

Manuscript No. ACP-2022-477

Title: 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:

Reviewer1:

The manuscript by Bao et al. present detailed observations of the chemical composition of PM_{2.5} in the Sichuan Basin (SCB), and the component responsible for the formation of haze during winter. The PM_{2.5} composition on site is driven by gas phase and aqueous-phase oxidation for nitrate, aqueous phase formation for sulfate, primary emission from Biomass burning and vehicle emissions and nitrate formation influenced by biomass burning. During fog events, primary organic aerosols were scavenged while secondary aerosol formation was enhanced by aqueous-phase reactions. The method applied and the case studies presented provide valuable knowledge on the species and mechanisms leading to haze and fog events in the SCB, but some restructuring and improvement in the discussion need to be addressed before publication.

General comments:

Page 11 lines 296-316: The discussion about night time nitrate formation is a bit confusing or not well constructed. During daytime, you attribute the nitrate formation to homogeneous reaction based on the fit of NO₃/SO₄ and NH₄/SO₄ molar ratios. Then, for night time, you conclude that aqueous reactions dominate nitrate formation based on the increasing trend of NO₃ with ALWC. Then you

justify not considering the fitting approach used for daytime based on the fact that NO_x and SO₂ emissions decreased and NH₃ emissions increased. Is the RH high throughout night time? Couldn't it mean that you have both homogeneous and heterogeneous reactions occurring? If you can show that "HNO₃ was firstly heterogeneously formed through the hydrolysis of N₂O₅, then excess NH₃ was uptake by wet particles and neutralised HNO₃ forming ammonium nitrate" dominate nitrate formation at night, then I would simply not mention the night time NO₃/SO₄ vs NH₄/SO₄ fitting. I suggest mentioning why it is not applicable first, and then talk about the aqueous reactivity because this could lead the reader to doubt the fitting relevance during daytime as well.

The regional transport discussion should be moved prior to the "Case studies for haze pollution" section as the content does not provide specific details or information that contribute to a better understanding of the haze episodes. And "Evolution of chemical composition during fog periods" would probably correspond more as the second subsection of "Case studies for haze pollution".

Reply: Thanks for the reviewer's good suggestion. As the reviewer mentions, the discussion of [NO₃⁻/SO₄²⁻] vs. [NH₄⁺/SO₄²⁻] fitting during night time indeed makes the fitting relevance during daytime doubtful. We have reconstructed the discussion of this part in the revised manuscript as the reviewer suggests, and added the part of discussion on the probable nocturnal nitrate formation pathways according to previous studies. (lines 273-292)

The intercept of the regression line on the [NH₄⁺]/[SO₄²⁻] axis was 1.56, which was close to 1.5, as suggested by Pathak et al. (2009), implying that the nitrate formation was mainly driven by the homogeneous reactions (Sun et al., 2011). Indeed, the nitrate concentration and nitrogen oxidation ratio (NOR = n(NO₃⁻)/[n(NO₂) + n(NO₃⁻)]) increased as the Ox concentration increased (as shown in Fig. 4), and exhibited a strong O₃/Ox ratio dependency, which further demonstrated the homogeneous daytime formation of nitrate.

The emission of NO_x and SO₂ had been reduced while NH₃ 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). Despite this, a recent study showed that the nocturnal nitrate formation was not sensitive to NH₃, and even increased slightly as NH₃ decreased, which was likely due to the aerosol acidity effects on the partitioning of nitrate (Wen et al., 2018). Thus, the fitting of [NO₃⁻]/[SO₄²⁻] vs. [NH₄⁺]/[SO₄²⁻] might not be applicable for identifying the nitrate formation process during

nighttime. The average O₃ concentration was 13.7 µg/m³ and the 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 implies the heterogeneous hydrolysis of N₂O₅ might dominate the formation of nocturnal nitrate. The results were consistent with the study of Tian et al. (2019), which showed that heterogeneous hydrolysis of N₂O₅ dominated nitrate formation during nighttime, while photochemical reactions also played an important role in nitrate formation during daytime in two megacities in Sichuan Basin.

As the reviewer suggests, we have put the discussion of regional transport before “Case studies for haze pollution” section. Also, we have put the “Evolution of chemical composition during fog periods” section as a subsection of “Case studies for haze pollution” in the revised manuscript.

Minor comments on manuscript:

Page 1 lines 21-23: “The fine aerosol chemical composition was characterised by using a time-of-flight aerosol chemical speciation monitor (ToF-ACSM) with the aim of inorganic and organic aerosol characterisation and source apportionment.” Please, rephrase.

Reply: Thanks for the reviewer’s careful check, we have rephrased this sentence in the revised manuscript. (lines 21-23)

The fine aerosol chemical composition was characterised by using a time-of-flight aerosol chemical speciation monitor (ToF-ACSM), which also provided detailed information on the sources for organic aerosols (OA).

Page 1 line 25: Please choose a more appropriate word than “occupied”

Reply: We have replaced this word with “took up” in the manuscript. (line 25)

The average concentration of non-refractory fine particles (NR-PM_{2.5}) was 98.5 ± 38.7 µg/m³, and organics aerosols (OA), nitrate, sulphate, ammonium, and chloride **took up** 40.3, 28.8, 10.6, 15.3 and 5.1 % of PM_{2.5}.

Page 3 lines 64-66: “The emission of SO₂ had been reduced dramatically over the past ten years in China; however, NO_x did not show a significant reduction.” Please add references to support these

trends.

Reply: Thanks for the reviewer's careful check. Relevant references have been added in the revised manuscript. (lines 65-66)

The emission of SO₂ had been reduced dramatically over the past ten years in China; however, NO_x did not show a significant reduction (Liu et al., 2019; Zhou et al., 2021).

