RE: A point-to-point response to reviewers' comments

"Unambiguous identification of N-containing oxygenated organic molecules using CI-Orbitrap in an eastern Chinese megacity" (acp-2022-774) by Yiqun Lu, Yingge Ma, Dan Dan Huang, Shengrong Lou, Sheng'ao Jing, Yaqin Gao, Hongli Wang, Yanjun Zhang, Hui Chen, Naiqiang Yan, Jianmin Chen, Christian George, Matthieu Riva, Cheng Huang

We are grateful to the helpful comments from this anonymous referee, and have carefully revised our manuscript accordingly. A point-to-point response to the comments, which are repeated in italic, is given below.

In addition to the reviewers' comments, we have noticed that an author has been added, who participated in the revision of the manuscript during the review process.

Reviewer #1's comments:

General comments

In this work, the authors characterized ambient OOMs in a densely populated urban site in Shanghai using an ultra-high resolution orbitrap coupled with a nitrate inlet. With its high mass resolving power, CI-Orbitrap gives more accurate identification of molecular composition and better separates N-containing OOMs in complex ambient data. The authors showed that aliphatic 2N-OOMs were the most abundant 2N-OOMs with significant contributions from those derived from long-chain aliphatic compounds, whose fraction was further increased on polluted days. This paper is overall well designed and nicely written. There is one point I am not very convinced about: the authors seemed to directly use the correlation between 2N-OOMs with solar radiation over NO3 radicals to reference daytime and nighttime formation pathways without considering the effects of meteorological dilution (e.g. the diurnal variation of boundary layer height). It can change or even flip the correlation in some cases. I also have some minor questions as listed below. I recommend publication after these issues are addressed.

Reply: We are very grateful to the positive viewing of our manuscript by Reviewer #1, and have now revised our manuscript accordingly.

We agree with reviewer #1 that meteorological dilution would bring some uncertainties and should be considered when discussing these correlations. We now scale the concentrations of 2N-OOMs and NO_3 radicals with the boundary layer height before calculating the correlation coefficients in Figure4a and Figure 5. Correction of this term does not lead to changes in our conclusions. A corresponding explanation has been added, which reads (L237-L239), "It should be noted that the concentrations of 2N-OOMs and NO_3 radicals were scaled with the boundary layer

height before calculating the correlation coefficients here and below for correcting the effects of meteorological dilution."

Specific comments:

1. Line 40-43: Most field measurements cited here were conducted in the United States and China. There are many available works from Europe, too. For example, the European sites included in Ng et al. (2017) show up to >70% ON in ambient submicron OA. Can the authors also include these data points to the paper, and if possible, more from other parts of the world?

Reply: We now include the data points in *Ng et al.* (2017) as well as those from other parts of the world and have revised our manuscript accordingly, which reads (L46-L50) "Field measurements also observed that up to 77 % of molecules in organic aerosol (OA) contain nitrate functional groups under different atmospheric conditions (Ditto et al., 2020; Kenagy et al., 2021; Kiendler-Scharr et al., 2016; Lee et al., 2016; Lee Ng et al., 2017; Lin et al., 2021; Rollins et al., 2013; Xu et al., 2015; Ye et al., 2021; Yu et al., 2019)."

2. Line 128, 131: Some references are needed for "widely used in previous studies" and "+-50% according to error propagation".

Reply: We now cite the corresponding literatures and have revised our manuscript accordingly, which reads (L135-L139) "…which is widely used in previous studies (Ehn et al., 2014; Yan et al., 2021; Yao et al., 2018). Among the low volatility vapors, it had been demonstrated that nitrate ions exhibit highest charging efficiency toward H_2SO_4 (Ehn et al., 2014; Hyttinen et al., 2015, 2018; Riva et al., 2019b). The estimated concentrations of OOMs thus can be considered as the lower limits with an uncertainty of $\pm50\%$ according to error propagation (Ehn et al., 2014)."

