Response to Referee #1

General comments:

This paper uses an SP-L-ToF-AMS to study the OA sources and SOA formation in urban Xi'an during winter 2018. The authors used AMS source apportionment techniques to study the contribution of different types/sources to OA and performed correlational analysis to identify key factors on the observed trends of different OA. They further focus on OOA derived from biomass burning (OOA-BB) and aq-OOA from aqueous reactions. In particular, aq-OOA was found to be dependent on SIA content and ALWC. The use of AMS type instruments for source apportionment analysis and the identification of SOA is quite routine now. POAs (HOA, COA, CCOA, BBOA etc) have been regularly identified. The observations of different types of OOAs, their VK plot characteristics and OSc trends are also widely reported. While the paper is a robust AMS "Measurement Report", I am most interested in the interplay between sulfate and nitrate and SOA formation, especially under different environments, BBOA dominant vs. aqueous phase chemistry dominant. Below I highlight a few comments for the consideration of the authors.

Response: We thank the referee to review our manuscript and particularly for the valuable comments and suggestions that are very helpful in improving the manuscript. We agree with the referee that the use of AMS type instruments for source apportionment analysis and the identification of SOA is routine now. However, multiple control measures have been implemented in Xi'an in recent years and aerosol composition is expected to have large variations, while direct elucidation and characterization are lack. In our study, PM_{2.5} composition was measured during the heating season of 2018 in Xi'an using a long-time-offlight AMS (LToF-AMS). Chemical composition and OA sources were analyzed and compared with those resolved in 2013 winter in Xi'an (Elser et al., 2016), in order to elucidate the aerosol variation in recent years due to emission controls. Our results indicated that the formation of OOA-BB was more favorable in the days with larger OA fraction and higher BBOA concentration. In comparison, aq-OOA was more dependent on SIA and ALWC. In particularly, the concentration of aq-OOA was not continuously increasing when ALWC increased from 10- $100 \ \mu g \ m^{-3}$ to >100 $\ \mu g \ m^{-3}$. Instead, the aq-OOA concentration was much affected by the mass increase of nitrate and sulfate, with similar aq-OOA concentration associated with similar sulfate or nitrate concentration level under different RH ranges, suggesting that SIA may play a much important role in the formation of aq-OOA in winter Xi'an. These results will further complete our understanding of SOA formation. We provide below point-by-point responses to the referee's comments. We also have made most of the changes suggested by the referee in the revised manuscript.

Page 4 line 135, what is the justification of using C2H3O+ as an identifier of OOA-BB? Also, the close relationship between BBOA and OOA-BB without much time lag can also mean that the OOA-BB measured could be a result of oxidation occurring very close to the source of the

burning instead of the result of atmospheric aging under "environmental conditions". Can the authors examine their data in more details or literature to address this issue? My main concern is that atmospheric aging does take time and a time lag is expected.

Response: We thank the referee's comment. m/z 43 (mainly C₂H₃O⁺) is an indicator of less oxidized oxygenated organics, while m/z 44 (mainly CO₂⁺) is an indicator of more oxidized oxygenated organics (Canonaco et al., 2015; Wang et al., 2017). The tight correlation between the time series of C₂H₃O⁺ and OOA-BB indicate its less oxidized property. And its source influence from biomass burning was further identified by the correlation between OOA-BB and BBOA as well as the formation mechanism discussed in section 3.2.

Meanwhile, we have also examined our data in more details, and found that although moderate correlation was observed between the time series of OOA-BB and BBOA ($R^2=0.59$), lags and differences between their time series were observed for certain periods (Fig. R1), as expected by the referee. However, as the chemical processes and atmospheric aging are influenced by many parameters such as meteorology, Ox concentration, solar radiation, the time lag between OOA-BB and BBOA was not consistent and showed variations over the entire measurement period.

In the revised manuscript page 10 lines 303-305, we have now added the sentence ".....Note that although moderate correlation was observed between the time series of OOA-BB and BBOA, lags and differences between their time series were observed, suggesting the atmospheric aging under environmental conditions".



Fig. R1 Time series of BBOA and OOA-BB during the measurement.

Page 7 line 213, did the SOA concentration increase? An increase in SOA% could be due to lower POA.

Response: We thank the referee for pointing this out. We checked the data and found that the average SOA concentration observed in our measurement (21.8 μ g m⁻³) was higher than that observed during reference days (5.4 μ g m⁻³), while lower than that during extreme haze (47.0 μ g m⁻³) in the winter of 2013 in Xi'an (Elser et al., 2016). To be more accurate, in the revised manuscript page 9 lines 276-278, we have now deleted ".....suggesting enhanced formation of SOA in recent years", and the sentence now reads "The contribution of SOA was much higher than that observed in the winter of 2013 in Xi'an (16%, 5.4 ± 8.9 μ g m⁻³ in reference days and 31%, 47.0 ± 12.0 μ g m⁻³ in haze days, respectively) (Elser et al., 2016)".

Page 7 line 221, what is the typical time scale for such BBOA reactions to form OOABB? Is it reflected in the correlation of time-lag profile of OOA-BB with time profile of BBOA? **Response:** We thank the referee's comment. In response above, time lag and difference between the time series of OOA-BB and BBOA were observed (Fig. R1). However, as the chemical processes and atmospheric aging are influenced by many parameters such as meteorology, Ox concentration, solar radiation, the time lag between OOA-BB and BBOA was not consistent and showed variations over the measurement.

Page 10 Fig.4, why was the slope larger at low RH? It is interesting and the authors should explain. The size of the symbols is meant to show the SIA concentration. But what is the scale? **Response:** We thank the referee's suggestion. As we discussed on page 14 lines 431-439 in the revised manuscript, the correlation slope (S) between aq-OOA and ALWC decreased from 0.74 for RH <70% to 0.12 for RH >90%, which means that when the ALWC exponentially increased with high RH, aq-OOA did not increase proportionally, and the slope decreased. In comparison, similar aq-OOA concentration was associated with similar SIA concentration levels under different RH ranges. These results suggest that SIA may play a much more important role in the formation of aq-OOA in winter Xi'an.

In addition, we have now added the scale of symbols to show the SIA concentration in Fig. 5 in the revised manuscript (see Fig. R2 below). Note the figure has also been updated according to suggestions from the other referee.



Fig. R2 The effects of ALWC on the formation of aq-OOA colored by RH, with the increase of SIA concentration shown as the size increase of the data points. Note "S" is defined as the slope between aq-OOA and ALWC in different RH ranges.

Page 10, line 295, as sulfate and nitrate increased, the aqOOA also increased to the same high level at some different ALWs. So, within certain range of ALW, its increase correlates with aqOOA increase. But at a very large increase of ALW, it does not give much higher max of aqOOA. What are the reasons for this?

Response: We thank the referee's comment. Condensed water would facilitate the partitioning of water-soluble, polar organics into condensed phases, and subsequent aqueous- phase SOA formation (Wu et al., 2018), thus within a certain range of ALWC, its increase correlates with aq-OOA increase. However, as we further discussed in Figs. 5 and 6 in the revised manuscript, the concentration of aq-OOA was not continuously increasing with a large increase of ALWC from 10-100 μ g m⁻³ to >100 μ g m⁻³. Instead, the aq-OOA concentration was much affected by the mass increase of nitrate and sulfate, with similar aq-OOA concentrations associated with similar sulfate or nitrate concentration level under different RH ranges. This further suggested that SIA may play a much more important role in the formation of aq-OOA in winter Xi'an.

Page 11 Fig. 5, the summer data are from Duan et al., (2021) should be stated in the captions. Also in Fig. 5, what are the scales for nitrate and sulfate concentrations?

Response: Change made. In the revised manuscript, the summer data from Duan et al. (2021) has been stated in the caption of the figure, and the scales of symbols to show the sulfate and nitrate concentrations are also added (see Fig. R3 below).



Fig. R3 Correlations between ALWC and aq-OOA, colored by RH during summer (a, b) and winter (c, d) in Xi'an. The effects of nitrate and sulfate are also shown in (a, c) and (b, d), respectively, in which the increase of sulfate or nitrate concentration is shown as the size increase of the data points. The summer data was from Duan et al. (2021), and the horizontal axes both in summer and winter were shown in exponential type for comparison.

More discussions on the role of sulfate and nitrate in Aq-OOA formation are needed. Do you see sulfate and nitrate playing other roles, e.g. nitrate photolysis, beyond ALW in the formation of Aq-OOA? Do you see a difference between daytime and nighttime trend?