Reference

Liu, M., Huang, X., Song, Y., Tang, J., Cao, J., Zhang, X., Zhang, Q., Wang, S., Xu, T., Kang, L., Cai, X., Zhang, H., Yang, F., Wang, H., Yu, J. Z., Lau, A. K. H., He, L., Huang, X., Duan, L., Ding, A., Xue, L., Gao, J., Liu, B., Zhu, T., 2019. Ammonia emission control in China would mitigate haze pollution and nitrogen deposition, but worsen acid rain. *Proceedings of the National Academy of Sciences* 116 (16), 7760-7765.

Zhou, W., Chen, C., Lei, L., Fu, P., Sun, Y., 2021. Temporal variations and spatial distributions of gaseous and particulate air pollutants and their health risks during 2015–2019 in China. *Environ. Pollut.* 272, 116031.

Page 3 line 68: “Compared to SIA, the formation process of SOA was more complicated (Chen et al., 2017).” Which formation process are you referring to? Or are you referring to SOA formation in general and therefore it includes multiple processes/pathways... As described later in the paragraph.

Reply: Sorry that we did not make this point clear. The “formation process” mentioned here refers to the multiple processes/pathways described in this paragraph.

Page 4 line 82: “was also suffering severe haze pollution”, if it is still happening, I would use present continuous tense.

Reply: Thanks for the reviewer's suggestion. The haze pollution is still a severe atmospheric problem in SCB, especially during winter. According to the report of ‘Sichuan Ecology and Environment Statement 2021’, the annual average PM_{2.5} concentration of Chengdu was ~40 µg/m³, which exceeded the grade II of National Ambient Air Quality Standard (AAQS, GB 3095-2012) (30

$\mu\text{g}/\text{m}^3$). We have changed the tense in the manuscript as the reviewer suggested. (line 83-85)

the Chengdu-Chongqing city cluster, located in the Sichuan Basin (SCB) in Southwest China, is also suffering severe haze pollution (Tao et al., 2017; Tan et al., 2019)

Page 5 line 148: “~84 cc/min” for consistency with previous flow (line 141) you should either write the equivalent value in L/min

Reply: Thanks for the reviewer’s suggestion. We have changed the flow rate of “~84 cc/min” to “~0.084 L/min” in the revised manuscript. (line 150)

Briefly, a 100 μm critical orifice and an aerodynamic lens were settled in the front inlet system to focus the ambient particles into a concentrated and narrow beam with a flow rate of ~0.084 L/min.

Page 7 – Data Process section: information on the elemental analysis with the TOF-ACSM is lacking.

Reply: We have added the information of the elemental analysis in the Data Process section in the revised manuscript. (lines 175-179)

The triangle plot of f44 (ratio of m/z 44 to total signal in the component mass spectrum) versus f43 (ratio of m/z 43 to total signal in the component mass spectrum) and f44 versus f60 (ratio of m/z 60 to total signal in the component mass spectrum) were applied to characterise the evolution of OA (Ng et al., 2010). The O/C and H/C were determined by the parameterization proposed by Canagaratna et al. (2015).

Reference

Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L., Donahue, N. M., DeCarlo, P. F., Lanz, V. A., Prévôt, A. S. H., Dinar, E., Rudich, Y., and Worsnop, D. R.: Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, *Atmos. Chem. Phys.*, 10, 4625-4641, <https://doi.org/10.5194/acp-10-4625-2010>, 2010.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and

Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, *Atmos. Chem. Phys.*, 15, 253-272, <https://doi.org/10.5194/acp-15-253-2015>, 2015.

Page 10 line 7: “planet boundary (PBL) height” I assume the “layer” is missing in that sentence.

Reply: Thanks for the reviewer’s check. Indeed, we left out “layer” in this sentence. We have deleted the discussion of the diurnal variation of gaseous pollutants and PM_{2.5} compositions in the revised manuscript as the other reviewer suggests. We have corrected it in other paragraphs in the revised manuscript. (lines 498-499)

Except for OOA and nitrate, all species kept decreasing during post-fog periods, which might be attributed to the increase of the planet boundary layer (PBL) height.

Page 10 line 261: You mention biomass burning as a source of Chloride. Any idea of fuel used or burning conditions?

Reply: The north and west of the observation site are croplands and villages. Crop residue (such as rice, wheat, rape and corn straws), wood with branches and leaves are commonly used as fuels for cooking and heating in the nearby villages. These biofuels are usually burned (flaming) in a cookstove and/or in a washbasin for cooking and heating, respectively (as shown in the figure below). We often saw the smoke of biomass burning in the morning and evening at the observation site.



Figure 1 Typical biomass burning for cooking in a cookstove in the villages.

Page 11 line 275: “If $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ linearly correlated with $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ under ammonium-rich conditions”, shouldn’t it be linearly correlated with “ $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ ”?

Reply: Thanks for the reviewer’s careful check. We have corrected it in the revised manuscript. (lines 259-260)

If $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ linearly correlated with $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ under ammonium-rich conditions ($[\text{NO}_3^-]/[\text{SO}_4^{2-}] \geq 1.5$)

Page 13 line 348: You mentioned that chloride is a biomass burning tracers and that these BB could be related to cooking and heating. Which of these sources would emit Cl^- ?

Reply: As discussed above, crop residues and wood with branches and leaves are commonly used for cooking and heating. Previous studies showed that wheat and rape straws burning (flaming) had high Cl^- emission factors (Hays et al., 2005; Engling et al., 2009), and the emission of these biofuels burning indeed contributed to high concentration Cl^- in SCB during the BB period (Tao et al., 2013). Although wood burning produced Cl^- , the amount of Cl^- emitted from wood burning was not as large as rice and wheat straws (Alves et al., 2011). Thus, cooking would contribute more Cl^- compared to heating, especially in the morning.

Reference

Alves, C., Gonçalves, C., Fernandes, A. P., Tarelho, L., and Pio, C.: Fireplace and woodstove fine particle emissions from combustion of western Mediterranean wood types, *Atmos. Res.*, 101, 692-700, <https://doi.org/10.1016/j.atmosres.2011.04.015>, 2011.

