Manuscript No. ACP-2022-477

Tittle: Measurement report: Intensive biomass burning emissions and rapid nitrate formation drive severe haze formation in Sichuan basin, China: insights from aerosol mass spectrometry

The authors gratefully thank all the reviewers for their comments and suggestions. We have revised our manuscript according to the two reviewers' suggestions and comments. **All the changes and responses to the reviewers' comments are listed below point-by-point. The changes are highlighted with red in the revised manuscript.** We sincerely hope this manuscript will be acceptable for publication in *Atmospheric Chemistry and Physics*.

Minor comments:

Page 6 - line 143 : "the flow rate was maintained at 3 L/min with a flow meter" I assume the author meant a mass flow controller instead of a flow meter to maintain the 3LPM flow rate.

Reply: Thanks for the reviewer's suggestion. Our flow meter has the function of controlling flow rate. Despite this, as the reviewer suggests, it is more precise to use 'flow controller' in the manuscript. We have changed the 'flow meter' to 'flow controller' in the revised manuscript. (line 143)

the flow rate was maintained at 3 L/min with a mass flow controller

Page 6 – line 145: "then was dried by a Nafion drier" was the RH below 30-40%? The author could maybe indicate a range of RH.

Reply: Sorry for missing the information of the RH after the Nafion drier. Except for the fog periods, the RH of the air samples dried by the Nafion drier ranged 35-46 % during the whole campaign. The RH of the air samples dried by the Nafion drier during fog periods could reach ~56 %. We have added the RH of the air samples dried by the Nafion drier in the revised manuscript. (lines 145-147)

the ambient air would go through a PM2.5 cyclone (URG-2000-30ED, USA) to remove coarse particles, then was dried by a Nafion drier. The relative humidity of the air samples dried by the Nafion drier usually ranged from ~35% to 46 %, and could reach ~56 % during fog events.

Page 6 line 151: "which made the PM2.5 measurement available". I suggest to rephrase this part,

e.g. “the PM2.5 allows to chemically characterize the PM2.5 fraction” or something similar.

Reply: Thanks for the reviewer’s suggestion. We have rephrased this part as the reviewer suggests. (lines 152-153)

It should be mentioned that a PM2.5 lens was used during the whole campaign, which allowed to chemically characterise the PM2.5 composition (Xu et al., 2017).

Page 9 – lines 218-219: “an arrival height of 500 m which is above ground level (AGL) for target analysis in the HYSPLIT model to diminish the effects of surface friction (Polissar et al., 2001) this height value and greater are regarded as in the open height of the planetary boundary layer in winter and are more useful for long-range transport”. Based on the PBL height reported in Figure S3d this height is most of the time above the PBL observed at the sampling site? Would using a fraction of the BL in HYSPLIT result in similar results/be more appropriate? Maybe you try to justify the height choice in the second part of this sentence but it doesn’t sound very conclusive, especially when you mentioned earlier in the manuscript that the landscape in the SCB basin “is unfavourable for either horizontal transport or vertical diffusion”.

Reply: The height of 500 m above ground level (AGL) exceeded the PBLH most of the time, as shown in the figure 1 below. As a fact, we had compared the simulation results for the arrival heights of 200 m, 500 m and 1000 m AGL (as shown in the figure 2 below). Although the appropriate number of mean trajectories for the arrival height of 1000 m was three, the origins and the transport paths of the cluster-mean trajectories for these three heights were similar. The air parcels from the east and northeast of Sichuan Province took up major parts in all air parcels.

The HYSPLIT model computation is a terrain following calculation, and the trajectories can never go below ground. The terrain issue of valley/basin can be ignored if the valley/basin is relatively wide and large, and the arrival height can be set to a value of interest (one is referred to https://www.arl.noaa.gov/hysplit-frequenctly-asked-questions for more detail information). Since the 500 m height covers the height above and below PBLH, we chose this height to achieve an overall consideration of both long-range transport and local transport. Tao et al. (2013) also used this height to analyse the transport paths in Sichuan Basin. Wang et al., (2018) even used a lower arrival height (300 m) in their study to identify major transport paths in two megacities in Sichuan Basin. As the reviewer suggests, the description ‘this height value and greater are regarded as in the

open height of the planetary boundary layer in winter and are more useful for long-range transport' is somewhat not conclusive. We have deleted this sentence in the revised manuscript.

