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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*.

Comments from the reviewers:

Reviwer2

The authors reported measurement results of PM2.5 components at a site in Sichuan basin, China, using a time-of-flight aerosol chemical speciation monitor (ToF-ACSM). General results of the one-month campaign in winter 2021/2022 were presented with routine but rigorous data analysis tools. Three haze events, each accompanied with a foggy period, were selected for case studies to identify the reasons behind haze formation. The authors concluded that intensive biomass burning and rapid nitrate formation might be the reason behind the formation of those haze events. The study is in general well designed and properly conducted, and the manuscript is fairly well written. I therefore recommend Minor Revision before publication.

Reply: Thanks for the reviewer's positive comment. We hope that the results of the present study will improve our knowledge of the factors driving haze formation in SCB.

Main:

The authors tried to make a point in the title that "intensive" biomass burning and "rapid" formation "drive" severe haze formation in their campaign. Yet, I do not see clear evidence supporting such a statement. First, for biomass burning, BBOA contributed 20-30% to OA, and maybe 10-15% of NR-PM2.5 during haze events (Figure 10a). Yes, it is non-negligible, but I would not say that it drives the haze formation. In addition, I do not see evidence for "intensive" biomass burning during haze events. Maybe showing some fire spot data from satellite archive will help. Second, for nitrate, the

contribution of around 30% to NR-PM2.5 during haze events is of course quite substantial. But I do not see any evidence of "rapid" formation of nitrate. Maybe showing some cases of fast growing of nitrate concentrations in some haze events would help.

Reply: Thanks for the reviewer's suggestion. We have added the discussion of satellite observation results showing fire spots during the haze episodes in the manuscript. (lines 465 -467)

The fire maps (as illustrated in Fig. S8) showed that more fire spots during H2 and H3 were observed around Deyang compared to non-haze episodes, suggesting the biomass burning activities were more intensive during these haze episodes.

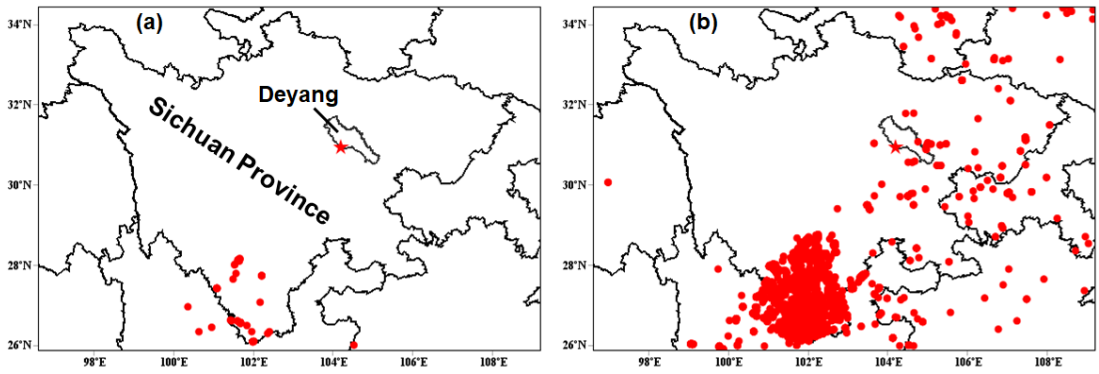

Fig. S8 Fire maps of areas around Deyang during (a) non-haze, (b) H2 and H3 periods. The Fire Maps were acquired from Fire Information for Resource Management System (FIRMS) developed by the National Aeronautics and Space Administration (NASA). The data of VIIRS (375m) was used (https://firms.modaps.eosdis.nasa.gov/active_fire/).

Also, as the reviewer suggested, we have added the growth rate of nitrate to support the fast nitrate formation during the evolution of haze pollution. (lines 450-457)

The average NO_3^- formation rate as a function of $PM_{2.5}$ concentration during H1 was depicted in Fig. S7. The NO_3^- formation rate increased fast as $PM_{2.5}$ concentration increased from 50 to 110 $\mu g/m^3$, which also showed the rapid formation of nitrate contributed to haze formation. In contrast, the average nitrate formation rates were below zero when the $PM_{2.5}$ concentration was < 130 $\mu g/m^3$ during H2 and H3, suggesting nitrate formation did not play an important role at the early stage of H2 and H3. Although the nitrate formation rate decreased when $PM_{2.5}$ concentration was > 110 $\mu g/m^3$ during H1, it remained positive, suggesting the nitrate concentration increased gradually.