Engling, G., Lee, J. J., Tsai, Y., Lung, S. C., Chou, C. C. K., Chan, C., and Chan, K. C. C.: Size-Resolved Anhydrosugar Composition in Smoke Aerosol from Controlled Field Burning of Rice Straw, *Aerosol Sci. Tech.*, 43, 662-672, <https://doi.org/10.1080/02786820902825113>, 2009.

Hays, M. D., Fine, P. M., Geron, C. D., Kleeman, M. J., and Gullett, B. K.: Open burning of agricultural biomass: Physical and chemical properties of particle-phase emissions, *Atmos. Environ.*, 39, 6747-6764, <https://doi.org/10.1016/j.atmosenv.2005.07.072>, 2005.

Tao, J., Zhang, L., Engling, G., Zhang, R., Yang, Y., Cao, J., Zhu, C., Wang, Q., and Luo, L.: Chemical composition of PM_{2.5} 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.

Page 14 lines 369-373: “The average OOA concentration did not change significantly with increasing ALWC during daytime, suggesting the less contribution of aqueous state reaction to the formation of OOA. During nighttime, the average OOA concentration showed an increasing trend when ALWC < 200 µg/m³ and kept relatively constant subsequently, suggesting the aqueous-phase reactions did not significantly affect the formation of OOA” You can maybe shorten this part by saying that aqueous reactions are not significant pathway toward OOA formation during day- and night-time.

Reply: Thanks for the reviewer’s suggestion. We have shortened this part in the revised manuscript. (lines 345-349)

Except that the average OOA concentration showed an increasing trend when ALWC < 200 µg/m³ during nighttime, OOA concentration did not change significantly with increasing ALWC during both day- and nighttime, suggesting the aqueous-phase reactions were not significant pathway toward OOA formation.

Page 15 lines 403-405: “Higher RH was observed for those data points within the region of aged BBOA in the f₄₄ vs. f₆₀ space”. Although, I agree that BBOA oxidation probably occurs in the aqueous phase, in Figure 8, it seems that the RH is high for most of the points falling in the f₄₄ vs f₆₀ triangle, except for the data with f₄₄ > 0.15 and 0.08 > f₆₀ > 0.05, where the RH seems lower. Also is there a reason behind using RH here instead of ALWC as used in the previous comparison?

Reply: It is a good question. We take the region of aged BBOA in the f₄₄ vs. f₆₀ reported by Paglione et al. (2020) as reference (as shown in the figure below). It can be found that most of the data points (including those with f₄₄ > 0.15 and 0.08 > f₆₀ > 0.05 as the reviewer mentions) in the present study are within this region and correspond to high RH conditions. It seems that our description might confuse the readers. We have made the description clearer in the revised manuscript. (lines 378 -

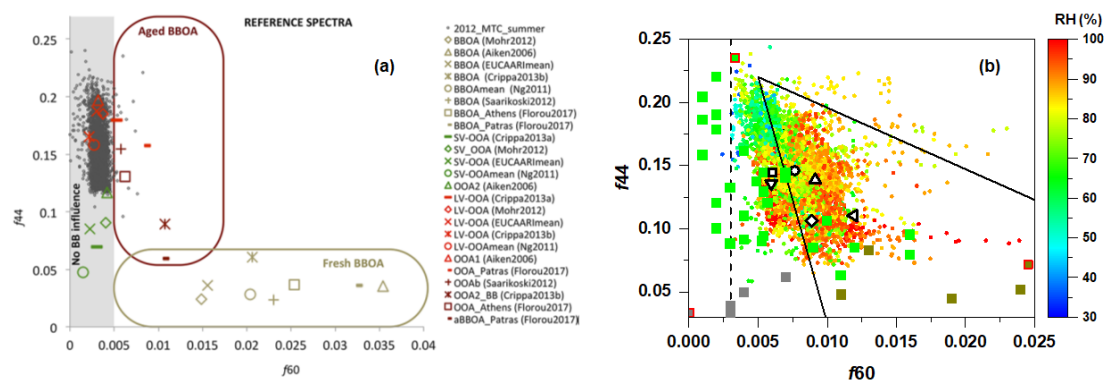


Figure 1 Triangle plots of f_{44} vs. f_{60} (a) reported by Paglione et al. (2020) and (b) in the present study. The ranges of f_{44} and f_{60} for 'Aged BBOA' and 'Fresh BBOA' are marked in (a).

The main reason why the data points in Figure 8(d) are mapped with RH instead of ALWC is that 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 RH to map the data points. However, the reviewer's suggestion reminds us that we can use the logarithm of ALWC to map the data points. We have changed $\lg(\text{ALWC})$ with RH in figure 8(d) in the revised manuscript.

Compared to the effects of Ox, the increasing ALWC did not seem to push f_{60} to the left upper region. Most of the data points, which corresponded to high ALWC, were within the region of aged BBOA in the f_{44} vs. f_{60} space as defined previously by Paglione et al. (2020), indicating the probable aqueous-phase oxidation of BBOA.