3. Line 142: Some references are needed for "one of our companion studies".

Reply: We now cite the corresponding literature and have revised our manuscript accordingly, which reads (L149-L150) "…as suggested by one of our companion studies (Zhang et al., 2022)."

4. Figure 1a: The font for pie chart percentages is too small (same for other figures).

Reply: We now enlarge the size of font for Figure 1a as well as other figures in the same situation.

5. Figure 1b: How did the authors explain 3N-OOMs fraction decreased when nC>12?

Reply: In fact, the fraction of 3N-OOMs as well as 1N-OOMs and 0N-OOMs overall showed a descending trend when nC>10 due to the ascending fraction of 2N-OOMs which seems more interesting. We now discuss the probable reason in the manuscript, which reads (L161-L168) "More

interestingly, we found 1N-OOMs prevailed among the OOMs with nC≤10, yet 2N-OOMs dominated the C>10 OOMs (41.8-84.2%), suggesting the increased importance of multi-step bimolecular oxidation in the formation of 2N-OOMs with nC>10. We also note that the fraction of 2N-OOMs increased stepwise with the increase of nC (Figure 1b) while 3N-OOMs don't exhibit a similar dependence. The potential reason is that, with the increase of nC, on the one hand, more active sites are potentially provided to promote the occurrence of multi-step oxidation, but on the other hand, the potential larger steric effect can hinder multi-step oxidation. From our observation, these two factors lead an overall positive coupling for 2N-OOMs, but result in a non-monotonic trend for 3N-OOMs."

6. *Line 185: How is the 2N-OOMs enhancement in polluted days compared to the enhancement of total OOMs?*

Reply: In daytime, the 2N-OOMs enhancement in polluted case was about 1.7 times higher than those in clean case while the enhancement of total OOMs was not that much bigger (about 1.3 times). In nighttime, the 2N-OOMs enhancement (about 2.7 times) in polluted case was quite comparable with the enhancement of total OOMs (about 2.8 times).

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We are grateful to the helpful comments from this anonymous referee, and have carefully revised our manuscript accordingly. A point-to-point response to the comments, which are repeated in italic, is given below.

In addition to the reviewers' comments, we have noticed that an author has been added, who participated in the revision of the manuscript during the review process.

Reviewer #2's comments:

This manuscript presents measurements of N-containing oxygenated organic molecules (N- OOMs) in a Chinese megacity made using a nitrate-orbitrap chemical ionization mass spectrometer (CIMS), with a focus on N-OOMs containing two N atoms (2N-OOMs). Using an established workflow, the 2N-OOMs are classified based on possible precursors, aliphatics, aromatics and monoterpenes, and the abundances and properties of the 2N- OOM classes are examined as a function of pollution level and time of day. Overall, the results presented in this manuscript are interesting but somewhat incremental given the recent companion paper by Zhang et al. 2022 (DOI: 10.1021/acs.est.1c08346). In several instances, the data/figures also do not appear to support the stated discussions/conclusions. As such, I recommend that publication as a Measurement Report be considered only after the comments detailed below are addressed.

Reply: We are very grateful to the viewing of our manuscript by Reviewer #2, and have now revised our manuscript accordingly. We think our manuscript has devoted a large space to discuss the potential formation pathway and the preference of oxidants during daytime and nighttime with a special focus on 2N-OOMs based on the field campaign. Therefore, it is better to be submitted as a research article.

Major comments:

1. *Nitroaromatics. It is assumed that all N atoms in N-OOMs are nitrate groups. For aromatics, however, recent laboratory work by Xu et al. 2020 (DOI: 10.1021/acs.est.0c04780) suggests that nitrate yields are low. Moreover, nitroaromatics are known to be significant products of aromatic oxidation under high- NO2 conditions. Accordingly, despite the authors stating that*

nitrophenol peaks were excluded (L269), the contribution of nitroaromatics should be accounted for. Additionally, relevant sections in the manuscript should be rephrased to state that OOMs were classified based on the number of N atoms not nitrate groups (e.g., L45 and L146).

