equations were obtained as $[NO_3^-]/[SO_4^{2-}] =$
504	$\underline{0.85[NH_4^{\pm}]/[SO_4^{2\pm}]-1.89 \text{ at CD and } [NO_3^{\pm}]/[SO_4^{2\pm}] = 0.92[NH_4^{\pm}]/[SO_4^{2\pm}]-1.82 \text{ at CQ}_{\overline{5}}. \text{ Based on these}$
505	equations, the molar ratio of $[NH_4^{\pm}]/[SO_4^{2-}]$ was defined as the threshold value separating
506	ammonium-rich and ammonium-poor conditions when the value of $[NO_3^-]/[SO_4^{2-}]$ was zero. In the
507	present study, the threshold value was 2.2 and 2.0 at CD and CQ, respectively. The molar ratio
508	$[NH_4^{\pm}]/[SO_4^{2-}]$ was higher than the threshold value at both sites, suggesting the prevalence of
509	ammonium-rich condition. The near-perfect fitting between the molar ratio $[NO_3^-]/[SO_4^{2-}]$ and
510	$[NH_4^{\pm}]/[SO_4^{2^-}]$ further demonstrated the characteristics of NO ₃ ⁻ formed through homogenous gas-phase
511	reaction. Moreover, NO_3^{\pm} showed a strong correlation with excess NH_4^{\pm} with correlation coefficients of
512	0.98-0.99 at both sites, providing an insight into the gas-phase reactions of ambient NH ₃ and HNO ₃ .
513	Using high-resolution inorganic ions data, (Tian et al., 2017) demonstrated that NO ₃ ⁻ was primarily
514	formed via homogeneous reaction when RH below 75% and through heterogeneous processes when RH
515	was above 75%. The increases in NOR with RH at both sites also revealed the possibility of the
516	heterogeneous processes, although this cannot be verified directly due to the lack of high-resolution
517	data.
518	The ratio of SOC/OC decreased with temperature at CD but increased with temperature at CQ
519	when T was lower than 10°C. Although SOC/OC did not correlate well with RH, an opposite trend was
520	also found between CD and CQ at high RH conditions. Heterogeneous reactions seemed to be dominant
521	in the formation of SOA at CD, whereas homogeneous reactions were prevalent at CQ. SOC/OC
522	showed no apparent dependency on O_3 concentrations at either site, indicating more complex formation
523	mechanisms of SOA than SO_4^{2-} and NO_3^{-} , were further based on the diurnal variations of their gaseous-
524	precursors and the relevant meteorological parameters. Considering the different characteristics of

PM_{2.5} pollution, the polluted days were further divided into moderate polluted days ($75 < PM_{2.5} \le 150$) 525 μ g m⁻³) and heavy polluted days (PM_{2.5}>150 μ g m⁻³). Figure 7 and Fig. S2 describe the diurnal-526 variations of T, RH, WS, SR, NO, CO, SO₂, NO₂ and O₃ concentrations in the cold season at CD and 527 CQ. Most gaseous species except O₃ showed relatively higher concentrations on polluted days, but 528 exhibited different diurnal patterns under different pollution levels. For example, NO and CO both-529 reached their peak values at around 10:00 am, consistent with the morning traffic rush hours (Fig. S2). 530 531 For SO₂ and NO₂, similar diurnal variations were seen on clean and moderate polluted days, but a different one on heavy polluted days, with the latter having long-lasting (from 12:00 to 18:00 pm) high-532 533 concentrations likely caused by transport as supported by stronger afternoon winds on these days (Fig. 7). O₃ showed a typical diurnal variation with a peak value at around 16:00 pm. Daytime (11:00-20:00-534 535 LT) O₃ was much higher on moderate polluted days, but slightly lower on heavy polluted days-536 compared to those on clean days. Aerosols were generally considered as a constrain factor to O₃production due to their absorbing or scattering the UV radiation, which would reduce solar radiation-537 538 and consequently decrease the photochemical activity and O₃ levels (Zhang et al., 2015b; Zheng et al., 539 2015b; Tian et al., 2016). The O₃ data on heavy polluted days seemed to support this hypothesis, but 540 not those on moderate polluted days. The diurnal variations of O₃ tracked the pattern of solar radiation-(Fig. S2), which might be associated with the special climate characteristics in Chengdu with extremely-541 low annual sunshine totals and mostly overcast days, especially in winter. As a result, the impact of 542 543 weather conditions on solar radiation might overwhelm that of aerosol pollution at CD and causedunusual diurnal variations of O₃ and solar radiation. In the warm season, no heavy PM_{2.5} pollution-544 occurred at CD and CQ, and the diurnal patterns of gaseous precursors and meteorological parameters-545 546 were similar as those in the cold season (Fig. 8 and Fig. S3). 547 While photochemical reactions are mostly influenced by temperature and solar radiation, 548 heterogeneous reactions are associated with high RH. Meteorological conditions and O₃ levels 549 associated with different pollution levels suggest that gas-phase oxidation reaction was likely the major-