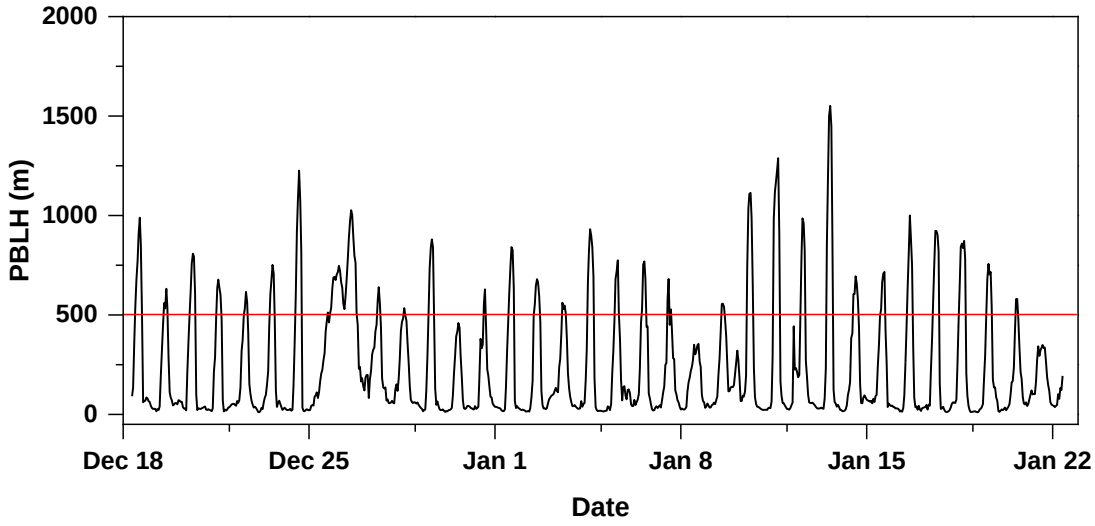

Figure 1 Temporal profile of planet boundary layer height (PBLH) during the campaign. The red line shows the 500 m height. The PBLH is derived from the European Centre for Medium-Range Weather Forecasts (ECMWF) dataset of ERA5 hourly data (https://cds.climate.copernicus.eu/cdsapp#!/home)

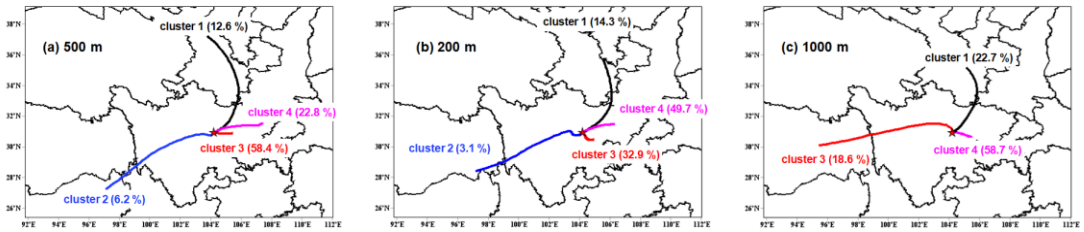

Figure 2 Simulation results of 48 h backward air parcels cluster-mean trajectories for arrival heights of (a) 500 m, (b) 200 m and (c) 1000 m during the campaign.

Reference

Tao, J., Zhang, L., Engling, G., Zhang, R., Yang, Y., Cao, J., Zhu, C., Wang, Q., and Luo, L.: Chemical composition of PM2.5 in an urban environment in Chengdu, China: Importance of springtime dust storms and biomass burning, Atmos. Res., 122, 270-283, https://doi.org/10.1016/j.atmosres.2012.11.004, 2013.