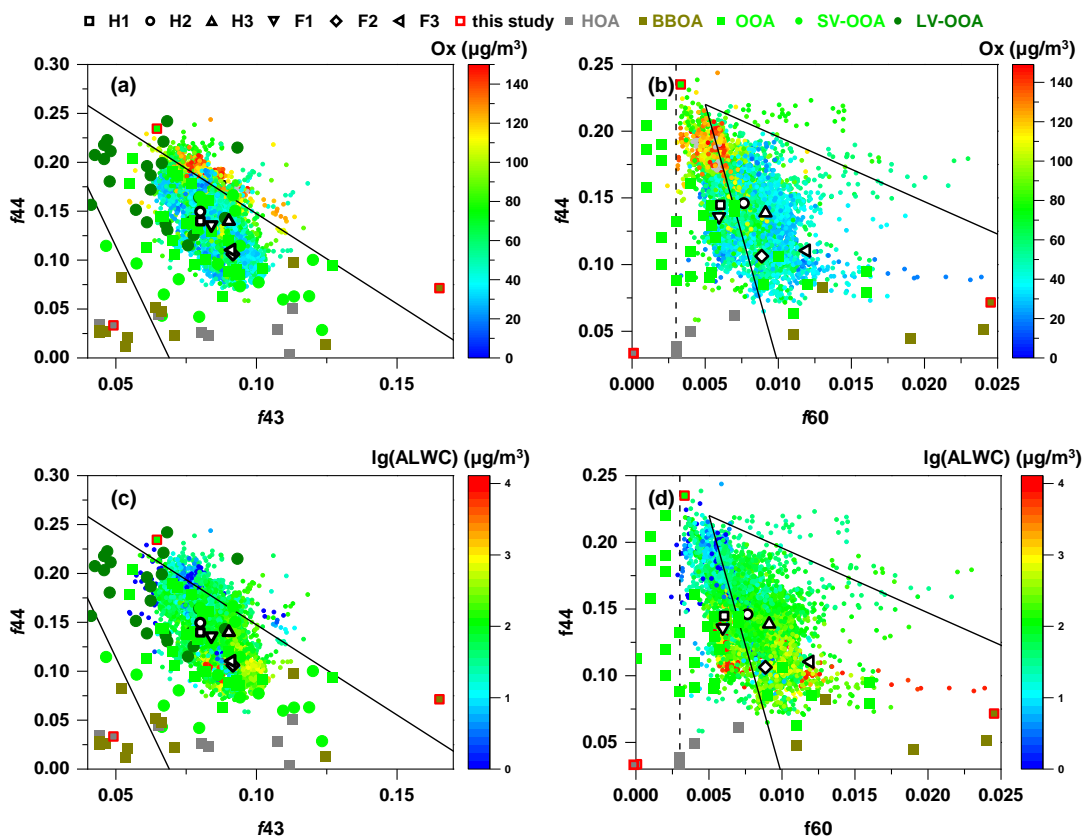


Fig. 8 Triangle plots of (a), (c) f44 (ratio of m/z 44 to total signal in the component mass spectrum) vs. f43 (ratio of m/z 43 to total signal in the component mass spectrum), and (b), (d) f44 vs. f60 (ratio of m/z 60 to total signal in the component mass spectrum) during the whole campaign. The colour scale in (a) and (b) represents Ox concentration, and that in (c) and (d) represents lg(ALWC). The solid lines in (a) and (c) are derived from the results reported by (Ng et al., 2010). The dashed line representing the background value of secondary aged OA and the solid guidelines in (b) and (d) are derived from (Cubison et al., 2011). The f44 vs. f43 and f44 vs. f60 for different OA sources reported in previous studies are also shown (Kim et al., 2019; Ng et al., 2011; Paglione et al., 2020; Wang et al., 2016; Zhao et al., 2019).

Page 16 line 428: change “Table S2” to Table S3.

Reply: Corrected. (line 431)

The synoptic conditions and aerosol chemical composition for each haze episode were summarised in Table. S3.

Page 17 line 460 and after: as a cluster represent several “air masses”, the plural form is probably

more adapted, especially that you use “air parcels” later on in the paragraph.

Reply: Thanks for the reviewer’s suggestion. We have replaced “air mass” with “air parcels” throughout the revised manuscript.

Page 18 PSCF discussion: more details about the threshold value used could be added in the text or in Figure 12.

Reply: Thanks for the reviewer’s suggestion. We have added the details of the threshold values used in Figure 12 in the revised manuscript. (lines 642-658)

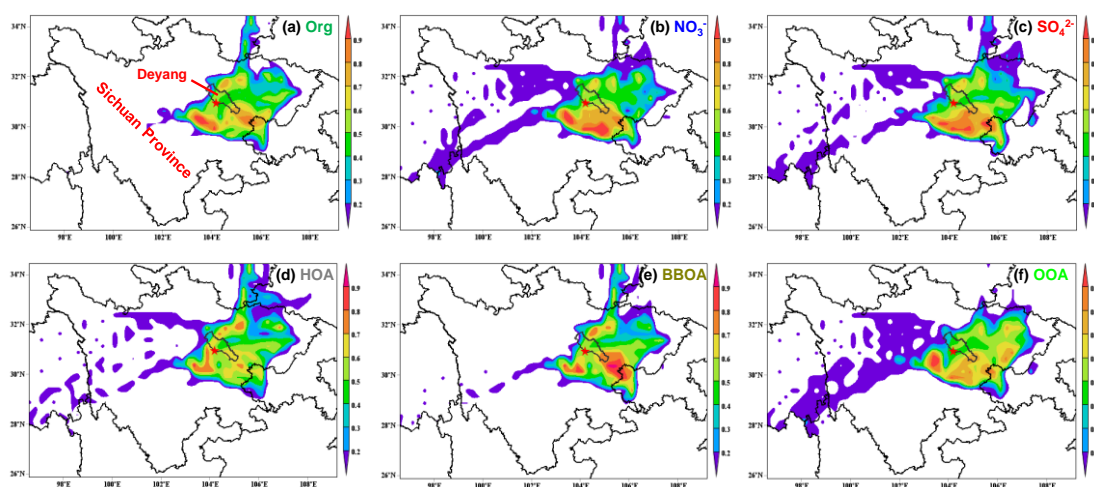


Fig. 10 Simulation results of PSCF for (a) organics, (b) nitrate, (c) sulphate, (d) HOA, (e) BBOA, and (f) OOA during the whole campaign. The 50th percentile of the concentrations for each composition (organics: 39.5 $\mu\text{g}/\text{m}^3$, nitrate: 27.8 $\mu\text{g}/\text{m}^3$, sulphate: 9.5 $\mu\text{g}/\text{m}^3$,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

Page 20 lines 534-540: “The average elemental O:C showed an increasing trend from pre-fog periods to post-fog/foggy periods, while H:C did not change significantly for different fog events, suggesting the OA became more oxidised. As shown in Fig. S6, 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. As a consequence, the O:C increased in line with the increased contribution of OOA.” The O:C and H:C could be added to Figure S6

Reply: Thanks for the reviewer’s suggestion. The O:C and H:C have been added in Figure S6 in the revised supplementary information.