Response: We thank the referee's suggestion. As we discussed in the manuscript, SIA may play

a much more important role in the formation of aq-OOA in winter Xi'an. We agree with the referee that more discussion on the role of sulfate and nitrate in aq-OOA formation is needed for improving the manuscript, such as nitrate photolysis. The photolysis of nitrate can produce in-particle oxidants including OH radicals, NO₂ radicals, and N(III) (NO₂/HONO) under sunlight, which has been found to contribute to sulfate formation and may also play a role in aq-OOA formation (Chen et al., 2021). As suggested by the referee, we further analyzed correlations between ALWC and aq-OOA influenced by sulfate or nitrate between daytime (8:00-18:00) and nighttime (19:00-7:00) in the winter campaign (Fig. R4), and found that similar trends were observed between daytime and nighttime. In addition, similar aq-OOA concentrations were also observed between daytime $(12.6 \pm 12.1 \mu \text{g m}^{-3})$ and nighttime $(12.8 \pm$ 13.0µg m⁻³). This suggests that nitrate photolysis under sunlight and nocturnal reactions such as NO₃ radical oxidation might play roles in the aq-OOA formation in daytime and nighttime, respectively, which results in the comparable increase of aq-OOA concentration between daytime and nighttime, and complicates this correlation analysis based on field data. Actually, we plan to conduct the nitrate photolysis as well as nocturnal chemistry effects in a laboratory in the future to further investigate the aq-OOA formation.



Fig. R4 Correlations between ALWC and aq-OOA colored by RH during daytime (a, b) and nighttime (c, d) in winter. The effects of nitrate and sulfate are also shown in (a, c) and (b, d), respectively, in which the increase of sulfate or nitrate concentration is shown as the size increase of the data points. The horizontal axes both in daytime and nighttime were shown in exponential type for comparison.

Similarly, do you see any correlation between BBOA and sulfate formation? There are a lot of recent interesting work suggesting that BBOA can form sulfate during its atmospheric aging **Response:** We thank the referee's suggestion. We further analyzed the correlation between BBOA and sulfate (Fig. R5), as suggested by the referee. A weak correlation was observed

 $(R^2=0.08)$ between BBOA and sulfate, which might suggest that BBOA played a minor influence on the sulfate formation in our winter campaign in Xi'an.



Fig. R5 Correlation between the time series of BBOA and sulfate during the winter campaign.

Response to Referee #2

General Comments

Duan and coauthors discuss the sources and processes contributing to organic aerosol (OA) composition in a recent Xi'an, China winter. Along with a general presentation of the aerosol characteristics, the observations were contrasted with the group's prior work in summer and in winter several years prior. A particular focus is on the aged biomass burning and aqueous processing contributions to the aerosol. The connection between various variables during two periods with high SIA concentrations is used to demonstrate both new and established observations about the fraction of the OA that was formed via aqueous processing.

My main suggestion is to add additional context and interpretation based on prior literature, both in the introduction and within the Results and Discussion. In some cases, proper attribution of ideas to prior work must also be added. The organization of the paper is good, but consolidating the many small figures and re-organizing the content in the final section of the Results and Discussion would improve the paper substantially. Some additions to the methods section, updates to grammar, and clarifications of results presented are needed.

Overall, the quality of the content and organization is quite good, and I recommend this paper for publication with minor revisions.

Response: The authors thank the referee to review our manuscript and particularly for the constructive comments and suggestions that are very helpful in improving the manuscript. All concerns have been carefully addressed. Below is our point-by-point response to each comment. We also have made most of the changes suggested by the referee in the revised manuscript.

Specific Comments

1. Major Content Suggestions:

1a. Additional clarity is needed to distinguish the new findings in this work from those of prior studies, and to give attribution to those works.

Lines 123-132: Please cite relevant papers for the sources of each PMF factor.

Response: Change made. In the revised supplement (according to the referee's suggestion below, this section has been moved to the revised supplement), we have now cited relevant papers for the sources of each PMF factor, and it now reads "......The HOA was emitted mainly from local traffic with mass peaks in traffic hours (Huang et al., 2010; Sun et al., 2011; Ge et al., 2012), and COA was dominantly associated with the cooking emissions (He et al., 2010;

Xu et al., 2016), exhibiting mass peaks at around breakfast, lunch and dinner times (Fig. S6). Meanwhile, the time series of COA correlated well with that of $C_6H_{10}O^+$ (*r*=0.85), which is a tracer fragment of cooking emissions (Sun et al., 2011; Hu et al., 2016) (Fig. S6). The mass spectrum of CCOA is dominated by unsaturated hydrocarbons, particularly polycyclic aromatic hydrocarbons (PAH)-related ion peaks (e.g., *m/z* 77, 91 and 115) (Dall'Osto et al., 2013; Hu et al., 2013). In comparison, BBOA was mainly emitted from the combustion of biomass fuel such as wood or straw (Wang et al., 2009; Zhang et al., 2015), with the tracer signal at *m/z* 60 (dominantly C₂H₄O₂⁺), which is mainly enhanced by biomass-burning tracer levoglucosan and related species (mannosan, galactosan, etc.) (Cubison et al., 2011)".

The following references have been added to the revised reference list:

- Ge, X., Setyan, A., Sun, Y., and Zhang, Q.: Primary and secondary organic aerosols in Fresno, California during wintertime: Results from high resolution aerosol mass spectrometry, J. Geophys. Res., 117, D19301, https://doi.org/10.1029/2012jd018026, 2012.
- He, L. Y., Lin, Y., Huang, X. F., Guo, S., Xue, L., Su, Q., Hu, M., Luan, S. J., and Zhang, Y. H.: Characterization of high-resolution aerosol mass spectra of primary organic aerosol emissions from Chinese cooking and biomass burning, Atmos. Chem. Phys., 10, 11535– 11543, https://doi.org/10.5194/acp-10-11535-2010, 2010.
- Huang, X.-F., He, L.-Y., Hu, M., Canagaratna, M. R., Sun, Y., Zhang, Q., Zhu, T., Xue, L., Zeng, L.-W., Liu, X.-G., Zhang, Y.-H., Jayne, J. T., Ng, N. L., and Worsnop, D. R.: Highly time-resolved chemical characterization of atmospheric submicron particles during 2008 Beijing Olympic Games using an Aerodyne High-Resolution Aerosol Mass Spectrometer, Atmos. Chem. Phys., 10, 8933–8945, https://doi.org/10.5194/acp-10-8933-2010, 2010.
- Sun, Y.-L., Zhang, Q., Schwab, J. J., Demerjian, K. L., Chen, W.-N., Bae, M.-S., Hung, H.-M., Hogrefe, O., Frank, B., Rattigan, O. V., and Lin, Y.-C.: Characterization of the sources and processes of organic and inorganic aerosols in New York city with a high-resolution timeof-flight aerosol mass apectrometer, Atmos. Chem. Phys., 11, 1581–1602, https://doi.org/10.5194/acp-11-1581-2011, 2011.
- Wang, Q., Shao, M., Zhang, Y., Wei, Y., Hu, M., and Guo, S.: Source apportionment of fine organic aerosols in Beijing, Atmos. Chem. Phys., 9, 8573–8585, https://doi.org/10.5194/acp-9-8573-2009, 2009.
- Zhang, Y. J., Tang, L. L., Wang, Z., Yu, H. X., Sun, Y. L., Liu, D., Qin, W., Canonaco, F., Prévôt,
 A. S. H., Zhang, H. L., and Zhou, H. C.: Insights into characteristics, sources, and evolution of submicron aerosols during harvest seasons in the Yangtze River delta region, China, Atmos. Chem. Phys., 15, 1331–1349, https://doi.org/10.5194/acp-15-1331-2015, 2015.

Lines 169-192: Please cite relevant papers that contain context for the variables discussed here, such as NO3/SO4, SOR and NOR.

Response: Change made. In the revised manuscript page 7 lines 234-248, we have cited

relevant papers and it now reads "......Meanwhile, the average mass ratio of NO₃^{-/}SO₄²⁻ (Sun et al., 2016) decreased from 1.9 during reference days to 1.5 during SIA_P1 and 1.4 during SIA_P2, respectively. Consistently, although both sulfur oxidation ratio (SOR, defined as $n[SO_4^{2^-}]/(n[SO_4^{2^-}] + n[SO_2])$, Ji et al., 2018; Chang et al., 2020) and nitrogen oxidation ratio (NOR, defined as $n[NO_3^-]/(n[NO_3^-] + n[NO_2])$, Ji et al., 2018; Chang et al., 2020) increased with RH..... These results suggested that high RH is favorable in sulfate formation than nitrate formation, especially in haze pollution in winter Xi'an".

And the following references have been added to the revised reference list:

- Chang, Y., Huang, R.-J., Ge, X., Huang, X., Hu, J., Duan, Y., Zou, Z., Liu, X., and Lehmannet, M.F.: Puzzling haze events in China during the coronavirus (COVID-19) shutdown, Geophys. Res. Lett., 47, e2020GL088533, https://doi.org/10.1029/2020GL088533, 2020.
- Ji, Y., Qin, X., Wang, B., Xu, J., Shen, J., Chen, J., Huang, K., Deng, C., Yan, R., Xu, K., and Zhang, T.: Counteractive effects of regional transport and emission control on the formation of fine particles: a case study during the Hangzhou G20 summit, Atmos. Chem. Phys., 18, 13581–13600, https://doi.org/10.5194/acp-18-13581-2018, 2018.