Wang, H., Tian, M., Chen, Y., Shi, G., Liu, Y., Yang, F., Zhang, L., Deng, L., Yu, J., Peng, C., and

Cao, X.: Seasonal characteristics, formation mechanisms and source origins of PM2.5 in two megacities in Sichuan Basin, China, Atmos. Chem. Phys., 18, 865-881, https://doi.org/10.5194/acp-18-865-2018, 2018.

Page 15 line 403: "Clsuter2" cluster 2

Reply: Corrected. (line 403)

Page 17 line 462: "the rest composition did not change significantly" could you rephrase.

Reply: Thanks for the reviewer's suggestion. We have rephrased this part. (lines 461-463)

During H3, the fractions of nitrate and BBOA in $PM_{2.5}$ increased, while OOA decreased and HOA, sulphate, ammonium, chloride did not change significantly as the $PM_{2.5}$ concentration increased.

Page 18 line 485: "due to the aqueous-phase reaction" "due to aqueous-phase reactions"

Reply: Corrected (lines 484-485)

The domination of secondary species in $PM_{2.5}$ during F1 was probably due to the aqueous-phase reactions

Page 19 line 502: "Distinguished from H1" rephrase

Reply: Thanks for the reviewer's suggestion. We have rephrased this part. (lines 502-503)

All species (except for HOA) increased during the foggy period from the pre-fog period during F2, which was different from the case during F1.

Page 19 lines 509-511: "The increase of BBOA in the present study was attributed to the intense emission from biomass burning during the foggy period, which overwhelmed the scavenging effects of fog droplet" Could it be that biomass burning VOCs partitioning is enhanced by the high RH?

Reply: This is a good question. As reported by a recent study by Xiao et al. (2022), biomass burning emits large quantities of phenols, which readily partition into the atmospheric aqueous phase and subsequently may react to produce aqueous secondary organic aerosol (aqSOA). At first, we also thought that the increase of BBOA could be attributed to the enhanced partitioning of biomass burning VOCs. However, the increase of BBOA (compared to pre-fog period) was only observed

during the foggy period of F2. If it was the case that high RH enhanced the partitioning of biomass burning VOCs, an increase of BBOA should be also observed during the foggy periods of F1 and F3. In fact, compared to pre-fog periods, BBOA decreased during the foggy periods of F1 and F3. Thus, we thought it more reasonable that the increase of BBOA during the foggy period of F2. However, as the reviewer mentions, it might be more comprehensive to add some discussions on the contribution of biomass burning VOCs partitioning. We have added relevant discussions in the revised manuscript. (lines 509-514)

The increase of BBOA in the present study was likely attributed to the intense emission from biomass burning during the foggy period, which overwhelmed the scavenging effects of fog droplets. The enhanced partitioning of biomass burning VOCs under high RH conditions might also contribute the increase of BBOA. For example, a recent study showed that the large quantities of phenols from biomass burning emission would readily partition into the atmospheric aqueous phase (Xiao et al., 2022).

Reference

Xiao, Y., Hu, M., Li, X., Zong, T., Xu, N., Hu, S., Zeng, L., Chen, S., Song, Y., Guo, S., and Wu, Z.: Aqueous secondary organic aerosol formation attributed to phenols from biomass burning, Sci. Total Environ., 847, 157582, https://doi.org/10.1016/j.scitotenv.2022.157582, 2022.

Page 19 lines 522-523: “the mass fractions of OOA increased, while the contribution of BBOA and HOA decreased from pre-fog periods to post-fog/foggy periods for the three fog events.” Scavenging is mentioned as the main reason for the decrease in HOA and BBOA. Would it be possible that BBOA and HOA would just get oxidized during the fog events and therefore contribute to the OOA fraction?