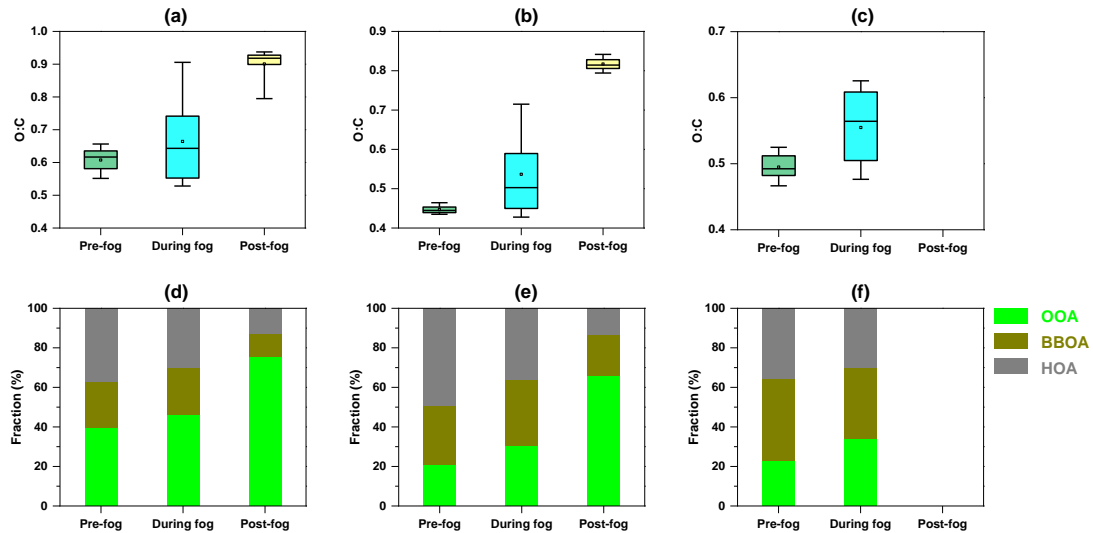


Fig. S9 Variation of O:C of OA and relative contribution of OOA, BBOA, and HOA to OA during the evolution of (a), (d) F1, (b), (e) F2, and (c), (f) F3.

Figure 2 would benefit from a different (perhaps lighter) background as the yellow makes it difficult to distinguish between SO₄, NH₄ and Chl.

Reply: Thanks for the reviewer's suggestion. The colour of the background has been replaced with a lighter one.

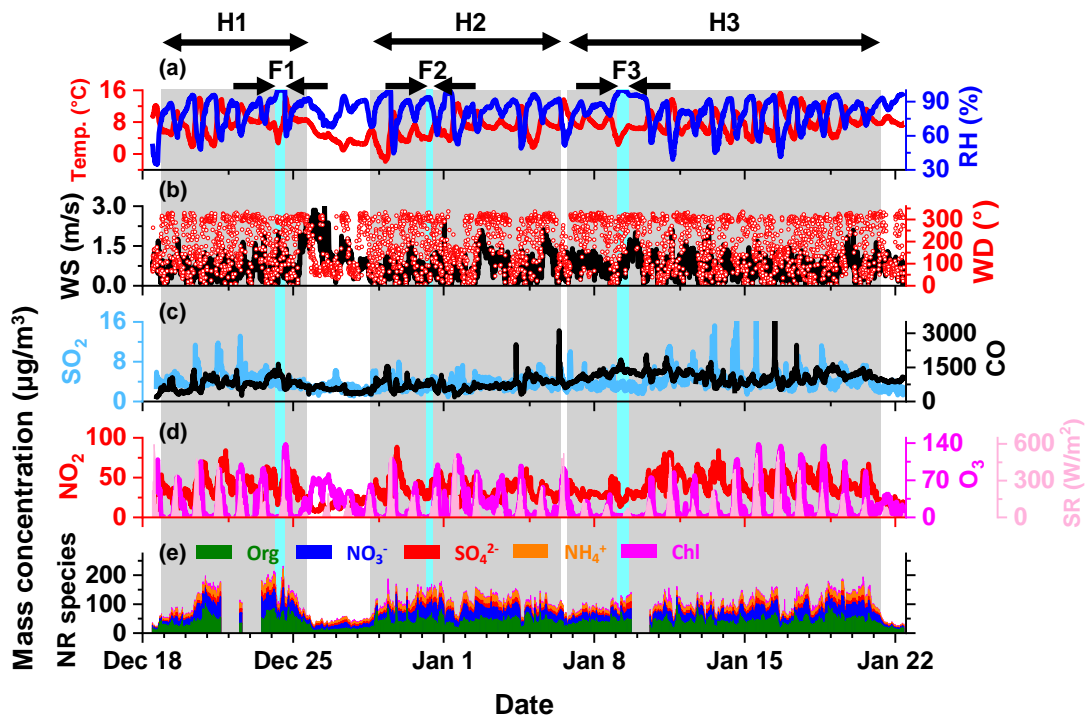


Fig. 2 Time series of (a) relative humidity (RH) and temperature (T); (b) wind direction and wind

speed; (c), (d) CO, NO₂, SO₂, and O₃ mass concentrations and solar radiation; (e) mass concentration of organics, nitrate, sulphate, ammonium, and chloride in NR-PM_{2.5}. The yellow-shaded areas represent the intervals of H1, H2, and H3, respectively. The light blue-shaded areas represent the intervals of F1, F2, and F3, respectively.

Figure 3: As you discuss day/night time nitrate formation and the effect of RH at night, could you perhaps add RH diurnal variation. Or a figure with the diurnal cycles of meteorological parameters and PBL could be added in the supplement.