- 550 formation mechanism of secondary aerosols on moderate polluted days (high O₃ levels and SR, low RH)
- 551 while heterogeneous reactions likely played a more important role on heavy polluted days (low O₃-
- 552 levels and slightly higher RH). This hypothesis needs further verification using high-resolution data.

553 **3.4.3 Impact of NH₃ amount and RH on NO₃⁻ concentrations-**

In Sect. 3.4.2, it was found that the CO-scaled NO₃⁻ increased dramatically in the cold season butdecreased in the warm season on polluted days at CQ. To explain the different season patterns, majorfactors affecting NO₃⁻ are explored, including NH₃ levels and RH. The neutralization ratio (NR) isdefined as -

558
$$\frac{NR = \frac{[NH_4^+]}{2[SO_4^{2-}] + [NO_3^-]}}{(4)}$$

559 Where the concentrations of NH_4^+ , $SO_4^{2^-}$ and NO_3^- were expressed as molar concentrations. NR in cold 560 season ranged from 1.0 to 1.2 at the two sites, indicating fully neutralization of $SO_4^{2^-}$ and NO_3^- by NH_3^- . 561 In this case, NH_3^- was not a limiting factor for NO_3^- . NR in the warm season was 1.05 at CD, but less-562 than 1.0 (0.94-0.95) at CQ. NH_3^- seemed to be a limiting factor for NO_3^- formation at CQ on both clean-563 and polluted days in the warm season. Although NH_4^+ increased on polluted days (by 30% based on-564 CO-scaled concentrations), $SO_4^{2^-}$ increased even more (by 60% based on scaled concentration), 565 resulting in incomplete neutralization of NO_3^- and little variations of its concentrations.

Another consideration is the thermodynamic equilibrium between particulate NH4NO3- and gaseous-566 567 HNO₂, which depends on temperature and RH. Kuprov et al. (2014) found that the equilibrium wouldbe shifted toward the particulate phase when RH was above the deliquescence relative humidity (DRH)-568 569 of NH₄NO₃, and the dissociation constant decreased to about an order of magnitude when RH wasabove 75%. As shown in Fig. S4, on polluted days, RH was lower than DRH most of the time in the-570 warm season at CQ estimated according to Mozurkewich (1993), which explains the lower NO3-571 concentrations. In contrast, RH was above the DRH most of the time at CD. Thus, despite similar-572 concentrations of SO₄²⁻ and NH₄⁺ between CD and CQ in summer, NO₃⁻ was 50% lower at CQ than-573 574 that at CD due to the lower ambient RH at CQ.

575 **3.2.3 Geographical origins of high PM_{2.5} pollution**

576 PSCF analysis was applied to investigate the potential source regions contributing to high $PM_{2.5}$

577 pollution. As can be seen from the PSCF maps in (Fig. 910)., all the pollutants including PM_{2.57} and its

- 578 chemical componentssitions and as well as gaseous precursors had similar spatial patterns of potential
- 579 <u>source areas.</u> Basically, all the major source areas for high <u>PM_{2.5} pollutants concentrations</u> were
- 580 distributed within the Basinbasin. Long-range transports as seennormally occurred in North Plain and

581	eastern coastal regions were not observed at CD and CQ site (Zhao et al., 2015;Zhang et al., 2013). At
582	CD, the major source areas in the cold seasonwinter included the areas of the northeastern, southeastern
583	and southern Chengdu and in some areas of eastern Chongqing, and in warm season included areas-
584	scattered between Chengdu and Chongqing (e.g., Neijiang) besides the area south of Chengdu. A
585	similar spatial distribution of PM _{2.5} potential sources was also found by (Liao et al., 2017) through
586	PSCF analysis in winter 2013, in which high PM _{2.5} concentrations were mostly associated with sources
587	broadly located in the southeast of the basin, covering Neijiang, Zigong, Yibin, Luzhou and east part of
588	Chongqing. At CQ in the cold season, the northeast area of Chongqing was identified as strong sources,
589	where a number of industries were located, such as Changshou chemical industrial ozone. In the warm-
590	season, the areas of the southern Chongqing were also found to be potential sources. Overall, PM2.5
591	pollution at CQ was characterized by significant local contribution from major sources located in or
592	nearby Chongqing. In contrast, regional transport in Sichuan Basin from southeast, south and southwest
593	of Chengdu had a major impact on PM _{2.5} pollution at CD.