Lines 224-250: Please cite relevant papers that contain context for OOA-BB and OOAaq

Response: Change made. We have now cited relevant papers in the revised manuscript page 10 lines 325-329, which now reads "OOA-BB (Paglione et al., 2020) resolved in the winter of 2018 was characterized by a $f_{C2H4O2+}$ value of 0.08 and a f_{CO2+} value of 0.13, which was located in the BB-influenced region, indicating the OOA-BB resolved in the winter of 2018 was largely influenced by BBOA emission. In comparison, the aq-OOA (Sun et al., 2016) resolved in the winter of 2018, OOA resolved in the winter of 2013, as well as the three SOA sources (LO-OOA, MO-OOA, aq-OOA) resolved in the......"

The cited papers including Paglione et al. (2020) and Sun et al. (2016) were already in the reference list.

2. More background, context, and interpretation is needed.

2a. Since a main focus of the paper is the roles of SIA, ALWC, aqueous processing, and BB in Xi'an aerosol composition, please include a summary of recent papers on these subjects from the Xi'an region and elsewhere in the introduction section.

Response: We thank the referee's suggestion. In the revised manuscript page 3 lines 78-90, we have now added a summary of recent papers on these subjects in the introduction section as follows: ".....Recent studies showed that biomass burning and secondary formation dominated OA concentration in Xi'an, which in total contributed >50% of total OA in both autumn and winter (Zhong et al., 2020). In addition, Xiao et al. (2020) reported that biomass burning sources, especially residential biofuel, can contribute to increased urban NH₃ emissions. Several studies also indicated that biomass burning is an important source of light absorption

components in Xi'an (Zhang et al., 2020; Yuan et al., 2021; Zhang et al., 2021; Li et al., 2022). Wu et al. (2018) revealed that simultaneously elevated RH and anthropogenic secondary inorganic aerosol resulted in an abundant ALWC, which can further facilitate the formation of heavy haze. Zhong et al. (2020) indicated that OOA formation was most likely dominated by aqueous-phase processes when Ox was <35 ppb in autumn and winter Xi'an, and Duan et al. (2021) found that persistently high RH/ALWC was the driving factor of aq-OOA formation in summer Xi'an, and the increasing trend of aq-OOA was much consistent with that of nitrate. These studies indicated the importance of biomass burning as well as aqueous-phase reactions in Xi'an, which need further elucidation".

Meanwhile, the following references have been added to the revised reference list:

- Li, X., Sun, N., Jin, Q., Zhao, Z., Wang, L., Wang, Q., Gu, X., Li, Y., and Liu, X.: Light absorption properties of black and brown carbon in winter over the North China Plain: Impacts of regional biomass burning, Atmos. Environ., 278, 119100, https://doi.org/10.1016/j.atmosenv.2022.119100, 2022.
- Xiao, H. W., Wu, J. F., Luo, L., Liu, C., Xie, Y. J., and Xiao, H. Y.: Enhanced biomass burning as a source of aerosol ammonium over cities in central China in autumn, Environ. Pollut., 266, 115278, https://doi.org/10.1016/j.envpol.2020.115278, 2020.
- Yuan, W., Huang, R. J., Yang, L., Ni, H., Wang, T., Cao, W., Duan, J., Guo, J., Huang, H., and Hoffmann, T.: Concentrations, optical properties and sources of humic-like substances (HULIS) in fine particulate matter in Xi'an, Northwest China. Sci. Total. Environ., 789, 147902, https://doi.org/10.1016/j.scitotenv.2021.147902, 2021.
- Zhang, T., Shen, Z., Zhang, L., Tang, Z., Zhang, Q., Chen, Q., Lei, Y., Zeng, Y., Xu, H., and Cao, J.: PM2. 5 Humic-like substances over Xi'an, China: Optical properties, chemical functional group, and source identification, Atmos. Res., 234, 104784, https://doi.org/10.1016/j.atmosres.2019.104784, 2020.
- Zhang, T., Shen, Z., Zeng, Y., Cheng, C., Wang, D., Zhang, Q., Lei, Y., Zhang, Y., Sun, J., Xu, H., Ho, S.S.H., and Cao, J.: Light absorption properties and molecular profiles of HULIS in PM2.5 emitted from biomass burning in traditional "Heated Kang" in Northwest China, Sci. Total. Environ., 776, 146014, https://doi.org/10.1016/j.scitotenv.2021.146014, 2021.

2b. In many paragraphs of the Results and Discussion, values are presented with little interpretation, making the section difficult to follow and leaving the reader wondering about the overall message. Please add specific interpretation of the many values presented, add context for whether the findings are new to this study, cite prior studies that have discussed similar findings, and discuss what these findings imply about aerosol regionally or generally. Examples: lines 169-192 and lines 224-250.

Response: We thank the referee's suggestion. In the revised manuscript, we have now added further specific interpretation and context for our findings and values presented, and also cited prior studies that have discussed similar findings. For example:

Page 7 lines 224-246 now reads ".....Specifically, in order to further analyze the relative importance of sulfate and nitrate in haze pollution, the increase ratio of sulfate or nitrate contribution from reference days to SIA periods was calculated following the equations below:

IR_{sulfate}= $f_{sulfate,SIA}/f_{sulfate,reference}$

IR_{nitrate}= $f_{nitrate,SIA}/f_{nitrate,reference}$

In which the IR_{sulfate} and IR_{nitrate} refers the increase ratio of sulfate contribution or nitrate contribution from reference days to SIA periods, respectively. $f_{sulfate,SIA}$ or $f_{nitrate,SIA}$ refers the mass fraction of sulfate or nitrate in total PM_{2.5} mass during SIA periods including SIA_P1 and SIA_P2, and $f_{sulfate,reference}$ or $f_{nitrate,reference}$ refers the mass fraction of sulfate or nitrate in total PM_{2.5} mass fraction of sulfate or nitrate in total PM_{2.5} mass fraction of sulfate or nitrate in total PM_{2.5} mass fraction of sulfate or nitrate in total PM_{2.5} mass fraction of sulfate or nitrate in total PM_{2.5} mass fraction of sulfate or nitrate in total PM_{2.5} mass during reference days.

The IR_{sulfate} from reference days to SIA_P1 (1.8) and to SIA_P2 (2.1) was higher than those of IR_{nitrate} (1.4 from reference days to SIA_P1 and 1.5 from reference days to SIA_P2, respectively). Meanwhile, the average mass ratio of NO₃^{-/}SO₄²⁻ (Sun et al., 2016) decreased from 1.9 during reference days to 1.5 during SIA_P1 and 1.4 during SIA_P2, respectively. These trends suggested that the increase of sulfate contribution during haze pollution was much obvious than that of nitrate contribution in winter Xi'an, although the absolute concentration of nitrate was higher than sulfate both in reference days and SIA periods. NO₃^{-/}SO₄²⁻ showed an evident decrease as a function of RH at higher NR-PM_{2.5} loading (> 50 µg m⁻³) (Fig. S1). Consistently, although both sulfur oxidation ratio (SOR, defined as n[SO₄²⁻]/(n[SO₄²⁻] + n[SO₂]), Ji et al., 2018; Chang et al., 2020) and nitrogen oxidation ratio (NOR, defined as n[NO₃^{-]}/(n[NO₃^{-]} + n[NO₂]), Ji et al., 2018; Chang et al., 2018; Chang et al., 2020) increased with RH,".

Page 10 lines 314-342 now reads ".....is usually used to analyze the influence of BBOA on SOA and their evolution processes (Cubison et al., 2011). As PM_{2.5} was measured in our campaign, in order to further analyze the influence of BBOA on SOA formation in Xi'an, OA sources in PM_{2.5} resolved using AMS were compared. Fig. 3a displays plots of f_{44} (f_{CO2+}) vs. f_{60} (f_{C2H4O2+}) of BBOA and SOA sources resolved in the winter of 2018 (this campaign), the winter of 2013 (Elser et a., 2016) and the summer of 2019 (Duan et al., 2021). According to Cubison et al. (2010), $f_{60}=0.003 \pm 0.002$ represented the threshold of BB influence. SOA sources have a f_{60} higher than 0.005 suggested the influence from BBOA, while $f_{60} < 0.003$ suggested a secondary source having no influence from BBOA, and sources from fresh biomass burning emission usually have high f_{60} and low f_{44} . As shown in Fig. 3, BBOA factor resolved in the winter of 2018 and 2013 were both located in the fresh BBOA region with higher $f_{C2H4O2+}$ (0.024 and 0.021, respectively, which were both higher than 0.005) and lower f_{CO2+} , suggesting they were fresh BBOA emissions. OOA-BB (Paglione et al., 2020) resolved in the winter of 2018 was characterized by a $f_{C2H402+}$ value of 0.08 and a f_{C02+} value of 0.13, which was located in the BB-influenced region, indicating the OOA-BB resolved in the winter of 2018 was largely influenced by BBOA emission. In comparison, the aq-OOA (Sun et al., 2016) resolved in the winter of 2018, OOA resolved in the winter of 2013, as well as the three SOA sources (LO-OOA, MO-OOA, aq-OOA) resolved in the summer of 2019 all showed higher f_{CO2+} and lower $f_{C2H4O2+}$ (< 0.005), and were located in the non-BB influenced region, suggesting that these SOA were formed from other processes independent on BBOA source. In addition, in order to further compare the BBOA influence on SOA between different regions, f_{44} vs. f_{60} for BBOA and SOA resolved in PM₁-OA from previous studies were also compared (see Fig. 3b, note that f_{44} and f_{60} values were not available in other group papers, only those resolved in our previous studies were summarized here). In most of studies, BBOA is located in the fresh BBOA region, except the BBOA resolved in the winter of 2012 in Xi'an (Zhong et al., 2020). Meanwhile, most of the SOAs were located in the non-BB influenced region, except the OOA resolved in the winter of 2012 (Zhong et al., 2020) which showed a higher f_{44} of 0.17 and a higher f_{60} of 0.09 (>0.05). This further indicated the influence of biomass burning on SOA formation in winter Xi'an. In comparison, the MO-OOA resolved in BaOji and the OOA resolved in Shijiazhuang also showed minor influence from BBOA, which are located in the edge of the aged-BB region (Wang et al., 2017; Huang et al., 2019)".