Reply: Thanks for the reviewer's suggestion. Since the discussions of diurnal variations of PM_{2.5} compositions and meteorological parameters have been deleted in the revised manuscript. We put the diurnal cycles of PM_{2.5} chemical compositions, gaseous pollutants, meteorological parameters and PBL together in the supplementary information.

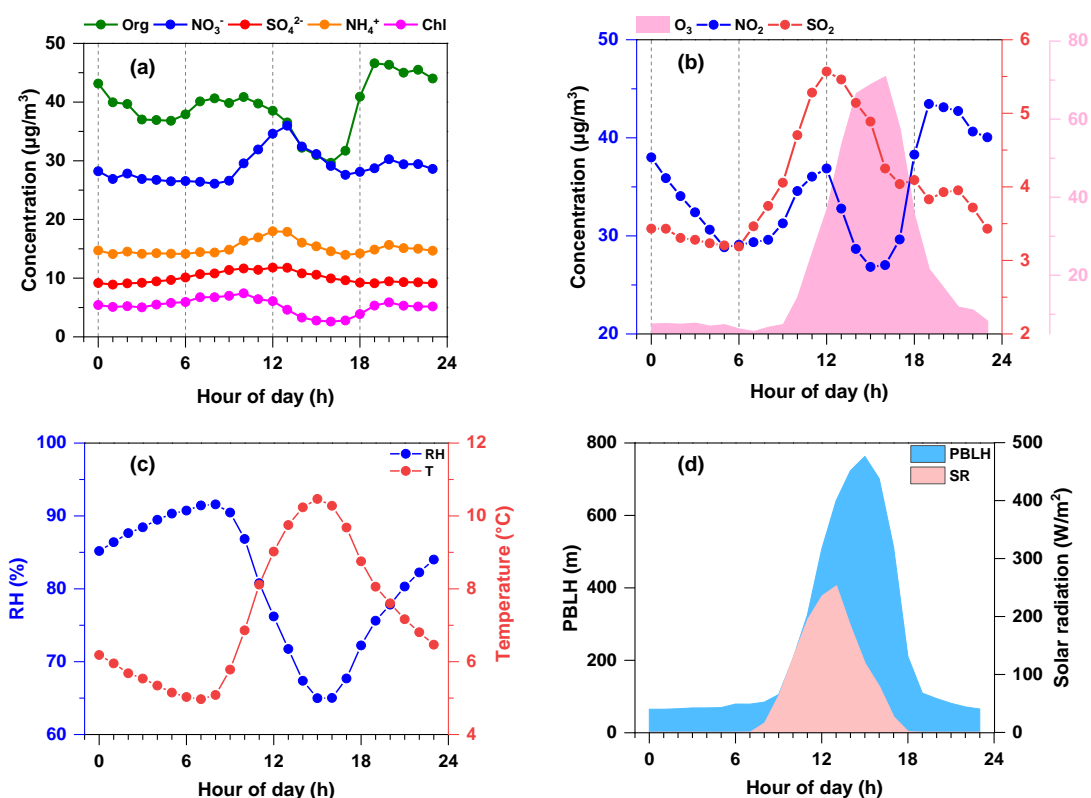


Fig. S3 Diurnal variations of (a) chemical composition in NR-PM_{2.5}, (b) O₃, NO₂, and SO₂, (c) RH and temperature, (d) planet boundary layer height (PBLH) and solar radiation (SR). The PBLH was derived from the European Centre for Medium-Range Weather Forecasts (ECMWF) dataset of ERA5 hourly data (<https://cds.climate.copernicus.eu/cdsapp#!/home>).

Figure 6: it would be helpful to add some background to evidence the fog periods on the time series of the OA sources.

Reply: Thanks for the reviewer's suggestion. We have added backgrounds to mark fog periods.

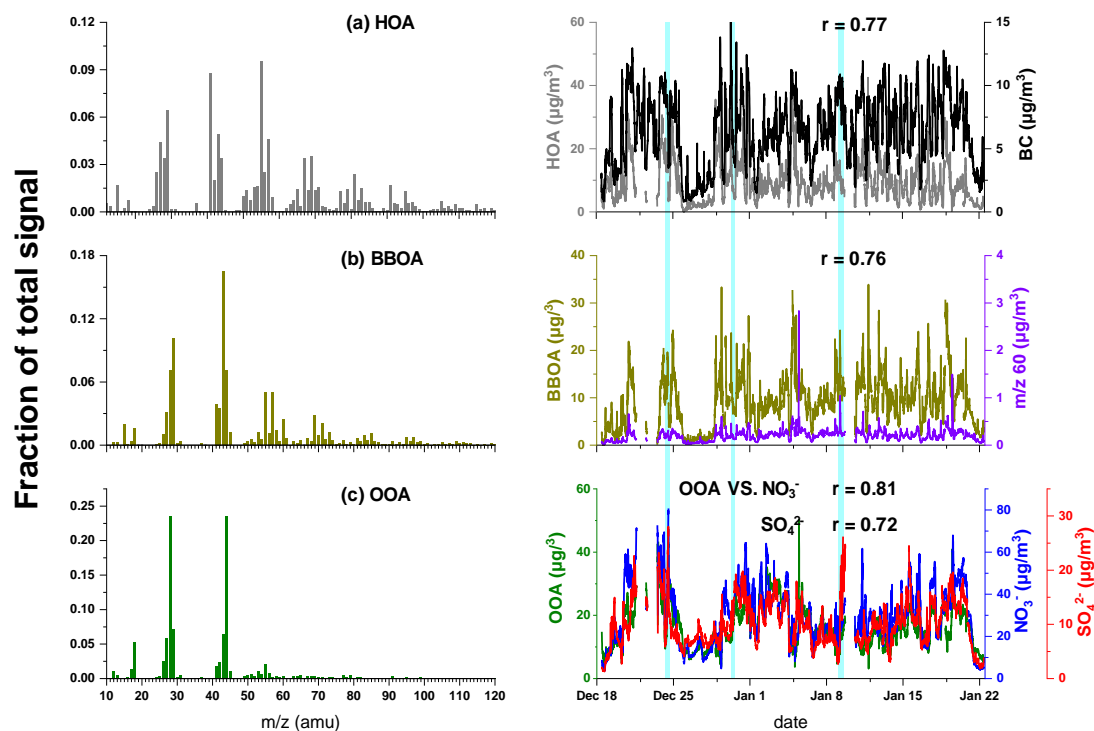


Fig. 5 Mass spectrum of (a) HOA, (b) BBOA, and (c) OOA resolved by PMF. The time series of each OA source and corresponding tracers are depicted in the right panel. The light blue shaded areas represent the intervals of foggy periods.