Reply: Thanks for the reviewer’s question. As reported by a previous study by Wang et al. (2020), the fossil fuel organic aerosols (FFOA) could be oxidised to aqSOA under high RH conditions. Nevertheless, we thought that the scavenging of fog droplets also played a role in the decrease of BBOA and HOA. Because not all BBOA and HOA were water-soluble (Qiu et al., 2019), and the insoluble parts could be scavenged by fog droplets, resulting in the decrease of BBOA and HOA in the interstitial particular matter. The results of Collet et al. (2008) also showed that the biomass

burning tracers were scavenged efficiently by fog droplets, while the vehicle emission tracers showed a relatively lower scavenging efficiency. However, as the reviewer mentions, we could not rule out the transformation of POA to OOA through aqueous-phase reactions. We have added relevant discussions in the revised manuscript. (lines 526-530)

As shown in Fig. S9, the mass fractions of OOA increased, while the contribution of BBOA and HOA decreased from pre-fog periods to post-fog/foggy periods for the three fog events. Except for the scavenging of fog droplets, BBOA and HOA could also be oxidised to OOA through aqueous-phase reactions (Wang et al., 2021), thus resulting in the decrease contribution of BBOA and HOA.

Reference

Qiu, Y., Xie, Q., Wang, J., Xu, W., Li, L., Wang, Q., Zhao, J., Chen, Y., Chen, Y., Wu, Y., Du, W., Zhou, W., Lee, J., Zhao, C., Ge, X., Fu, P., Wang, Z., Worsnop, D. R., and Sun, Y.: Vertical Characterization and Source Apportionment of Water-Soluble Organic Aerosol with High-resolution Aerosol Mass Spectrometry in Beijing, China, ACS Earth and Space Chemistry, 3, 273-284, https://doi.org/10.1021/acsearthspacechem.8b00155, 2019.

Wang, J., Ye, J., Zhang, Q., Zhao, J., Wu, Y., Li, J., Liu, D., Li, W., Zhang, Y., Wu, C., Xie, C., Qin, Y., Lei, Y., Huang, X., Guo, J., Liu, P., Fu, P., Li, Y., Lee, H. C., Choi, H., Zhang, J., Liao, H., Chen, M., Sun, Y., Ge, X., Martin, S. T., and Jacob, D. J.: Aqueous production of secondary organic aerosol from fossil-fuel emissions in winter Beijing haze, P. Natl. Acad. Sci. USA, 118, https://doi.org/10.1073/pnas.2022179118, 2021.

Page 20 line 533: “which are still unclear.” In the introduction the author describe pretty well the topography and meteorological conditions of the SCB. If what the author meant is that their effects, together with emission sources, on haze formation processes are unclear, then the author may want to rephrase this sentence accordingly.

Reply: Thanks for the reviewer’s suggestion. We have rephrased this part. (lines 538-540)

The formation process of haze pollution in SCB might be different from those in NCP, YRD, and PRD due to the unique topography, meteorological conditions and emission sources, which are still unclear.

Page 20 lines 545-548": "Due to the limitation of the present study, the parameters which are indicative of the pathways of nitrate formation are not characterised. The major precursors contributing to a large amount of OOA are not clear yet. In addition, how controlling BBOA will affect the atmospheric visibility, radiative forcing, and climate change in SCB needs further investigation." I would rephrase these sentences. The author emphasize the need to further investigate how controlling BBOA will affect radiative forcing etc.. while a better understanding of the gas/particles emitted by biomass burning (and not solely BBOA) and how they will contribute/affect the Haze formation processes, may help to implement appropriate POA emission control to reduce the occurrence of haze.