Reply: In fact, we could identify a number of nitrated phenols. However, these nitrated phenol molecules are characterized by remarkably high concentrations (as this reviewer said) and high volatility (Cheng et al., 2021; Dang et al., 2019) but negligible contribution to SOA via condensation (Wang et al., 2021). On the other hand, the formation of nitrated phenol from aromatics is unlikely to pass through RO_2 process as other N-containing OOMs based on the Master Chemical Mechanism. These reasons led us to finally exclude them in this study.

We also note that in some review and research articles on OOMs/HOMs, the authors also tend to exclude these nitroaromatics (Bianchi et al., 2019; Nie et al., 2022; Yan et al., 2021).

We now revise the description of the classification of OOMs in L51-52, which reads "The N-containing OOM molecules can be classified into 1N-OOMs, 2N-OOMs, and 3N-OOMs, according to the number of N atoms in the molecule" and in L155-156, which reads "We further classified the detected OOMs into four groups based on the number of N atoms they possessed, …".

2. *Concentration Determination. Given that the calibration factor for H2SO4 was applied for all detected OOMs, the detailed derivation (L116–125) is unnecessary.*

Reply: In combination with the opinion of reviewer #3, we should describe the methodology of concentration determination as much detail as possible.

3. *L154: Multistep Oxidation. By this argument, the fraction of 3N-OOM should exhibit a similar dependence with on carbon number (nC), with a maximum at higher nC than the 2N-OOM. A discussion of potential reasons for the absence of this behavior should be included.*

Reply: We now discuss the probable reason and rephrase the description in the manuscript, which reads (L161-L168) "More interestingly, we found 1N-OOMs prevailed among the OOMs with nC≤10, yet 2N-OOMs dominated the C>10 OOMs (41.8-84.2%), suggesting the increased importance of multi-step bimolecular oxidation in the formation of 2N-OOMs with nC>10. We also note that the fraction of 2N-OOMs increased stepwise with the increase of nC (Figure 1b) while 3N-OOMs don't exhibit a similar dependence. The potential reason is that, with the increase of nC, on the one hand, more active sites are potentially provided to promote the occurrence of multi-step oxidation, but on the other hand, the potential larger steric effect can hinder multi-step oxidation. From our observation, these two factors lead an overall positive coupling for 2N-OOMs, but result in a non-monotonic trend for 3N-OOMs."

4. *Percentages. Percentages reported throughout the manuscript should specify the period over which the calculations were performed (e.g., campaign averages, daytime averages, or nighttime averages).*

Reply: We now specify the period at a very beginning position in the result and discussion section, which reads (L144-L146) "In total, we have identified 562 OOMs, which concentrated in the nC range of 5 to 10, taking up 84.6% of total OOMs during the whole campaign (unless otherwise stated, all the reported values hereafter were corresponding to the average of the whole campaign)."

5. *Figure 1. It is difficult to distinguish the different shades of red, blue, green, and gray from one another. The authors should consider using hatching/patterns to differentiate carbon numbers within each class.*

Reply: We found that it would be difficult to distinguish the group that occupied only a small proportion in the pie when using hatching patterns. Now we adjust the color selection to make the different groups more distinguishable.

6. *Section 3.2. The analysis in this section does not appear to reflect the key takeaways from Table 1 and Figures 2 and 3. Table 1 indicates that with the exception of aromatic 2N-OOM (2N-OOMAro) during the day, the abundances of all 2N-OOM classes during both day and night were higher during the polluted (PL) as compared to clean (CL) period, not just aliphatic 2N-OOM (2N-OOMAli) as the authors highlight. The pie charts in Figure 2 show that the relative fractions of the different 2N-OOM classes do not vary considerably as a function of pollution level, especially at night. Figure 3 illustrates that this is also true for the fraction of 2N-OOMAli comprised of C4–10 vs. C>10 species. As such, the authors should consider restructuring this section to emphasize that pollution levels modulate the absolute concentrations of 2N-OOM but not the relative fractions of 2N-OOM classes or subclasses, whereas daytime vs. nighttime chemistry exerts modest control over the fractional contribution of 2N-OOM classes but does not alter the relative importance.*