Minor comments on supplement:

Page 3 Figure S2: It may be easier to use a lighter blue for nitrate as the mean is hard to distinguish.

Could the dataset be separated between day/night time as it supports the discussion between secondary inorganic aerosol day/night formation?

Reply: Thanks for the reviewer's suggestion. We have changed the colour of nitrate to a lighter blue in the relevant figures. Also, we have separated the dataset into day- and nighttime ones to show the difference of SIA formation during day- and nighttime.

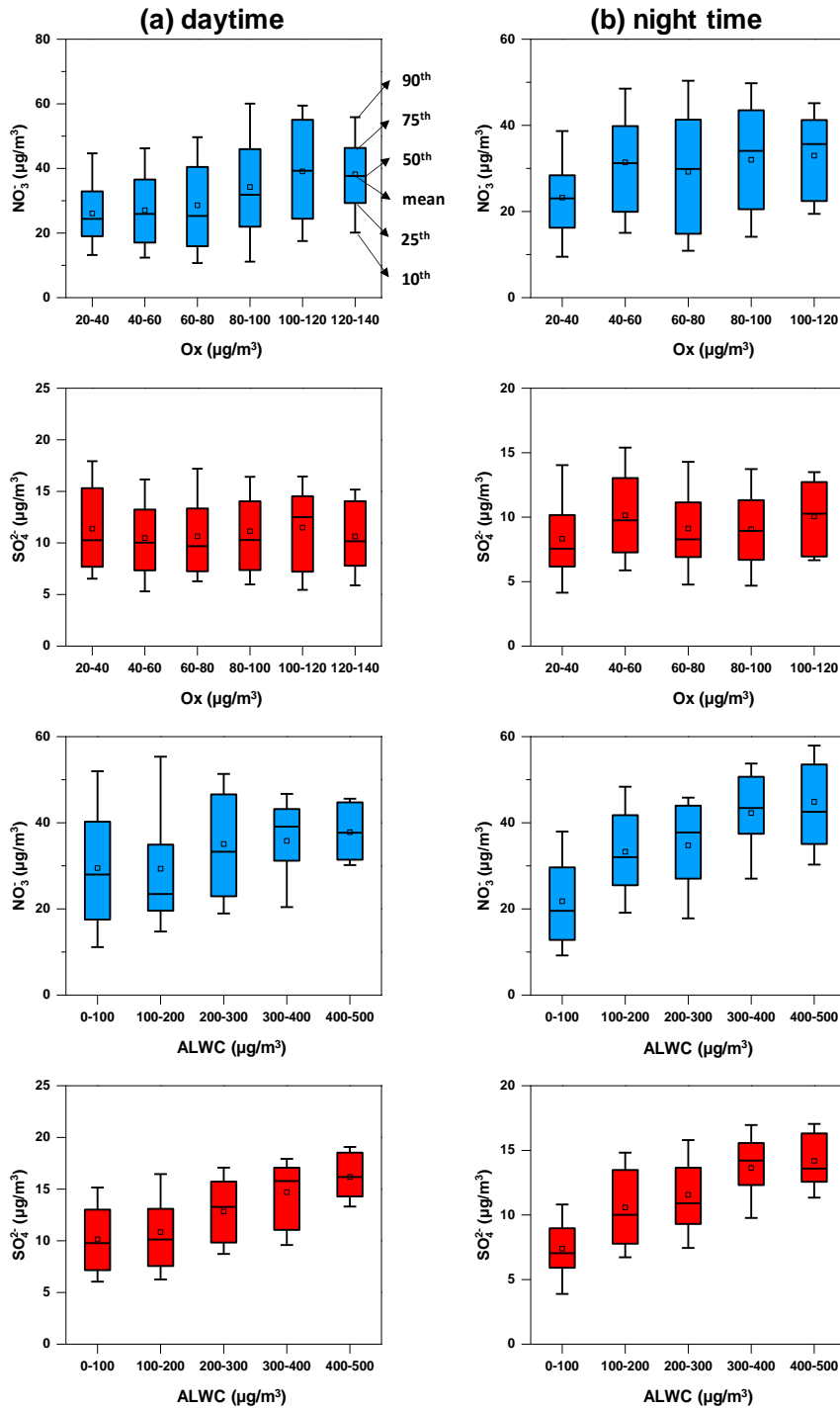


Fig. S1 Variation of nitrate and sulphate as Ox/ALWC increases during (a) daytime (left column) and (b) nighttime (right column). The data of nitrate and sulphate concentrations were grouped into different bins according to 20 µg/m³ increment of Ox, and 100 µg/m³ increment of ALWC. The mean (square), 50th (horizontal line inside the box), 25th and 75th percentiles (lower and upper box), and 10th and 90th percentiles (lower and upper whiskers) of the box chart are marked in (a).

Reviewer2

The authors reported measurement results of PM_{2.5} 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-PM_{2.5} 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-PM_{2.5} 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.

