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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characterizations and source analysis of atmospheric inorganic ions at a national background site in the northeastern Qinghai-Tibet Plateau: insights into the influence of anthropogenic emissions on a high-altitude area of China" *by* Bin Han et al.

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We appreciate the comments from Anonymous Referee #1. His or her comments gave us a lot of chances to reevaluate our manuscript. We have made corresponding revision according to his comments. We attached our revised manuscript in Supplement. All our responses are as follows:

In this work, the authors did a field observation in the northeast of Tibetan Plateau, in-

cluding the particulate matters as well as trace gases. Although such study is meaningful for the better understanding the atmospheric chemistry over this region, the current version of the manuscript suffer major problems. Specific comments:

1. In the introduction parts, the authors should state the motivates of this study more clearly. Several papers have been published for this site (Menyuan) in this special issue. Based on the previous studies, line 80-88, what the knowledge gaps or questions still exist for this region? Response to reviewer: We added some sentences in line 88-97 to better express the gaps that still exist and the advantage by using high resolution monitoring equipment.

2. In the section of Methods (sampling site), the Qinghai lake (major source of sulfate found later of this study) and major traffic roads (major source of NOx in this study) should also be introduced. Response to reviewer: We added the introductions on the Qinghai Lake and surrounding major road in line 127-128 and 134-136.

3. In the section 2.2, why Cl- data was missing? What's the data quality of this online monitoring? Did you compare it with the traditional method (filter sampling + IC)? What's the detection limits of the trace gases? Response to reviewer: 1) Cl- data missing: The analysis of Cl- was greatly interfered during whole sampling period. There are some interference/background peaks near the retention time of Cl-. After background peak being removed, we got negative value of Cl-. Therefore, we believed there were some problems in the analysis of Cl- during this time. We chose to remove all the data of Cl-. 2) Comparison between URG and traditional filter sampling: Actually we didn't do any comparison sampling with filter during our campaign, and we should admit it is our problem on initial study design. 3) The detection limits of the trace gases: We added the limits of detection of equipment for trace gases in line 145-146.

4. For the ion balance, without the Cl- data, it is somewhat strange to see that anion is only composed of sulfate and nitrate. Response to reviewer: We totally understand the concern of reviewer. We should admit that it does seem strange without Cl- in

ion balance analysis. However, given that the analysis data of Cl- was not good and had been removed in our preliminary analysis, we can do nothing now on present ion balance discussion. In our future potential observation, we will try to solve this problem.

5. Line 158-173, there is no need to describe the basic theory of PMF in such detailed way Response to reviewer: We moved some parts of introduction on miss data treatment and choice on the number of the factors to supplementary material.

6. Regarding the contents in table 2, some locations may be unnecessary to include. Line 221, are you sure the study site of Kumar and Sarin (2010) is urban area? Response to reviewer: 1) We deleted some locations in the table 2. 2) We checked the study of Kumar and Sarin (2010) again, and it turned out we were wrong. But it is unnecessary to the Table 2 now, so we chose to delete it.

7. I understand the NO3-/SO42- is frequently used to indicate the relative importance of vehicle and coal combustion. Such works were mostly based in urban or populated area like North China Plains or South Asia. However, such ratio seems not applicable for this study (Menyuan) for several reasons. First, as stated in Line 257 and later (by PMF results), biomass burning is also important source of nitrogen species. For sulfate, besides the coal combustion, salt lakes (like Qinghai Lake) were also proposed at important source of sulfate (see more details in PMF parts).

Response to reviewer: We totally agree with reviewer's opinion on this point. The NO3-/SO42- is really more applicable in urban area. In the QTP where we studied, it is questionable to use it as a marker. So we deleted all the expressions on NO3-/SO42- to avoid some possible misinterpretations.

8. Line 267-269, actually, this is no data of concentration abundance of organic matters yet. So it is not so conniving to say the particle growth is caused by organics. Response to reviewer: It is true we don't have data to prove that, and can only refer to other studies. So we deleted the expressions on the organic matter, and added a sentence "Therefore, more observational campaign should be implemented in the future

to investigate the driver compositions on the increase of PM2.5 mass concentrations."

9. Some time, the authors say "particle growth" sometime, "PM2.5 increase" were used. So is there any difference between such two expression? particle growth means hydroscopic growth in terms of mass or size?? Response to reviewer: We changed all "particle growth" to "PM2.5 increase". When we said "particle growth" or "PM2.5 increase", we both meant the concentration increase of PM2.5. Obviously, "particle growth" doesn't mean this. Just like the reviewer said, it should mean hydroscopic growth in terms of mass or size. So we corrected it.

10. Section 3.2, regarding the diurnal variations, what's the role of meteorologic factors like PBL? Response to reviewer: We didn't do any observations on PBL, and it is our fault in the study design. We also asked some other collaborators to see if we can be accessible to the PBL data of Mount Waliguan. Unfortunately, no data could be available during our observation period in that site, either. We are not sure if the PBL data in Xining city is suitable here, given that the altitude difference between our site and Xining city is quite large. Therefore, we have to leave this analysis blank for further study.

11. Line 298, what's the meaning of remote transportation? Response to reviewer: It is supposed to mean the long-range transportation. To avoid confusion on the understanding of oxidation ratio, we deleted the sentence " Furthermore, remote transportation also contributed to the concentrations of SO42- and NO3-, thus increasing the oxidant ratio, despite not being products of local oxidation."

12. Line 308-311, maybe crustal materials is responsible for the increase of PM2.5 Response to reviewer: We showed the trends of the percentages of all WSI in PM2.5 in Figure 3, and none of them turned out to be responsible for the increase of PM2.5. So here we added a sentence " Crustal materials are either not responsible for it as shown in Figure 3." at line 338 to make it more clear.