Reply: We agree with reviewer #2's comment on emphasizing the impact of pollution level on the absolute concentration of OOMs. On the other hand, the pie charts in Figure 2 show that the fraction of 2N-OOM$_{Ali}$ were considerably higher in polluted cases (66-66%) than those in clean cases (56-61%), which represented the most abundant 2N-OOMs class. In Figure 3, we could also see the enhanced fractions of 2N-OOM$_{Ali}$ with nC>10 in polluted cases especially for the nighttime cases (from 10% to 16%). Therefore, we think it is also meaningful to discuss the relative fractions of different 2N-OOM classes under different pollution levels.

We now revise the discussion in L197-L199, which reads "Table 1 further indicates that the absolute abundances of almost 2N-OOM classes were higher during the polluted cases as compared to clean case no matter in the daytime or nighttime except for the daytime 2N-OOM$_{Aro}$. Specifically…", in

L219-L224, which reads "To summarize, the absolute concentrations of 2N-OOM were greatly affected by the pollution level for the most cases. Both the concentrations and fractions of 2N-OOM$_{Ali}$ were significantly promoted by pollution condition, whereas the 2N-OOM$_{Aro}$ were predominantly affected by photochemical production, whose formation was less sensitive to pollution levels compared to 2N-OOM$_{Ali}$ in the daytime. In contrast, the absolute concentrations of 2N-OOM$_{MT}$ were also significantly influenced by pollution levels but seem not solely/almost depend on daytime/nighttime formation pathway", in Abstract (L28-L29), which reads "…The absolute concentrations of 2N-OOMs were greatly affected by the pollution level for the most cases…" and in conclusion (L336-L337), which reads "…The absolute concentrations of 2N-OOMs were greatly affected by the pollution level for the most cases…".

7. *Importance of Nighttime Monoterpene Chemistry. In L200, the authors state that monoterpene 2N-OOM (2N-OOMMT) "showed overall higher concentrations during nighttime than those in daytime." In L242, they state that "nighttime chemistry dominated the formation of 2N-OOMMT...supported by the stronger correlation between 2N-OOMMT and NO3 radicals than solar radiation." However, in Table 1, the daytime and nighttime concentrations of 2N-OOMMT during the CL period were the same (2.3 x 106molec. cm-3) and only slightly higher at night than in the day during the PL period (5.3 vs. 4.3 x 106 molec. cm-3). Furthermore, Figure 4 shows that the R values for 2N- OOMMT with solar radiation and NO3 radicals are similarly weak, ~0.15 and ~0.18, respectively, while Figure 5 suggests that the number of 2N-OOMMT species that exhibit a strong correlation (R > 0.5) with solar radiation is greater than that with NO3 radicals. As such, these data do not appear to support the conclusion that nighttime chemistry dominated 2N-OOMMT formation.*

Reply: Thanks for this valuable comment. We should emphasize the comparable importance of nighttime chemistry for 2N-OOM$_{MT}$ in contrast to the dominating effect of daytime oxidation for 2N-OOM$_{Aro}$ and 2N-OOM$_{Ali}$.

We now revise the description in L214-L218, which reads "… 2N-OOM$_{MT}$ showed significant higher concentrations but similar fractions in polluted cases. On the other hand, equivalent or even slightly higher concentrations during nighttime than those in daytime suggest the comparable importance of nighttime chemistry in 2N-OOM$_{MT}$ formation in contrast to 2N-OOM$_{Ali}$ and 2N-OOM$_{Aro}$, which will be discussed in later sections.", in L262-L266, which reads "Nighttime chemistry plays a more important role in the formation of 2N-OOM$_{MT}$. This is further supported by the slightly stronger correlation between 2N-OOM$_{MT}$ and NO$_3$ radicals than solar radiation. For some specific 2N-OOM$_{MT}$ species, the formation is likely a result of NO$_3$ radical initiated oxidation. As shown in Figure 5, we have identified a series of 2N-OOM$_{MT}$ molecules with molecular composition of $C_{10}H_{16}O_{7,9,11}N_2$, which showed strong positive correlations with NO$_3$ radical.", in Abstract (L31-L32), which reads "…nighttime NO$_3$-initiated oxidation played a comparable role as the daytime photochemistry in the formation of 2N-OOM$_{MT}$…" and in conclusion (L345-L348),