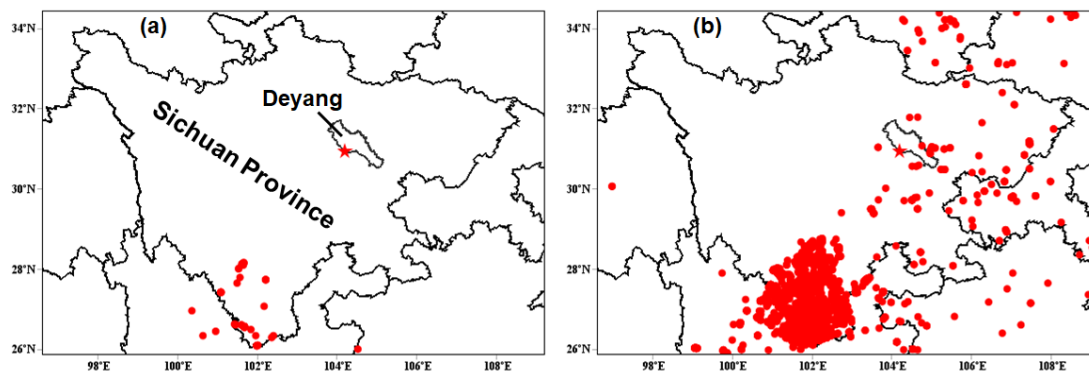


Fig. S8 Fire maps of areas around Deyang during (a) non-haze, (b) H2 and H3 periods. The Fire Maps were acquired from Fire Information for Resource Management System (FIRMS) developed by the National Aeronautics and Space Administration (NASA). The data of VIIRS (375m) was used (https://firms.modaps.eosdis.nasa.gov/active_fire/).

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 $\text{PM}_{2.5}$ concentration during H1 was depicted in Fig. S7. The NO_3^- formation rate increased fast as $\text{PM}_{2.5}$ concentration increased from 50 to 110 $\mu\text{g}/\text{m}^3$, which also showed the rapid formation of nitrate contributed to haze formation. In contrast, the average nitrate formation rates were below zero when the $\text{PM}_{2.5}$ concentration was < 130 $\mu\text{g}/\text{m}^3$ 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 $\text{PM}_{2.5}$ concentration was > 110 $\mu\text{g}/\text{m}^3$ during H1, it remained positive, suggesting the nitrate concentration increased gradually.

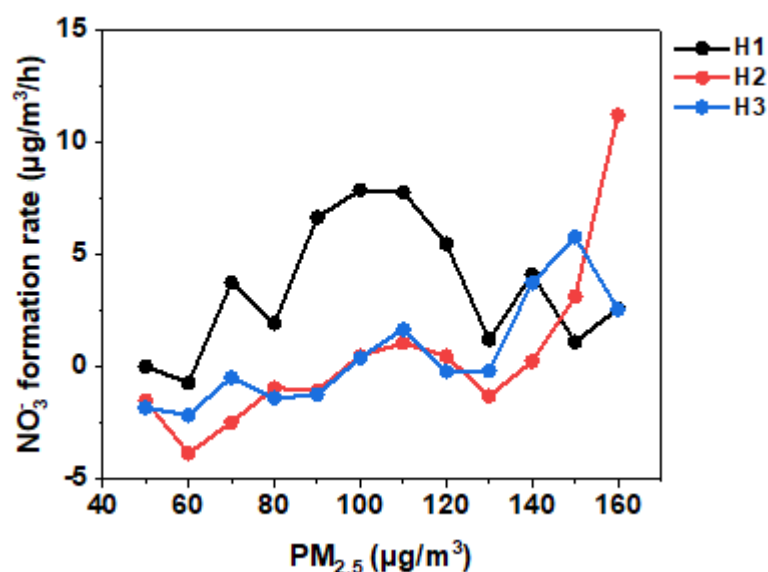


Fig. S7 Average nitrate formation rate as a function of PM_{2.5} concentration during H1, H2 and H3

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 PM_{2.5} 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/m³ 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 NO_x 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 $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ vs. $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ might not be applicable for identifying the nitrate formation process during nighttime. The average O_3 concentration was $13.7 \mu\text{g}/\text{m}^3$ 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

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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.

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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

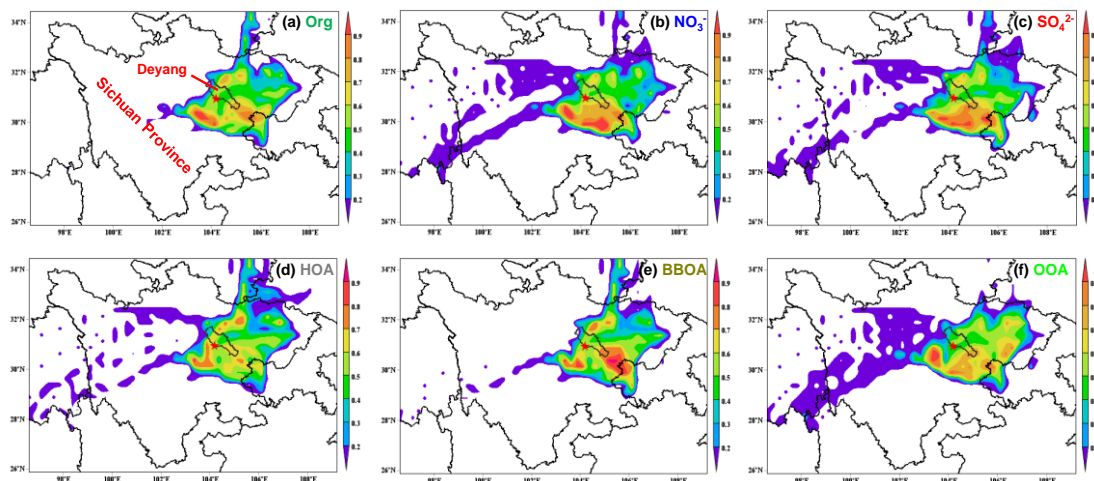


Fig. 10 Simulation results of PSCF for (a) organics, (b) nitrate, (c) sulphate, (d) HOA, (e) BBOA, and (f) OOA during the whole campaign. The 50th percentile of the concentrations for each composition (organics: 39.5 $\mu\text{g}/\text{m}^3$, nitrate: 27.8 $\mu\text{g}/\text{m}^3$, sulphate: 9.5 $\mu\text{g}/\text{m}^3$,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