Reply: Thanks for the reviewer's suggestion. Indeed, our description in this part might not be comprehensive. We have rephrased this part as the reviewer suggests. (lines 552-560)

Due to the limitation of the present study, the parameters which are indicative of the pathways of nitrate formation are not characterised. The major precursors contributing to a large amount of OOA are not clear yet. In addition, further investigation is needed to gain a better understanding of the gas/particles emitted by biomass burning or other primary emissions and how they will affect the haze formation processes, which may help to implement appropriate POA emission control to reduce the occurrence of haze. Nonetheless, the results in this study implied that controlling primary emissions (such as biomass burning and vehicle exhaust) and precursors of secondary aerosols (e.g., NOx, SO_2, and VOCs) during severe haze periods will benefit the improvement of air quality in SCB.

Page 20 line 549: "In spite of the deficiencies". I would simply use "Nonetheless," as the author already stated the limitation of the approach beforehand.

Reply: Thanks for the reviewer's suggestion. We have replaced 'In spite of the deficiencies' with 'Nonetheless' in the revised manuscript. (lines xxx)

Nonetheless, the results in this study implied that controlling primary emissions (such as biomass burning and vehicle exhaust) and precursors of secondary aerosols (e.g., NOx, SO2, and VOCs) during severe haze periods will benefit the improvement of air quality in SCB.

Page 27 – line 609 - Figure 6 "of different OA compositions" OA sources or OA factors

Reply: Corrected. (line 618)

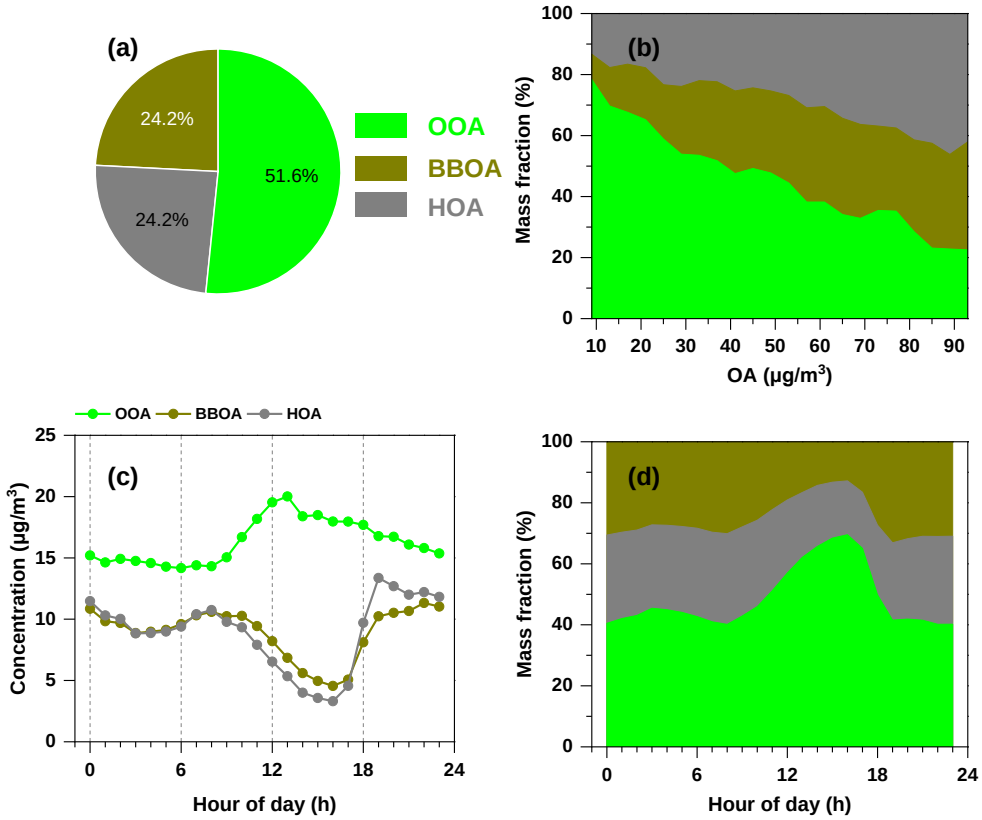

Fig. 6 Average mass fraction of different OOA, BBOA, and HOA (a) in OA and (b) as a function of OA mass concentration. The diurnal variation of different OA factors compositions and their mass contributions are shown in (c) and (d).