which reads "…2N-OOM$_{MT}$ prevailed both in daytime and nighttime, some specific 2N-OOM$_{MT}$ species showed strong positive correlations with NO$_3$ radical and were likely a result of NO$_3$ radical initiated oxidation, suggesting the comparable importance of nighttime NO$_3$ chemistry in 2N-OOM$_{MT}$ formation…".

8. *PMF Results. Given that a combination of "up-to-date understanding of VOC oxidation as well as PMF results" was used to derived the 2N-OOM classes that are the focus of this manuscript, the PMF analysis and factors discussed in L188–191 and L224–241 seem superfluous. The authors should consider moving these discussions to the SI.*

Reply: The PMF analysis in L188–191 and L224–241 were not only used to derive the 2N-OOM classes but also compare the timeseries of factors with tracer gases. Therefore, we think it's better to keep these parts.

9. *NOx vs. NO vs. NO2. In L282, the authors state that "high NOx concentrations during the nighttime (Table 1)...could efficiently suppress the RO2 radicals from autoxidation reactions." In L298 they state that "nOeff of 2N-OOMAro and 2N-OOMMT increased with the decrease of NOx concentrations...likely due to the prevailing of NOx termination reactions." In Figure 7, the authors plot nOeff as a function of NOx. As shown in Table 1, however, the increase in nighttime vs. daytime NOx concentrations is driven by NO2; NO concentrations during both the CL and PL periods are actually lower at night than during the day. Given that reaction with NO not NO2 modulates the fate of RO2 (except for acyl RO2) and that reaction of NO2 with aromatic alkyl radicals represents an important mechanism of N incorporation, the authors should reanalyze these trends as a function of NO and NO2 independently.*

Reply: In combination with the fourth minor comment of reviewer #3, we now explore the effects of NO as well as the total NO$_x$ concentrations on the average oxygenation levels of 2N-OOMs in this part, and have revised the Figure 7 as well as the corresponding paragraph accordingly, which reads (L313-L327) "It is known that NO is also critical in determining the fate of RO$_2$ radical during the oxidation, forming RO radicals or organonitrates. Formation of RO radicals and organonitrates will have opposite effects on the oxidation state of the termination products since the former will significantly increase the oxygenation state of carbon through initiating propagation reactions before termination. We thus explore the effects of NO as well as the total NO$_x$ concentrations on the average oxygenation levels of 2N-OOMs from different precursors during the whole campaign (Figure 7). Consistent with previous studies in polluted urban environment (Qiao et al., 2021; Yan et al., 2021), the detected 2N-OOMs were also of low oxygenation with nO$_{eff}$ of 3.9-5.4 (25-75% percentile) compared to those measured in forest or in laboratory studies (Berndt et al., 2016; Ehn et al., 2014; Jokinen et al., 2014; Rissanen et al., 2014; Yan et al., 2016). nO$_{eff}$ of 2N-OOM$_{Aro}$ and 2N-OOM$_{MT}$ increased with the decrease of NO/NO$_x$ concentrations. This is likely due to the

prevailing of NO termination reactions because the maximum autoxidation rate constant of alkylbenzenes with long-chain substituents (e.g., isopropyl-benzene, ethyl-benzene) and monoterpene are comparable to the bimolecular reaction rate between RO_2 and NO (Bianchi et al., 2019). The oxygenation levels of 2N-OOM$_{Ali}$ appears to be insensitive to the pollution levels and NO/NO$_x$ concentrations, which should be further investigated in future studies."