The following references have also been added to the revised reference list:

- Chang, Y., Huang, R.-J., Ge, X., Huang, X., Hu, J., Duan, Y., Zou, Z., Liu, X., and Lehmannet, M.F.: Puzzling haze events in China during the coronavirus (COVID-19) shutdown, Geophys. Res. Lett., 47, e2020GL088533, https://doi.org/10.1029/2020GL088533, 2020.
- Ji, Y., Qin, X., Wang, B., Xu, J., Shen, J., Chen, J., Huang, K., Deng, C., Yan, R., Xu, K., and Zhang, T.: Counteractive effects of regional transport and emission control on the formation of fine particles: a case study during the Hangzhou G20 summit, Atmos. Chem. Phys., 18, 13581–13600, https://doi.org/10.5194/acp-18-13581-2018, 2018.

Lines 181-182 state that, "...high RH and liquid phase condition may drive the large production of SIA." Further discussion and attribution for this idea is needed. In addition, there is an inherent dependence of ALWC on SIA because their concentrations are used to calculate ALWC. The explanations for Figs. 4 and 5 also require more discussion of this topic. Please further discuss the prior work demonstrating causality between SIA and heightened ALWC, and also heightened OOA-aq, and new implications of this study.

Response: We thank the referee's suggestion. According to our measurement results, the major difference between SIA-enhanced periods and reference days was the much frequent occurrence of higher relative humidity and ALWC concentration during SIA_P1 and SIA_P2 than reference days. These indicated the much frequent occurrence of liquid conditions during SIA periods than reference days. According to previous studies, high RH and liquid phase reactions play important roles in the formation of secondary inorganic aerosol, such as sulfate and nitrate (Sun et al., 2016: Wu et al., 2018). Therefore, we supposed that high RH and liquid phase conditions may drive the large production of SIA. We agree with the referee that there is an inherent dependence of ALWC on SIA as their concentrations are used to calculate ALWC.

As analyzed in Wu et al. (2018), a feedback mechanism driven by Henry's law and thermodynamic equilibrium was present between the SIA and ALWC. Higher RH levels and SIA concentrations resulted in an abundant ALWC. The condensed water could in turn act as an efficient medium for multiphase reactions, thereby facilitate the formation of SIA. In addition, Condensed water also facilitates the partitioning of water-soluble, polar organics into condensed phases, and subsequent aqueous-phase reactions into more oxygenated organic components (aq-OOA). The enhanced aerosol liquid water facilitates the aqueous phase SOA formation, similar to that we discussed in Figs. 5 and 6 in the revised manuscript. However, as we further discussed, the concentration of aq-OOA was not continuously increasing when ALWC increased from 10-100 μ g m⁻³ to >100 μ g m⁻³. Instead, the aq-OOA concentration was much affected by the mass increase of nitrate and sulfate, with similar aq-OOA concentration associated with similar sulfate or nitrate concentration level under different RH ranges. This further suggested that SIA may play a much more important role in the formation of aq-OOA in winter Xi'an.

To be more accurate, in the revised manuscript, further discussion and attribution have been added. For example:

Page 6 lines 209-214: "..... These indicated the more frequent occurrence of liquid condition during SIA periods than reference days. According to previous studies, high RH and liquid phase reactions played important roles in the formation of secondary inorganic aerosol, such as sulfate and nitrate (Sun et al., 2016: Wu et al., 2018). These indicated that high RH and liquid phase condition may drive the large production of SIA in winter Xi'an.....".

Page 13 lines 399-402: ".....As discussed by Wu et al. (2018), simultaneously elevated RH levels and SIA concentrations resulted in an abundant ALWC. Condensed water also facilitates the partitioning of water-soluble, polar organics into condensed phases, and subsequent facilitate the SOA formation.....".

2c. Van Krevelen analysis can be useful to summarize complex organic composition, but not to determine the specific molecular pathways in long datasets. Factors such as mixing of aerosol populations can affect O/C and H/C, and integrated composition over long time periods cannot show what's happening at the molecular level. Please instead focus on the shorter-term and non-molecular Van Krevelen analyses, or perhaps cautiously discuss the similarities between your results and those of lab studies, as in Heald et al., 2010.

Response: We thank the referee's suggestion. We agree with the referee that factors such as the mixing of aerosol populations can affect O/C and H/C, while the LToF-AMS provides mass spectra of an ensemble of submicron OA particles in real time, with sufficiently high mass resolution that the chemical formulae of all important ions (especially below $m/z \le 100$) can be unambiguously determined (DeCarlo et al., 2006). The VK analysis has been used in many AMS studies in order to elucidate the OA evolution mechanism in field observation with long datasets. For example, Ng et al. (2011) derived that the evolution from SV-OOA to LV-OOA

was mainly along with a slope of approximately -0.5, and was associated with the replacement of carboxyl functional group (OH-(CHO)-). Gilardoni et al. (2016) and Paglione et al. (2020) used the VK diagram of the BBOA and SOA factors resolved in field observations to analyze the oxidation pathway of BBOA to SOA. Xu et al. (2016) characterized the OA evolution in winter Lanzhou, and found that the observed OA data in the VK diagram followed a slope of -0.8, which suggested that SOA formation chemistry was a combination of carboxylic acid and alcohol/peroxide formation. Liu et al. (2020) reported that a much lower slope of -0.13 was found in VK diagram when the BBOA mass concentration was $>10 \ \mu g \ m^{-3}$ in Qinghai–Tibet Plateau, corresponding to the addition of alcohol/peroxide functional groups without fragmentation alone. According to these studies, VK analysis was also used to discuss the OA evolution mechanism during the field measurement in our manuscript.

3. Structural suggestions:

3a. There are many figures, and some present duplicate information. Many of the figures are barely discussed in the text (fig. 6(a), for example). I suggest consolidating or moving some additional figures to the Supplemental.

Response: We thank the referee's suggestion. Fig. 6(a) compared the concentration of OA composition and elemental ratios between reference days and SIA-enhanced periods. We agree with the referee that the consolidation of some figures would improve the structure of our manuscript. According to the referee's suggestion, Fig. 6(a) has been moved to the revised supplement as Fig. S9.

3b. Section 3.4: The organization of this section is confusing. The content seems to be a mixture of continued discussions about the BB influence and SIA period source/process characterization, then Van Krevelen analysis for SIA periods, then back to general Van Krevelen periods. I suggest reorganizing the material, renaming the section, and perhaps fitting relevant pieces into 3.1 and 3.2.

Response: We thank the referee's valuable suggestion. In the revised manuscript, we have now reorganized the section 3.4. The first paragraph "As discussed above.....much higher than those during reference days and SIA_P1" has been moved to section 3.1 on page 9 lines 280-293. The second paragraph "The scatterplot of f_{44} vs. f_{60} was also applied to further investigate OA transformation during different periods.....and the aq-OOA contribution increased largely from 19% and 39% to 61%" has been moved to section 3.2 on page 12 lines 359-375. And the rest of the section has been renamed as "3.4 Van Krevelen analysis: importance of aqueous-phase processes". Meanwhile, related figures have also been moved and the sequence of figures throughout the results has been updated accordingly.

3c. Some material in lines 117 through 140 (Methods, Data Analysis section) is Results material

rather than Methods, and should be moved.

Response: Change made. The material in lines 117-140 of Data analysis section is the OA source apportionment result, which has been moved to the revised supplement, SI-text: OA source apportionment (also see response 4b below).

4. Methods questions:

4a. Were averaged ratios such as O/C calculated following Aiken et al., 2008? (https://cires1.colorado.edu/jimenez-group/wiki/index.php/FAQ_for_AMS_Data

_Users#How_do_I_average_OA_elemental_composition_variables_.28O:C.2C_H:C_OA:OC _and_OSc.29.3F)

Response: Average ratios such as O/C, H/C, and OM/OC were calculated based on the Improved Ambient (I-A) method following Canagaratna et al. (2015). This reference was also cited in the manuscript.

4b. Please discuss (in the supplemental is fine) the process for selecting the solution with the six PMF factors chosen.