4 Conclusions

595	Chemically-resolved PM _{2.5} data collected during four seasons at two urban sites in Sichuan basin,
596	southwest China were analyzed in the present study. The concurrent occurrences of heavy pollution
597	events at the two sites and similarities in pollutants characteristics between the two sites demonstrated
598	the regional-scale phenomenon of PM _{2.5} episodes inside the Basin, which was mainly caused by the
599	surrounding mountainous topography under typical stagnant meteorological conditions. Such a finding
600	was also supported by back trajectory analysis which showed that air masses reaching at both sites were
601	originated within the basin and only traveled for short distances on heavy polluted days. Differences
602	between the two sites with regards to several major chemical components provided evidences of
603	sub-regional characteristics of emission sources and chemical transformation processes under different
604	meteorological conditions. For example, an additional source factor from motorcycle traffic was
605	identified for VOCs emission in Chongqing, which led to higher high OC concentrations, and lower
606	relative humidity in Chongqing caused lower nitrate concentration in this city despite similar levels of
607	its gaseous precursors in the two cities. The present study also identified different driving mechanisms
608	for the polluted PM _{2.5} episodes in the Sichuan Basin than in the other regions of China. For example,
609	sharply increased relative humidity was thought to be one of the main factors causing high inorganic

- 610 aerosol concentrations during the polluted periods in eastern coastal China and North China Plain, while
- 611 in Sichuan Basin the special topography and meteorological conditions are driving forces for such
- 612 events considering humidity was high throughout the year and did not differ much between polluted and
- 613 clear periods. However, on annual basis heterogeneous reactions might be more important in this basin
- 614 <u>than in other regions of China due to the consistent high humidity conditions, as revealed in the case of</u>
- 615 <u>sulfate formation in the present study. Future studies should use high-resolution data to verify the</u>
- 616 <u>findings related to chemical transformation paths proposed here. More importantly, a detailed emission</u>
- 617 inventory of aerosol particles and related gaseous precursors in the basin should be developed promptly,
- 618 which is needed for further investigating $PM_{2.5}$ formation mechanisms and for making future emission
- 619 <u>control policies. Source-receptor analysis using monitored chemical-resolved PM_{2.5} data should be</u>
- 620 <u>conducted to verify such emission inventories.</u>

Seasonal patterns, formation mechanisms, and sources geographical origins of PM25 at the two 621 megacities in Sichuan Basin were explored using chemically resolved daily PM25 samples collected in 622 623 four consecutive seasons. On about 30% of the days, daily PM25 exceeded NAAQS, with SNA and OC concentrations 1.7-2.8 and 2.1-3.4 times, respectively, higher than those on clean days. During the 624 severe PM_{2.5}-pollution episodes in winter, The the percentage contributions of SNA and OM to PM_{2.5} 625 mass only differed slightly between polluted and clean days at CD, while it increased significantly for 626 OM at CO in cold season. This phenomenon was different from those found in the other regions of 627 China, implying the unique roles played by local special topography, meteorology, and emissions 628 sources in this region. Most chemical components of PM2.5 exhibited the highest concentrations in the 629 winter (with exception of FS) and the lowest in the summer (with exception of SO_4^{2-}). The site 630 differences in PM_{2.5} and SNA between CD and CQ were not significant in all the seasons except in the 631 summer, while higher OC and FS concentrations were observed at CO than at CD in most seasons. The 632 different diurnal patterns of gaseous precursors and meteorological parameters under different PM25 633 level implied the more important roles of heterogeneous transformation on the heavy polluted days. The 634 ammonia limited and high temperature conditions also played a critical role in low NO3⁻ levels in the 635 warm season at CQ.. Major sources of PM25 were concentrated in Chengdu, Chongqing, and the areas 636 637 in between, with the regional sources affecting more at CD site and the local emissions at CQ site. Future studies should aim to combine high-resolution PM25 data and at suburban and rural locations to 638 gain a thorough understanding of PM_{2.5}-sources and formation mechanisms. 639

640

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

642

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Table 1 <u>Meteorological parameters</u>, <u>Annual annual</u> and seasonal mean concentrations of $PM_{2.5}$, <u>gaseous pollutants</u> and major chemical components ($\mu g \text{ m}^{-3}$) at CD and CQ during 2014-2015.