Page 28 – Figure 7 and caption: why using "lg(ALWC)" instead of ALWC?

Reply: The ALWC simulated by ISORRIPIA increased dramatically for the conditions with RH > 95 %. The ALWC simulated for the conditions with RH > 95 % are higher 2-3 orders of those with RH ranging from 60-90 %. It is not obvious to observe the effect of ALWC on OOA if mapping the data points with ALWC directly, so we used the logarithm of ALWC to map the data points, which could show the variation of OOA with ALWC clearer.

Page 30 - Figure 9: Have height axis in meter might be easier for the reader

Reply: Thanks for the reviewer's suggestion. We have changed the height axis to height above ground level (AGL) in Figure 9.

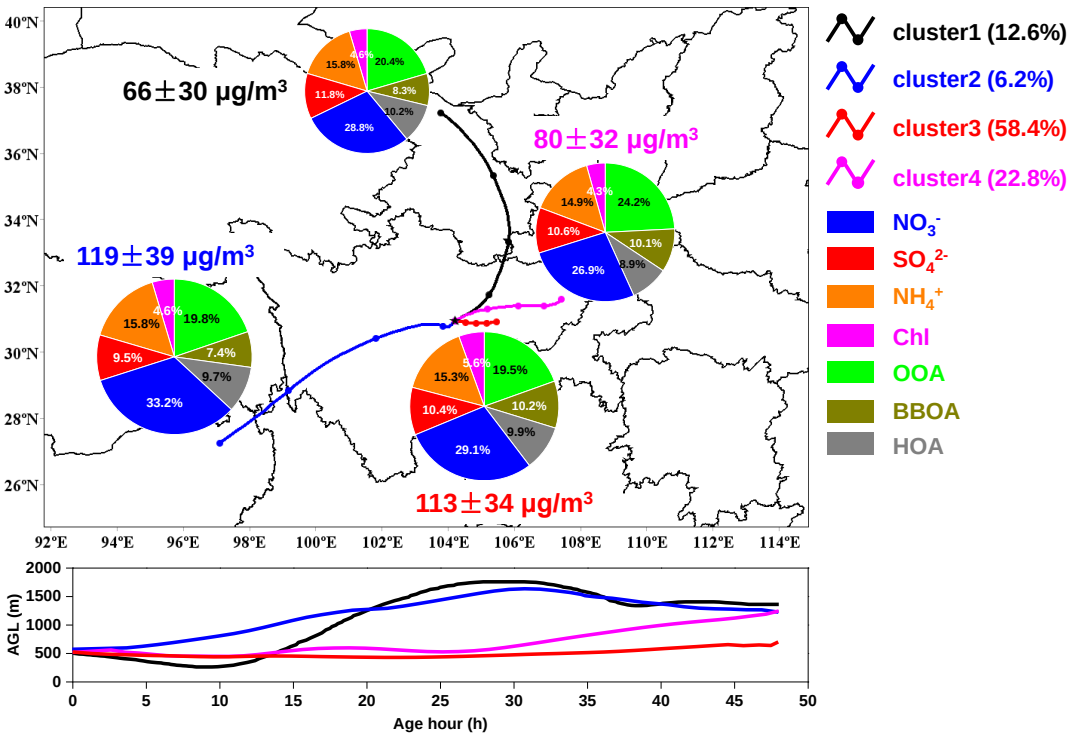

Fig. 9 Simulation results of 48 h backward air parcels cluster-mean trajectories during the campaign. The lines in black, blue, red, and purple represent the mean trajectories of Cluster1 to Cluster4, respectively. The pie charts show the average mass contribution of different chemical compositions to $PM_{2.5}$ for each cluster. The lower panel shows the height profile (above ground level, AGL) for different air parcels clusters along their transport paths.