Response: We thank the referee's suggestion. In the revised manuscript page 8 lines 257-260, the following sentence has been added:

"Six OA sources were resolved, including a hydrocarbon-like OA (HOA), a cooking OA (COA), a biomass burning OA (BBOA), a coal combustion OA (CCOA), a biomass burning influencedoxygenated OA (OOA-BB), and an aqueous phase processed-oxygenated OA (aq-OOA) (Fig. 2, the OA source apportionment was detailed in the supplement)".

In the revised supplement, we have now added the process for selecting the solution with the six factors as follows:

"SI-text: OA source apportionment

OA source apportionment was performed on high resolution mass spectra for m/z 12-120 using PMF combined with the multilinear engine (ME-2) in Igor Pro (Paatero, 1999; Canonaco et al., 2013). First, a range of solutions with two to ten factors from unconstrained runs were examined. The OA factors are mixed with each other seriously in less factor number solutions, and increasing the number of factors can improve the separation. As shown in Fig. S4, four POA factors including HOA, COA, CCOA and BBOA were resolved in the 6-factor solution, while high signal of CO₂⁺ was mixed in CCOA and COA factors. Meanwhile, two SOA factors with different oxidation states were also resolved, referred to as LO-OOA with O/C ratio of 0.42 and MO-OOA with O/C ratio of 1.02, respectively. However, much hydrocarbon-like ions in higher m/z were observed in LO-OOA, also suggesting the mixture between POA factors and SOA factors. In seven factors solution, the mixture of CO₂⁺ in COA was reduced, while the mixture in CCOA and LO-OOA were still observed, and MO-OOA was separated into MO-OOA1 and MO-OOA2. When further increasing the factor into eight, clear POA sources including CCOA,

BBOA, COA, and HOA were resolved. and the mixture in LO-OOA was also reduced. However, the MO-OOA is still separated into MO-OOA1 and MO-OOA2, and there was no new meaningful factor resolved. Therefore, six sources including HOA, COA, CCOA, BBOA, LO-OOA and MO-OOA should be resolved. Note that reasonable POA sources could not be resolved in six PMF solution, while SOA was separated in the seven and eight factor solutions. To optimize the source apportionment, we further conducted 6-factor solution using ME-2 approach in order to obtain a more environmentally meaningful result (Canonaco et al., 2013). The clear profiles of HOA, COA, CCOA and BBOA resolved in 8-factor PMF solution were used to constrain these four sources, and a *a*-value of 0.1 was applied for a reasonable variation range. Finally, six OA sources including HOA, COA, BBOA, CCOA, LO-OOA, and MO-OOA were identified (Fig. S5).

As for POAs, both the mass spectrum of HOA and COA are characterized by prominent hydrocarbon ion series of C_nH_{2n-1} and C_nH_{2n+1} , while the COA contains higher signal at C_nH_{2n-1} than C_nH_{2n+1} , an especially much higher signal ratio of $C_4H_7^+/C_4H_9^+$ which is the typical characteristic of COA profile as reported in previous studies at various urban sites (He et al., 2011; Ng et al., 2011). The HOA was emitted mainly from local traffic with mass peaks in traffic hours (Huang et al., 2010; Sun et al., 2011; Ge et al., 2012), and COA was dominantly associated with the cooking emissions (He et al., 2010; Xu et al., 2016), exhibiting mass peaks at around breakfast, lunch and dinner times (Fig. S6). Meanwhile, the time series of COA correlated well with that of $C_6H_{10}O^+$ (r=0.85), which is a tracer fragment of cooking emissions (Sun et al., 2011; Hu et al., 2016) (Fig. S6). The mass spectrum of CCOA is dominated by unsaturated hydrocarbons, particularly polycyclic aromatic hydrocarbons (PAH)-related ion peaks (e.g., *m/z* 77, 91 and 115) (Dall'Osto et al., 2013; Hu et al., 2013). In comparison, BBOA was mainly emitted from the combustion of biomass fuel such as wood or straw (Wang et al., 2009; Zhang et al., 2015), with the tracer signal at m/z 60 (dominantly C₂H₄O₂⁺), which is mainly enhanced by biomass-burning tracer levoglucosan and related species (mannosan, galactosan, etc.) (Cubison et al., 2011). Consistently, a good correlation between the time series of BBOA and the $C_2H_4O_2^+$ fragment was also observed (*r*=0.95) (Fig. S6).

As for SOAs, the mass spectrum of LO-OOA shows a higher peak at m/z 43 (mainly C₂H₃O⁺) and a lower O/C ratio (0.57) than that of MO-OOA (0.82). The tight correlation between the time series of C₂H₃O⁺ and LO-OOA (r = 0.83) also suggests its less oxidized property (Fig. S6). In addition, obvious m/z 60 (C₂H₄O₂⁺) and m/z 73 (C₃H₅O₂⁺) peaks were found in the mass spectrum of LO-OOA and the time variation of LO-OOA correlated well with that of BBOA (R²=0.59) (Fig. S7), suggesting the possible influence of BBOA source on the formation of LO-OOA. Therefore, LO-OOA was further referred to as OOA-BB and discussed in detail in section 3.2. In comparison, MO-OOA has a mass spectrum with a much higher peak at m/z 44 (mainly CO₂⁺) than m/z 43, and a largely different time series with LO-OOA, implying different formation processes. Meanwhile, the time series of MO-OOA was correlated well with the typical fragment ions of aqueous-phase processing products including CH₂O₂⁺ (R² = 0.91),

 CH_3SO^+ ($R^2 = 0.89$), and $CH_3SO_2^+$ ($R^2 = 0.75$) (Fig. S8) (Tan et al., 2009; Chhabra et al., 2010; Ge et al., 2012; Sun et al., 2016), suggesting the dominant role of aqueous-phase processes in its formation. Therefore, MO-OOA was further referred to as aq-OOA and discussed in detail in section 3.3".

Fig. R6 and Fig. R7 have been added as Fig. S4 and Fig. S5, respectively, in the revised supplement.



Fig. R6 Profiles (HR) of OA sources for six, seven and eight factors PMF solutions during the winter campaign in Xi'an.



Fig. R7 Profiles (HR) of OA sources for six factors ME-2 solution during the winter campaign in Xi'an.

4c. Please define the equations described by NOR and SOR.

Response: Change made. In the revised manuscript page 7 lines 242-246, the equations described by NOR and SOR have been added. It now reads ".....Consistently, although both sulfur oxidation ratio (SOR, defined as $n[SO_4^{2^-}]/(n[SO_4^{2^-}] + n[SO_2])$, Ji et al., 2018; Chang et al., 2020) and nitrogen oxidation ratio (NOR, defined as $n[NO_3^-]/(n[NO_3^-] + n[NO_2])$, Ji et al., 2018; Chang et al., 2020) increased with RH.....".

4d. Please add the calculation for odd oxygen here (difficult to find definition for "Ox" within the introduction).

Response: Change made. The definition of odd oxygen has been added in the revised manuscript page 2 line 59, which now reads "..... according to the correlation between SOA and odd oxygen, which defined as $Ox (Ox = O_3 + NO_2)$ (Sun et al., 2014; Elser et al., 2016; Hu et al., 2016)".

4e. Please add the gas analyzer models.

Response: Change made. The gas analyzer models have been added in section 2.1 in the revised manuscript page 4 lines 115-118: ".....Meanwhile, gases species including CO, NO₂, O₃ and SO₂ were measured using a Thermo Scientific Model 48i carbon monoxide analyzer, a Thermo Scientific Model 42i NO–NO₂–NO_x analyzer, a Thermo Scientific Model 49i ozone analyzer, and an Ecotech EC 9850 sulfur dioxide analyzer, respectively.....".

4f. Please mention the wind speed and direction measurement methods.

Response: Change made. In the revised manuscript page 4 lines 119-122, we have added such statement and the sentence now reads ".....The meteorological parameters including relative humidity (RH), temperature, wind speed, and wind direction were measured by an automatic weather station (MAWS201, Vaisala, Vantaa, Finland) and a wind sensor (Vaisala Model QMW101-M2), respectively".

4g. Please discuss the precise metrics used to define the beginnings and ends of SIA_P1 and SIA P2.

Response: We thank the referee's suggestion. During our measurement, A continuous and large increase of secondary inorganic aerosol (SIA, nitrate + sulfate + ammonium) was observed during two periods. the first SIA-enhanced period was beginning at 2018/12/30 0:00, and end at 2019/1/15 6:00, thus the period from 2018/12/30 0:00 to 2019/1/15 6:00 was defined as SIA_P1. Similarly, the secondary SIA-enhanced period was beginning at 2019/2/7 0:00, and end at 2019/3/4 23:00, the period from 2019/2/7 0:00 to 2019/3/4 23:00 was defined as SIA_P2. In the revised manuscript page 6 lines 194-197, the precise metrics have been updated for the definition of SIA_P1 and SIA_P2, which now reads "....., including period 1 from 2018/12/30 0:00 to 2019/1/15 6:00 (SIA-enhanced period 1, SIA_P1) and period 2 from 2019/2/7 0:00 to 2019/3/4 23:00 (SIA-enhanced period 2, SIA_P2)."

4h. Please highlight the assumptions and considerations made to account for changes in volatility or other losses during sampling at high humidity. For example:

Were tests with wetted standard particles performed to determine whether the humidity impacted the concentrations?