			CD					_		
	Autumn	Winter	Spring	Summer	Annual	Autumn	Winter	Spring	Summer	Annual
Meteorological parameters										
<u>T (°C)</u>	<u>15.8±2.9</u>	<u>9.3±2.5</u>	<u>20.4±4.4</u>	<u>28.3±2.9</u>	<u>18.5±7.7</u>	<u>16.0±3.2</u>	<u>10.0±2.3</u>	<u>20.5±4.5</u>	<u>28.4±3.4</u>	<u>18.8±7.6</u>
<u>P (hPa)</u>	<u>960±3.8</u>	<u>963±4.7</u>	<u>954±7.9</u>	<u>946±2.1</u>	<u>955±8.1</u>	<u>981±4.2</u>	<u>984±5.2</u>	<u>974±8.4</u>	<u>963±2.2</u>	<u>975±7.7</u>
<u>RH (%)</u>	<u>81.9±9.0</u>	<u>80.9±6.8</u>	<u>70.5±8.6</u>	<u>72.2±11.3</u>	<u>76.3±10.3</u>	<u>76.1±5.7</u>	<u>68.7±8.8</u>	<u>60.7±13.6</u>	<u>61.0±13.3</u>	<u>66.5±12.5</u>
<u>SR (w m⁻²)</u>	<u>54.9±40.3</u>	<u>37.8±27.2</u>	<u>128.9±65.0</u>	<u>123.6±94.2</u>	<u>67.2±56.7</u>	<u>na.</u>	<u>na.</u>	<u>na.</u>	<u>na.</u>	<u>na.</u>
<u>WS (m s⁻¹)</u>	<u>0.5±0.2</u>	<u>0.4±0.3</u>	<u>0.7±0.4</u>	<u>0.5±0.2</u>	<u>0.5±0.3</u>	<u>0.7±0.2</u>	<u>0.7±0.3</u>	<u>1.0±0.4</u>	<u>0.7±0.3</u>	<u>0.8±0.3</u>
<u>PBLH_{max}</u>	<u>890±305</u>	<u>852±273</u>	<u>1296±491</u>	<u>1422±529</u>	<u>1119±481</u>	<u>821±252</u>	<u>928±260</u>	<u>1310±491</u>	<u>1329±505</u>	<u>1101±453</u>
Concentration	s of gaseous	pollutants (µş	<u>g m⁻³)</u>							
<u>O</u> ₃	<u>19.3±10.5</u>	<u>11.9±7.6</u>	<u>69.3±22.9</u>	<u>90.5±33.3</u>	<u>48.2±39.6</u>	<u>13.3±8.9</u>	<u>12.5±7.7</u>	<u>56.3±23.5</u>	<u>42.8±17.2</u>	<u>31.5±24.5</u>
<u>SO</u> 2	<u>15.8±7.0</u>	<u>21.5±9.5</u>	<u>11.2±6.3</u>	<u>11.3±4.7</u>	<u>14.9±3.7</u>	<u>16.4±4.6</u>	<u>23.3±9.2</u>	<u>13.9±5.3</u>	<u>14.4±5.4</u>	<u>17.0±7.3</u>
<u>NO2</u>	<u>60.2±18.7</u>	<u>75.3±24.5</u>	<u>51.8±26.8</u>	<u>54.2±9.4</u>	<u>60.4±22.5</u>	<u>66.5±15.0</u>	<u>81.3±19.8</u>	<u>50.8±16.7</u>	<u>51.7±20.8</u>	<u>62.4±22.0</u>
Concentration	$\begin{array}{ c c c c c c c c } \hline CD & CQ & CQ \\ \hline Autumn & Winter & Spring & Summer & Annual & Autumn & Winter & Spring & Summer & Annual & Autumn & Winter & Spring & Summer & Annual & Autumn & Winter & Spring & Summer & Annual & Autumn & Winter & Spring & Summer & Annual & CQ & Vectorological parameters & Vectorolog$									

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
SO4 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
\mathbf{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	\mathbf{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} -75th percentiles, box), and the central 90% data (5^{th} -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 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 O_3 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).