

***Interactive comment on* “Seasonal characteristics, formation mechanisms and source origins of PM_{2.5} in two megacities in Sichuan Basin, China” by Huanbo Wang et al.**

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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.

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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 PM_{2.5} 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 PM_{2.5} 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.

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(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 additional in-depth analyses and innovative results, we hope the reviewer will find the paper meets the standard of the journal.

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 seem not ideal to understand the characteristics of PM_{2.5} in two basin 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

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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 PM_{2.5} 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 regional-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

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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 analysis and the other one was equipped with quartz filter for water-soluble inorganic ions and carbonaceous components analysis. At the CQ site, a low-volume aerosol sampler (BGI Corp., fr-mOmni, USA) operating at a flow rate of 5 L min⁻¹ was used to collect PM_{2.5} samples on Teflon filter, and another sampler (Thermo Scientific Corp. Partisol 2000i, USA) with a flow rate of 16.7 L min⁻¹ was used to collect PM_{2.5} samples on quartz filter. Sampling 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 carefully 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

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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. SO₄²⁻ 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.

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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 meteoro-

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logical 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, PM_{2.5} 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, SO₄₂/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 ev-

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idence 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 in 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 SO₄²⁻/OC. Such an analysis revealed that SO₄²⁻ 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 NO₃⁻ 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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