Response: We thank the referee's comment. Tests with wetted standard particles were not performed in our measurement. According to Middlebrook et al. (2012), RH has important effects on the collection efficiency of particulate measured in AMS, and a Nafion dryer (MD-700-24S, Perma Pure, Inc.) was used to make the particulate RH into the range of 20%-30%, and the RH effects on collection efficiency were much reduced.

Was RH considered in composition-dependent collection efficiency calculations?

Response: We thank the referee's comment. In response above, RH has important effects on the collection efficiency of particulate measured in AMS, thus a Nafion dryer (MD-700-24S, Perma Pure, Inc.) was used to make the particulate RH into the range of 20%-30%. The RH effects on collection efficiency were much reduced, and RH was not further considered in the composition-dependent collection efficiency calculations in our measurement.

In the revised manuscript page 4 lines 130-132, highlight of this assumption has been added, which now reads "Meanwhile, the composition-dependent collection efficiency (CDCE) was used to calibrate and compensate for the incomplete detection due to particle bounce (Middlebrook et al., 2012). Note RH was not considered in the CDCE calculations as a Nafion dryer was used and the RH effects on collection efficiency were much reduced".

4i. If a soot particle long time-of-flight aerosol mass spectrometer (SP-LToF-AMS) was used, why were the elemental carbon concentrations not discussed?

Response: We thank the referee's comment. We used the SP-LToF-AMS in the "laser off" mode as that in Duan et al. (2021). Therefore, the elemental carbon was not measured, and we stated "The contribution of black carbon (BC) was not considered, and only NR-PM_{2.5} composition, including organics (OA), nitrate (NO₃⁻), sulfate (SO₄²⁻), ammonium (NH₄⁺), and chloride (Cl⁻) were analyzed" in the manuscript.

5. Additional content questions:

5a. Were the different PMF factors identified here versus in summer Xi'an expected? What does this imply about these factors and atmospheric chemistry of the region? For example, Sun et al., 2016 found a substantial summertime agricultural burning source at Xianghe, but there is no BB factor in Duan et al., 2021.

Response: We thank the referee's comment. We expected that PMF factors identified in winter

would be different compared to that in summer in Xi'an, which implies different sources and atmospheric chemistry between winter and summer. For example, a CCOA factor was resolved in winter but not in summer in Xi'an, due to the heating season began from November in north China every year. A BBOA factor was also resolved in winter due to domestic heating. Sun et al. (2016) found a substantial summertime biomass burning source, suggesting a large impact of agricultural burning on air pollution in summer at Xianghe. In comparison, f_{60} was lower than 0.005 (f_{60} =0.003 ± 0.002 represented the threshold of BB influence, according to Cubison et al. (2010)), and no biomass burning factor was resolved in summer at Xi'an, indicating negligible contribution from agricultural burning activities in Xi'an during summer. Agricultural burning was an important contributor to OA in harvest season before 2013. However, agricultural burning in harvest season has been banned after 2013 and BBOA source becomes a negligible contributor to OA in summertime, especially in urban city in recent years (Huang et al., 2021).

5b. Ammonium is included in the SIA concentrations but is never discussed separately even though it is emitted separately from nitrate and sulfate. Have ammonium concentrations or the competition by nitrate and sulfate for ammonium changed? How do they relate to the organic aerosol (OA) and OA fraction concentrations? Also see Zhang et al., 2021 (DOI: 10.1021/acs.estlett.0c00756).

Response: We thank the referee's suggestion. During our measurement, the concentration of ammonium increased from $3.3 \pm 2.2 \ \mu g \ m^{-3}$ during reference days to $13.3 \pm 6.5 \ \mu g \ m^{-3}$ during SIA P1 and $10.8 \pm 4.6 \ \mu g \ m^{-3}$ during SIA P2, respectively. This was consistent with the variation trends of sulfate and nitrate, in which sulfate increased from $3.5 \pm 2.8 \ \mu g \ m^{-3}$ during reference days to $18.4 \pm 10.2 \ \mu g \ m^{-3}$ during SIA P1 and $14.7 \pm 7.2 \ \mu g \ m^{-3}$ during SIA P2, and nitrate increased from 6.8 \pm 4.9 µg m⁻³ during reference days to 27.4 \pm 13.4 µg m⁻³ during SIA_P1 and 19.9 \pm 9.3 μg m $^{-3}$ during SIA_P2. As shown in Fig. R8, the equivalent molar concentration of ammonium correlated tightly with that of the total of sulfate and nitrate with a slope ≈ 1 during all the three periods including reference days (R²=0.96), SIA P1(R²=0.99), and SIA P2($R^2=0.99$), suggesting that ammonium was mainly neutralized by sulfate and nitrate in winter Xi'an both in reference days and SIA-enhanced periods. Therefore, we mainly discussed variations of sulfate and nitrate in our results. According to Zhang et al. (2020), nonagricultural sources are important contributor to NH₃ in urban city, which transferred to NH₄⁺ and plays a very important role in the formation of sulfate and nitrate. We further analyzed the correlations between ammonium and organic aerosol (OA) as well as OA factor concentrations during different periods. As shown in Table R1, weak correlations were found between ammonium and POAs, while a tight correlation between ammonium and aq-OOA during all the three periods was observed, consistent with the important influence of sulfate and nitrate in aq-OOA formation.

In the revised manuscript page 6 lines 215-223, the discussion of ammonium concentration

changes has been added, which now reads ".....During our measurement, the concentration of ammonium increased from $3.3 \pm 2.2 \ \mu g \ m^{-3}$ during reference days to $13.3 \pm 6.5 \ \mu g \ m^{-3}$ during SIA_P1 and $10.8 \pm 4.6 \ \mu g \ m^{-3}$ during SIA_P2, consistent with the variation trends of sulfate and nitrate, in which sulfate increased from $3.5 \pm 2.8 \ \mu g \ m^{-3}$ during reference days to $18.4 \pm 10.2 \ \mu g \ m^{-3}$ during SIA_P1 and $14.7 \pm 7.2 \ \mu g \ m^{-3}$ during SIA_P2, and nitrate increased from $6.8 \pm 4.9 \ \mu g \ m^{-3}$ during reference days to $27.4 \pm 13.4 \ \mu g \ m^{-3}$ during SIA_P1 and $19.9 \pm 9.3 \ \mu g \ m^{-3}$ during SIA_P2. The equivalent molar concentration of ammonium correlated tightly with that of the total of sulfate and nitrate with a slope ≈ 1 during all the three periods including reference days, SIA_P1, and SIA_P2, suggesting ammonium was mainly neutralized by sulfate and nitrate in winter Xi'an both in reference days and SIA-enhanced periods (Fig. S2)".



Fig. R8 Correlations between the equivalent molar concentration of ammonium and the sum of sulfate and nitrate during different periods (reference, SIA_P1, and SIA_P2) in winter Xi'an.

OA sources during the three periods including reference days, SIA_11, and SIA_12.							
\mathbb{R}^2	OA	HOA	COA	BBOA	CCOA	Aq-OOA	OOA-BB
Ammonium (reference)	0.55	0.22	0.06	0.27	0.41	0.78	0.42
Ammonium (SIA_P1)	0.65	0.06	0.01	0.09	0.08	0.96	0.29
Ammonium (SIA_P2)	0.68	0.02	0.09	0.07	0.01	0.95	0.02

Table R1 Correlations (R²) between the concentration of ammonium and OA as well as different OA sources during the three periods including reference days, SIA_P1, and SIA_P2.

6. Minor comments:

Some grammar should be updated. In particular, the word "promoted" is used in a confusing way in many places.

Response: Change made. In the revised manuscript, grammar has been checked and updated accordingly. For example, on page 6 lines 187-188, the sentence ".....likely due to the much lower temperature in winter which promoted the transformation of nitrate from gas-phase to particle-phase....." has been updated to ".....likely due to the much lower temperature in winter which facilitated the transformation of nitrate from gas-phase to particle-phase....."; on page 7 lines 248-249, the sentence "These results suggested that high RH is favorable in promoting sulfate formation than nitrate formation especially in haze pollution in winter Xi'an" has been updated to "These results suggested that high RH is favorable in sulfate formation than nitrate formation especially in haze pollution in winter Xi'an"; on page 13 lines 402-403, the sentence ".....Consistently, higher SIA concentration also showed positive promotion on the aq-OOA increase....." has been updated to ".....Consistently, higher SIA concentration also showed positive effect on the aq-OOA increase....."; on page 14 lines 417-418, the sentence "In addition, nitrate displayed a more positive promotion on the aq-OOA formation than sulfate....." has been updated to "In addition, nitrate displayed a more positive effect on the aq-OOA formation than sulfate....."; on page 14 lines 423-424, the sentence ".....and both nitrate and sulfate displayed positive promotions on aq-OOA increase" has been updated to ".....and both nitrate and sulfate displayed positive effects on aq-OOA increase"; on page 16 lines 483-484, the sentence ".....and higher ALWC also promoted the increase of O/C ratio, suggesting the promotion of SIA and aqueous-phase processes on the OA oxidation enhancement during winter Xi'an" has been updated to ".....and higher ALWC also facilitated the increase of O/C ratio, suggesting the positive effects of SIA and aqueous-phase processes on the OA oxidation enhancement during winter Xi'an".