13. Line 332-334, it is strange to see such description here. You know such points

actually were established after the discussion for Figure 6. Response to reviewer: We moved the description to the line 374-377.

14. In the previous studies, the aerosols and rain over Tibetan Plateau were found to be alkaline. However, in this study, the aerosols were found to be acid. So more discussion (more references for Tibetan Plateau) is also expected, to make this point more convincing. Response to reviewer: We summarize some papers published about the aerosol ions on the QTP and rewrote the discussion in this section. The results are found to be quite different at different locations. In the studies of South edge of the QTP, the aerosols were found to be alkaline at Qomolangma (Mt. Everest) Station for Atmospheric and Environmental Observation and Research Station (TSP, C/A=4.1) (Cong et al. 2015), four sites in central Himalayan region (TSP, C/A=3.7) (Tripathee et al. 2017), and Shigatsz, China (PM2.1, C/A=1.5) (Yang et al. 2016). While in the studies of the northeastern QTP, the results varied with locations. Two studies at Qilan Shan Station at different time achieved difference values of C/A (C/A=1.3, sampling time: summertime of 2011; C/A=0.95, sampling time: summertime of 2012) (Xu et al. 2014; Xu et al. 2015). Another study at the Qinghai Lake also got slightly acidic result (PM2.5, C/A=0.8) (Zhao et al. 2015). In their study at the summer of 2012, Xu et al. (2015) also found that the equivalent balances of water-soluble species in different size modes indicate that the accumulation mode particles were somewhat acidic (with the linear regression slope of [NH4++Ca2++Mg2++K+] vs. [SO42-+NO3-] being 0.6) and that the coarse mode particles were almost neutral (the slope was 0.999), indicating that small size of particles show tendency of acid.

15. For the source apportionment by PMF, the ions were only ascribed to two factors. I.e., factor 1, salt lake and factor 2, mixed. It seems PMF failed to identify the sources of those inorganic ions adequately. Response to reviewer: Integrating other comments of the reviewer, we changed the input of the PMF model and also rearranged the structure of the paper. First, we excluded all gases pollutants in the PMF model and allowed only ion data in the model. Thus we got five factors including animal waste emission

and biomass burning, crustal dust, salt lake emissions, secondary sulfate, secondary nitrate. Second, we moved the PMF model results to section 3.2 to use some of them (the results of secondary sulfate and nitrate) for the following SOR and NOR calculation.

16. Currently, the writing of the conclusion part is very weak. What's the values and implications of this work for the international scientific communities? Compared with the statements in the Introduction parts, what's questions have been addressed after the study? Response to reviewer: We rewrote part of the conclusion and added some implications of this work for the international scientific communities "To our knowledge, there is no such real-time measurement on WSIs associated with PM2.5 at rural sites in the QTP yet. This study provides some preliminary results on aerosol ion compositions on the QTP, and proposes the potential formation mechanism of secondary sulfate and nitrate. These findings are supposed to be useful for further studies on aerosol chemistry in this area." We also addressed some questions after the study by saying "In this study, we finished some analysis on WSIs by taking advantage of real-time data to: 1) analyze the diurnal variations of WSIs; 2) discuss the formation of secondary sulfate and nitrate at the QTP; and 3) investigate source apportionment on hourly data within short-term observation. All these above are difficult by using traditional manual PM2.5 sampling, given that it usually takes hours or even days for sample collection, and is unable to detect more variations on aerosol compositions and supply more data on finer temporal scale for further analysis. "

17. Line 487-488, the authors stated that "Our analysis suggests that photochemical reactions played a critical role in the formation of SO42- and NO3- during our observation period." However, salt lake emission was identified as the first factor (for SO42-) by PMF. Such expressions seem contradict. Response to reviewer: We added "After excluding the emission of sulfate from the salt lake" here. Also in the section of "results and discussion", we ran the PMF model again by using only ions data, and excluded the ratio of sulfate emitted from the salt lake. Thus we used sulfate and nitrate concen-

trations after modelling calculation for SOR and NOR discussion.

Reference:

Cong Z, Kang S, Kawamura K, Liu B, Wan X, Wang Z, et al. 2015. Carbonaceous aerosols on the south edge of the tibetan plateau: Concentrations, seasonality and sources. Atmos Chem Phys 15:1573-1584. Tripathee L, Kang SC, Rupakheti D, Cong ZY, Zhang QG, Huang J. 2017. Chemical characteristics of soluble aerosols over the central himalayas: Insights into spatiotemporal variations and sources. Environ Sci Pollut Res 24:24454-24472. Xu J, Wang Z, Yu G, Qin X, Ren J, Qin D. 2014. Characteristics of water soluble ionic species in fine particles from a high altitude site on the northern boundary of tibetan plateau: Mixture of mineral dust and anthropogenic aerosol. Atmospheric Research 143:43-56. Xu JZ, Zhang Q, Wang ZB, Yu GM, Ge XL, Qin X. 2015. Chemical composition and size distribution of summertime pm_{2.5} at a high altitude remote location in the northeast of the qinghai–xizang (tibet) plateau: Insights into aerosol sources and processing in free troposphere. Atmos Chem Phys 15:5069-5081. Yang YJ, Zhou R, Yan Y, Yu Y, Liu JQ, Di YA, et al. 2016. Seasonal variations and size distributions of water-soluble ions of atmospheric particulate matter at shigatse, tibetan plateau. Chemosphere 145:560-567. Zhao ZZ, Cao JJ, Shen ZX, Huang RJ, Hu TF, Wang P, et al. 2015. Chemical composition of pm2.5 at a high-altitude regional background site over northeast of tibet plateau. Atmos Pollut Res 6:815-823.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-1345/acp-2018-1345-AC2-supplement.pdf

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