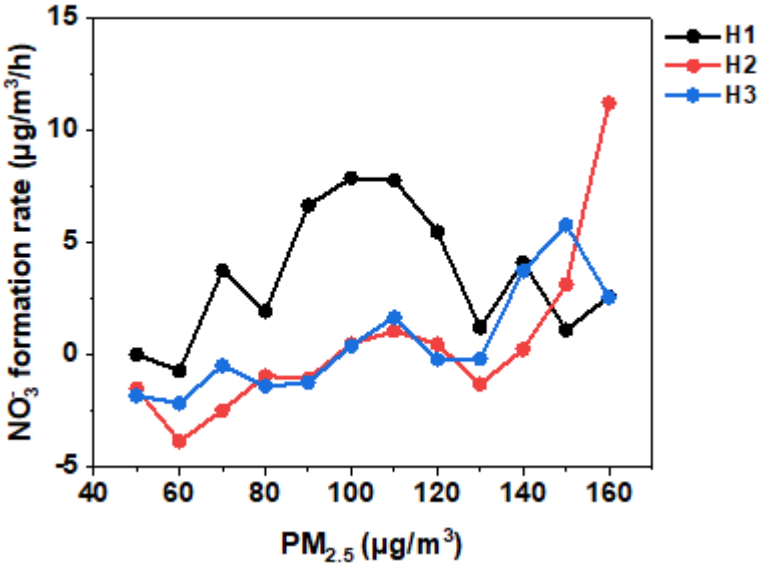

Fig. S7 Average nitrate formation rate as a function of $PM_{2.5}$ concentration during H1, H2 and H3

Sections 3.1 – 3.3 are quite routine and do not contribute much to the value of this study. I suggest shortening these three sections and focus on (expanding) discussion of the reasons behind haze formation (i.e., section 4).

Reply: Thanks for the reviewer's suggestion. As the reviewer suggests, we have cut some discussions on the diurnal variations of gaseous pollutants and PM2.5 chemical compositions. We have also shortened the discussion on nitrate formation during nighttime. Besides, we have added some discussions on the nitrate formation rate and fire spots to support the result of the rapid nitrate formation and biomass burning in section 3.5 as the reviewer suggests.

There are a few contradictory statements in the manuscript that I suggest the authors to resolve in the revision. For instance, it was suggested that aqueous-phase reaction was not important in OOA formation (L557), but in the discussion in L511 the authors suggested otherwise; the discussion on nitrate formation (L309-316) is interesting, but I do not follow 1) why the abundant ammonia can accommodate plenty of basic species (L310), and 2) how did the authors reach the conclusion that nitric acid was formed heterogeneously (which the authors thought that was not important in L290 and L303), and then take up ammonia?

Reply: Thanks for the reviewer's questions. Except that the average OOA concentration showed an increasing trend when ALWC < 200 μg/m^3 during nighttime, OOA concentration did not change significantly with increasing ALWC during both daytime and nighttime, suggesting the aqueous-

phase reactions were not significant pathway promoting OOA formation. In spite of this, it did not mean that aqueous-phase reactions did not occur during foggy periods. In fact, previous studies showed that SOA could be formed through aqueous-phase reactions under high RH conditions (Kuang et al., 2020; Duan et al., 2021). Thus, we thought that OOA could be formed through aqueous-phase reactions during foggy period, and offset the scavenging effect of fog droplets.

For the second and third questions, our description might be confusing and not appropriate. Since the atmosphere was under ammonium-rich conditions during nighttime, we deduced that wet particles would uptake NH_3 and neutralise HNO_3 subsequently, thus generating ammonium nitrate. However, the simulation results of Wen et al. (2018) showed that the NH_3 in excess would decrease the aerosol acidity and allow the reaction of NO_2^+ with Cl^- to happen during nighttime, hence restricting the formation of nitrate. Thus, the nitrate formation was primarily formed via the heterogeneous hydrolysis of N_2O_5, instead of the neutralisation between HNO_3 (aq, s) and NH_3 (g). As the other reviewer suggests, we have reconstructed this part in the revised manuscript. (lines 279-289)

The emission of NOx and SO_2 had been reduced while NH_3 increased in the past almost ten years, which resulted in the ammonium-rich condition in the atmosphere (Fu et al., 2017; Liu et al., 2018). In spite of this, a recent study showed that the nocturnal nitrate formation was not sensitive to NH_3, and even increased slightly as NH_3 decreased, which was likely due to the aerosol acidity effects on the partitioning of the nitrate formation (Wen et al., 2018). Thus, the fitting of $[NO_3^-]/[SO_4^{2-}]$ vs. $[NH_4^+]/[SO_4^{2-}]$ might not be applicable for identifying the nitrate formation process during nighttime. The average O_3 concentration was 13.7 μg/m^3 and average RH was 83.3 % during nighttime, which favoured the aqueous-phase reactions to occur. Higher nitrate concentration was observed with increasing ALWC during nighttime (as illustrated in Fig. S2), and so was NOR. This phenomenon further demonstrated the heterogeneous hydrolysis of N_2O_5 might dominate the formation of nocturnal nitrate.