Introduction lines 49-50: I suggest adding more recent references to support the statement that SOA is, "...becoming a critical concern for air pollution research".

Response: We thank the referee's suggestion. In the revised manuscript page 2 lines 50-51, more recent references have been added and the sentence now reads "However, the formation and evolution of secondary aerosol, especially secondary organic aerosol (SOA), is still not well understood and becoming a critical concern for air pollution research (Gilardoni et al., 2016; Xu et al., 2017; Kuang et al., 2020; Zhang et al., 2021; Li et al., 2022; Lv et al., 2022)". Meanwhile, the following references have been added to the revised reference list:

- Li, J., Deng, S., Li, G., Lu, Z., Song, H., Gao, J., Sun, Z., and Xu, K.: VOCs characteristics and their ozone and SOA formation potentials in autumn and winter at Weinan, China, Environ. Res., 203, 111821, https://doi.org/10.1016/j.envres.2021.111821, 2022.
- Lv, S., Wang, F., Wu, C., Chen, Y., Liu, S., Zhang, S., Li, D., Du, W., Zhang, F., Wang, H., Huang, C., Fu, Q., Duan, Y., and Wang, G.: Gas-to-Aerosol Phase Partitioning of

Atmospheric Water-Soluble Organic Compounds at a Rural Site in China: An Enhancing Effect of NH3 on SOA Formation, Environ. Sci. Technol., 56, 7, 3915–3924, https://doi.org/10.1021/acs.est.1c06855, 2022.

Zhang, H., Chen, C., Yan, W., Wu, N., Bo, Y., Zhang, Q., and He, K.: Characteristics and sources of non-methane VOCs and their roles in SOA formation during autumn in a central Chinese city, Sci. Total. Environ., 782, 146802, https://doi.org/10.1016/j.scitotenv.2021.146802, 2021.

Line 69: "...Research on aerosol composition and SOA formation mechanisms are still limited" would be well qualified with "in the region".

Response: Change made. In the revised manuscript page 2 line 70, the sentence has been updated, which now reads ".....while research on aerosol composition and SOA formation mechanisms are still limited in the region (Elser et al., 2016; Zhong et al., 2020; Duan et al., 2021)".

Introduction, line 60: Are there recent papers to support the statement that aqueous phase chemistry is missing in SOA simulations? I suggest also saying here that aqueous SOA is difficult to identify.

Response: We thank the referee's suggestion. In the revised manuscript page 2 lines 60-62, some recent papers have been added to support the statement that aqueous phase chemistry is missing in SOA simulations and the difficulty of aqueous SOA identify. The sentence now reads "However, recent studies also revealed the important contribution of aqueous-phase chemistry to SOA formation, which is also missing in SOA simulation and difficult to identify (Guo et al., 2014; Sun et al., 2016; Xu et al., 2017, 2019; Huang et al., 2020; Li et al., 2021)".

Meanwhile, the following reference has been added to the revised reference list:

Li, J., Han, Z., Sun, Y., Li, J., and Liang, L.: Chemical formation pathways of secondary organic aerosols in the Beijing-Tianjin-Hebei region in wintertime, Atmos. Environ., 244, 117996, https://doi.org/10.1016/j.atmosenv.2020.117996, 2021.

Introduction, line 75: Please add a reference for the "13th five-year energy conservation and emission reduction plan".

Response: Change made. In the revised manuscript page 3 line 76, a reference has been added, and the sentence now reads ".....such as the 13th five-year energy conservation and emission reduction plan (Wan et al., 2022)".

- Meanwhile, the following reference has been added to the revised reference list:
- Wan, J., Qin, C., Wang, Q., Xiao, Y., Niu, R., Li, X., and Su, J.: A Brief Overview of the 13th Five-Year Plan for the Protection of Ecological Environment, Environmental Strategy and Planning in China, 57-85, https://doi.org/10.1007/978-981-16-6909-5_3, 2022.

Throughout the Results and Discussion: Values are presented that are apparently averages, and some with an error calculation (X +/- Y). Please clarify that these values are the arithmetic means and standard deviations of the per-minute samples over the campaign or specified sub-period.

Response: We thank the referee's suggestion. These values are the arithmetic means and standard deviations of the per-minute samples over the campaign or specified sub-period. In the revised manuscript page 5 lines 172-174, this clarify has been added at the begin of the Results and Discussion. The sentence now reads "During the winter of 2018 in Xi'an, NR-PM_{2.5} concentration varied from 5.9 μ g m⁻³ to 205.6 μ g m⁻³, with an average of 68.0 ± 42.8 μ g m⁻³ (see Fig. 1 and Table S1, note that all the values throughout the results and discussion are the arithmetic means and standard deviations of the per-minute samples over the campaign or specified sub-period)".

Throughout the Results and Discussion: Concentrations of the OA fractions should be included to support the trends in emissions (for example, at lines 200-214). A change in contribution does not necessarily demonstrate an absolute change in abundance.

Response: We thank the referee's suggestion. In the revised manuscript, concentrations of OA fractions have been added to support the trends in emission throughout the Results and Discussion.

For example, the paragraph on page 8 lines 260-278 now reads "POA including HOA, COA, CCOA and BBOA in total contributed 42% to OA mass. HOA contributed 8% ($3.0 \pm 3.9 \ \mu g \ m^{-1}$ ³) to the total OA mass (Fig. 2). This contribution was lower than that observed in winter 2013 $(18\%, 23.0 \pm 27.0 \ \mu g \ m^{-3}$ in reference days and 16%, $49.0 \pm 41.0 \ \mu g \ m^{-3}$ in extreme haze, respectively) (Elser et al., 2016), which may be related to the better traffic control in recent years in urban Xi'an. COA on average contributed 13% ($4.8 \pm 4.2 \ \mu g \ m^{-3}$) to total OA, which was higher than that observed during winter 2013 (9%, $15.8 \pm 8.7 \ \mu g \ m^{-3}$ in reference days and 4%, $33.0 \pm 16.0 \ \mu g \ m^{-3}$ in extreme haze, respectively) in Xi'an (Elser, et al., 2016; Duan et al., 2021). CCOA on average contributed 9% $(3.2 \pm 2.5 \,\mu g \, m^{-3})$ to total OA in this winter campaign, consistent with that observed in the winter of 2013 (14%, $5.7 \pm 4.1 \ \mu g \ m^{-3}$ in reference days and 6%, $7.7 \pm 8.0 \ \mu g \ m^{-3}$ in extreme haze, respectively) (Elser et al., 2016). In comparison, BBOA was more significant contributor than CCOA, and on average accounted for 12% (4.3 \pm $5.9 \,\mu g \, m^{-3}$) of total OA mass. However, this contribution was much lower than that observed in the winter of 2013 in Xi'an (42%, 22.0 \pm 20.0 μ g m⁻³ in reference days and 43%, 67.0 \pm 40.0 ug m⁻³ in extreme haze, respectively) (Elser et al., 2016), suggesting the reduction of BBOA emissions in recent years in Xi'an and surrounding areas. SOA contributed a higher fraction of 58% (21.8 \pm 7.4 μ g m⁻³) than POA to total OA, with OOA-BB and aq-OOA accounting for 24% and 34% of OA mass, respectively. The contribution of SOA was much higher than that observed in the winter of 2013 in Xi'an (16%, $5.4 \pm 8.9 \ \mu g \ m^{-3}$ in reference days and 31%, 47.0 \pm 12.0 µg m⁻³ in haze days, respectively) (Elser et al., 2016)".

Results and Discussion, lines 173 and 176: The OA/NR-PM5 percentage is presented differently as 65 % and 66 % at these lines, respectively.

Response: We thank the referee for pointing this out. The OA/NR-PM_{2.5} percentage has been changed to 66% in the revised manuscript.

Results and Discussion, line 183: Please clarify the equations used to calculate the, "...increase ratio of sulfate contribution from reference days to SIA P1" ... "and to SI P2...".

Response: We thank the referee's suggestion. In the revised manuscript page 7 lines 224-232, the calculation equations have been added, which now reads ".....Specifically, in order to further analyze the relative importance of sulfate and nitrate in haze pollution, the increase ratio of sulfate or nitrate contribution from reference days to SIA periods were calculated following the equations below:

$IR_{sulfate} = f_{sulfate,SIA}/f_{sulfate,reference}$

IRnitrate=fnitrate,SIA/fnitrate,reference

In which the IR_{sulfate} and IR_{nitrate} refers the increase ratio of sulfate contribution or nitrate contribution from reference days to SIA periods, respectively. $f_{sulfate,SIA}$ or $f_{nitrate,SIA}$ refers the mass fraction of sulfate or nitrate in total PM_{2.5} mass during SIA periods including SIA_P1 and SIA_P2, and $f_{sulfate,reference}$ or $f_{nitrate,reference}$ refers the mass fraction of sulfate or nitrate in total PM_{2.5} mass fraction of sulfate or nitrate in total PM_{2.5} mass fraction of sulfate or nitrate in total PM_{2.5} mass fraction of sulfate or nitrate in total PM_{2.5} mass fraction of sulfate or nitrate in total PM_{2.5} mass fraction of sulfate or nitrate in total PM_{2.5} mass during reference days".