Reference

Duan, J., Huang, R., Gu, Y., Lin, C., Zhong, H., Wang, Y., Yuan, W., Ni, H., Yang, L., Chen, Y., Worsnop, D. R., and O'Dowd, C.: The formation and evolution of secondary organic aerosol during summer in Xi'an: Aqueous phase processing in fog-rain days, Sci. Total Environ., 756, 144077,

https://doi.org/10.1016/j.scitotenv.2020.144077, 2021.

Kuang, Y., He, Y., Xu, W., Yuan, B., Zhang, G., Ma, Z., Wu, C., Wang, C., Wang, S., Zhang, S., Tao, J., Ma, N., Su, H., Cheng, Y., Shao, M., and Sun, Y.: Photochemical Aqueous-Phase Reactions Induce Rapid Daytime Formation of Oxygenated Organic Aerosol on the North China Plain, Environ. Sci. Technol., 54, 3849-3860, https://doi.org/10.1021/acs.est.9b06836, 2020.

Wen, L., Xue, L., Wang, X., Xu, C., Chen, T., Yang, L., Wang, T., Zhang, Q., and Wang, W.: Summertime fine particulate nitrate pollution in the North China Plain: increasing trends, formation mechanisms and implications for control policy, Atmos. Chem. Phys., 18, 11261-11275, https://doi.org/10.5194/acp-18-11261-2018, 2018.

Minor:

L30: add “processes” after “aqueous-phase”?

Reply: Thanks for the reviewer’s careful check. We have added “processes” after “aqueous-phase” in the revised manuscript. (line 30)

Nitrate formation was promoted by gas-phase and aqueous-phase oxidation, while sulphate was mainly formed through aqueous-phase process.

L61 and a few other places: citation format not in accordance with that of ACP.

Reply: Thanks for the reviewer’s careful check. We have corrected the citation format in accordance with the requirement of ACP in the revised manuscript.

L387: aqueous-state should be aqueous-phase?

Reply: Corrected. (lines 347-349)

OOA concentration did not change significantly with increasing ALWC during both daytime and nighttime, suggesting the aqueous-phase reactions were not a significant pathway toward OOA formation.

Figure 12: better to clearly indicate the site, and Deyang and Sichuan in the maps. It is hard to follow when they are referred to in L475-485.

Reply: Thanks for the reviewer's suggestion. We have adjusted the scale of the map in figure 12 and made it clear to distinguish Deyang and Sichuan

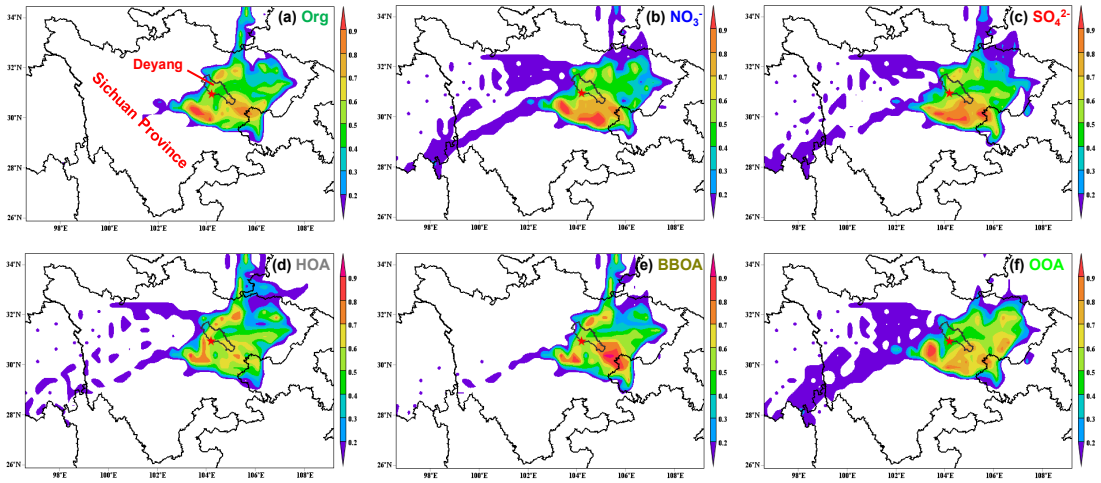

Fig. 10 Simulation results of PSCF for (a) organics, (b) nitrate, (c) sulphate, (d) HOA, (e) BBOA, and (f) OOA during the whole campaign. The 50th percentile of the concentrations for each composition (organics: 39.5 μg/m^3, nitrate: 27.8 μg/m^3, sulphate: 9.5 μg/m^3, HOA: 7.6 μg/m^3, BBOA: 8.7 μg/m^3, OOA: 15.2 μg/m^3) were used as thresholds in the PSCF analysis. The areas of Deyang and Sichuan Province are marked in (a).