Figure 4: The data in (a) are already plotted in a prior plot. Suggest adding ALWC to Fig. 1 and removing 4(b).

Response: We thank the referee's suggestion. In the revised manuscript, the ALWC in Fig. 4(a) has been added to Fig.1, and the Fig. 4(a) has been removed. Figure 1 is now updated as Fig. R9 below, and Figure 4 is now updated as Fig. R2 above.



Fig. R9 Time series of meteorology parameters (relative humidity (RH), temperature (T), wind speed (WS), and wind direction (WD) (a, b); gases species (SO₂, O₃, NO₂ and CO) (c, d); and NR-PM_{2.5} composition as well as the aerosol liquid water content (ALWC) (e, f) in the winter of 2018 in Xi'an. The average composition of NR-PM_{2.5} for the entire winter campaign, as well as reference days and SIA-enhanced periods (SIA_P1 and SIA_P2) are also shown.

Results and Discussion, lines 272-274: these ions are not listed in Tan et al., 2009.

Response: We thank the referee for pointing this out. We have now checked and updated the references cited in the revised manuscript page 13 line 395, and the sentence now reads ".....which are the typical fragment ions of aqueous-phase processing products (Tan et al., 2009; Chhabra et al., 2010; Ge et al., 2012; Sun et al., 2016)".

Meanwhile, the following references have been added to the revised reference list:

- Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Elemental analysis of chamber organic aerosol using an aerodyne high-resolution aerosol mass spectrometer, Atmos. Chem. Phys., 10, 4111–4131, https://doi.org/10.5194/acp-10-4111-2010, 2010.
- Ge, X., Zhang, Q., Sun, Y., Ruehl, C. R., and Setyan, A.: Effect of aqueous-phase processing on aerosol chemistry and size distributions in Fresno, California, during wintertime, Environ. Chem., 9, 221–235, https://doi.org/10.1071/EN11168, 2012.

Fig. 3(b): Are there additional studies using high resolution AMS data in China that could be added to demonstrate work done outside of your research group?

Response: We thank the referee's suggestion. There are also additional studies using high resolution AMS data in China and resolved BBOA, OOA or aged BBOA sources. However, the f_{44} and f_{60} are not available in those papers, and could not be added for the comparison and demonstrate our finding.

In the revised manuscript page 10 lines 332-335, we have now added the following state: "..... in order to further compare the BBOA influence on SOA between different regions, f_{44} vs. f_{60} for SOA and BBOA resolved in PM₁-OA from previous studies were also compared (see Fig. 3b, note that f_{44} and f_{60} values are not available in other groups' papers, only those resolved in our previous studies are summarized here)......".

Fig. 4(b) and Fig. 5: These patterns are surprising and very stark. Would you please confirm that the different slope groupings are not the result of the ALWC ISORROPIA modeling? (Wu et al., 2018 also used ISORROPIA). Additionally, please define "S" in the figure caption. **Response:** We thank the referee's comment. We calculated the ALWC based on the ISORROPIA in "metastable" mode, in which all components are assumed to be deliquescent and no solid matter is present. This calculation mode was consistent with that conducted in Wu et al. (2018). The thermodynamic equilibrium and phase state were then simulated and the ALWC was resolved. Therefore, we confirm that the different slope groupings are not the result of the ALWC ISORROPIA modeling.

Additionally, the definition of "S" has been added in the figure caption of Fig. 5 in the revised manuscript, which now reads "Fig. 5 The effects of ALWC on the formation of aq-OOA colored by RH, with the increase of SIA concentration shown as the size increase of the data points. Note "S" is defined as the slope between aq-OOA and ALWC in different RH range".

Results and Discussion, lines 305-307 ("This may suggest that aq-OOA..."): This is an interesting statement, but I'm not sure I understand how this conclusion was drawn. Please further explain the logic.

Response: We thank the referee's comment. As we discussed in the manuscript, aq-OOA was dominantly formed in fog-rain days with abundant liquid water environment, and the concentration of aq-OOA continuously increased as ALWC increased from 10 μ g m⁻³ to 100 μ g m⁻³ and further to 1000 μ g m⁻³ in summer. This suggested the formation of aq-OOA was much dependent on ALWC, which might be a bulk water reaction in summer Xi'an (Duan et al., 2021). In comparison, the concentration of aq-OOA was not continuously increasing with the increase of ALWC. Instead, the aq-OOA concentration was much affected by the mass increase of nitrate and sulfate, with similar aq-OOA concentration associated with similar sulfate or nitrate concentration level under different RH and ALWC ranges. As discussed in Wu et al. (2018), increased hygroscopic particle constituents such as sulfate and nitrate associated with

condensed water may provide the relevant media and increase the aerosol surface area, which leads to the increasing of heterogeneous reaction rate and modulate the formation and properties of SOA. Therefore, we stated here that aq-OOA formation is more driven by heterogeneous surface reactions.

In the revised manuscript page 14 lines 428-432, more explanation has been added, which now reads ".....This may suggest that aq-OOA formation is more driven by heterogeneous surface reactions in winter, as sulfate and nitrate associated with condensed water may provide the relevant media and increase the aerosol surface area, which leads to the increasing of heterogeneous reaction rate and modulate the formation and properties of SOA (Wu et al., 2018)".

Fig. 6(b): Pie charts do not have labels. Also, when characterizing aqueous processes, the f44 vs f43 space has been used (for example, Lee et al., 2011; DOI: 10.1029/2011GL047439), and might be more relevant for aq-OOA discussion here.

Response: We thank the referee's suggestion. In the revised manuscript, labels of pie charts have been added in Fig.4 (see Fig. R10 below). Meanwhile, according to the referee's suggestion and study conducted by Lee et al. (2011), we have now added the discussion of f_{44} vs f_{43} space on page 11 lines 375-383 as follows:

".....The scatterplot of f_{44} vs f_{43} was also discussed in Fig. 4b in order to study the evolution of SOA. The data points substantially fell into the triangle space derived by Ng et al. (2010), in which higher f_{44} and lower f_{43} are characteristics of more oxidized and aged aerosol, while lower f_{44} and higher f_{43} values represent less oxidized and fresh organics. From reference days to SIA_P1 and SIA_P2, OA showed the evolution trends moving from the lower right to the upper left in the triangle, suggesting the increased oxidation of OA during SIA-enhanced periods (Ng et al., 2010). Consistently, the POA factors (HOA, COA, CCOA, and BBOA) were concentrated in the bottom of the triangle, while OOA-BB was in an intermediate location with a higher oxidation state, and aq-OOA was at the top left of the triangle with the highest oxidation state".

Meanwhile, Fig. R10 has been added as Fig. 4 in the revised manuscript.



Fig. R10 The plots of f_{44} vs f_{60} , as well as the average OA composition during these three periods (a). The size of the pie chart identifies the mass concentration of total OA, and the plots of f_{44} vs f_{60} in summer 2019 was also shown for comparison. And the scatterplots of f_{44} vs f_{43} (b). The corresponding values of the six OA factors identified in this study are also shown, and the triangle range is from Ng et al. (2010).

Results and Discussion, lines 345-354: Do the meteorological parameters or mesoscale meteorological observations help explain the differences between SIA_P1 and SIA_P2? **Response:** We thank the referee's comment. As shown in Fig. S1, except temperature which is slightly higher in SIA_P2 than SIA_P1 due to seasonal variation from winter to spring, the patterns of other meteorological parameters including wind speed, wind direction, and RH are rather similar between SIA_P1 and SIA_P2. This suggests that meteorology might not the main reason to explain the differences between SIA_P1 and SIA_P2.

Supplement: Figure S5 (b) is confusing. What data are included in the aq-OOA profile resolved in summer? It seems like they are data from Duan et al., 2021, but it would not be possible to pair summer with winter concentrations. Please explain.

Response: We thank the referee's comment. In Figure S5 (b), we didn't compare the absolute concentrations of aq-OOA between summer and winter, instead we compared the normalized mass spectra profile of aq-OOA between summer and winter. The fraction of each ion in the total signal of the aq-OOA mass spectrum was compared, and a good correlation was observed between summer and winter.

Author contributions: Several authors are simply listed as having. "...commented on and discussed the manuscript". Please ensure that the integrity of co-authorship is preserved (https://www.springer.com/journal/10874/submissionguidelines#

Instructions%20for%20Authors_Authorship%20principles).

Response: We thank the referee's suggestion. We ensure that all authors made substantial contributions to the manuscript, and agreed with the content and submission. In the revised

manuscript, we have updated the author contributions according to the referee's suggestion, which now reads "*Author contributions*. RJH designed the study. JD, YFG, CSL, and HBZ conducted the field observation. Data analysis and source apportionment were done by JD and RJH, with help from WX, QL, and YY. JD and RJH wrote the manuscript. JD and RJH interpreted data and prepared display items, and JO, DC, TH, and CO all commented on and discussed the manuscript".

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