The extension of analysis on this issue does not lead to changes in our conclusions.

Minor comments:

1. *L99. A map indicating the location of the field site in the SI would be beneficial.*

Reply: We now add a map that indicates the location of the field site in the SI, and adjust the number of figures accordingly.

2. *L142. Reference to companion study is missing.*

Reply: We now cite the corresponding literature and have revised our manuscript accordingly, which reads (L149-L150) "…as suggested by one of our companion studies (Zhang et al., 2022)."

3. *L143. How were saturation mass concentrations of OOMs calculated?*

Reply: We now add a clear explanation in combination with the corresponding literature, which reads (L152-L153) "…based on a volatility parameterization proposed by Donahue and co-workers (Donahue et al., 2011, 2012; Schervish and Donahue, 2020)…".

4. *L164. A detailed description of the approach used to classify the 2N-OOMS should be included.*

Reply: We now add a clear explanation in combination with the corresponding literature, which reads (L174-L177) "We thus further classified the 2N-OOMs to their possible VOC precursors following a recently developed workflow proposed by Nie and co-workers, which is based on the up-to-date understanding of VOC oxidation and molecular characters (*i.e.,* number of different elements, DBE) as well as PMF results (Nie et al., 2022), …".

5. *L158. Reference is missing.*

Reply: Together with the third major comments of the reviewer #2. We have revised our manuscript accordingly, which reads (L161-L168) "More interestingly, we found 1N-OOMs prevailed among the OOMs with nC≤10, yet 2N-OOMs dominated the C>10 OOMs (41.8-84.2%), suggesting the increased importance of multi-step bimolecular oxidation in the formation of 2N-OOMs with nC>10. We also note that the fraction of 2N-OOMs increased stepwise with the increase of nC (Figure 1b) while 3N-OOMs don't exhibit a similar dependence. The potential reason is that, with

the increase of nC, on the one hand, more active sites are potentially provided to promote the occurrence of multi-step oxidation, but on the other hand, the potential larger steric effect can hinder multi-step oxidation. From our observation, these two factors lead an overall positive coupling for 2N-OOMs, but result in a non-monotonic trend for 3N-OOMs."

6. *L240. Given that isoprene is not emitted at night, is the hypothesis that this N-OOM is forming from residual isoprene? Does the diurnal profile support this?*

Reply: The diurnal pattern of isoprene showed peaks in the traffic rush-hour during our campaign, plausibly indicating the vehicle source.

Reference

Bianchi, F., Kurtén, T., Riva, M., Mohr, C., Rissanen, M. P., Roldin, P., Berndt, T., Crounse, J. D., Wennberg, P. O., Mentel, T. F., Wildt, J., Junninen, H., Jokinen, T., Kulmala, M., Worsnop, D. R., Thornton, J. A., Donahue, N., Kjaergaard, H. G. and Ehn, M.: Highly Oxygenated Molecules (HOM) from Gas-Phase Autoxidation Involving Organic Peroxy Radicals: A Key Contributor to Atmospheric Aerosol, Chem. Rev., 119, 3472–3509, doi:10.1021/acs.chemrev.8b00395, 2019.

Cheng, X., Chen, Q., Li, Y., Huang, G., Liu, Y., Lu, S., Zheng, Y., Qiu, W., Lu, K., Qiu, X., Bianchi, F., Yan, C., Yuan, B., Shao, M., Wang, Z., Canagaratna, M. R., Zhu, T., Wu, Y. and Zeng, L.: Secondary Production of Gaseous Nitrated Phenols in Polluted Urban Environments, Environ. Sci. Technol., 55(8), 4410–4419, doi:10.1021/acs.est.0c07988, 2021.

Dang, C., Bannan, T., Shelley, P., Priestley, M., Worrall, S. D., Waters, J., Coe, H., Percival, C. J. and Topping, D.: The effect of structure and isomerism on the vapor pressures of organic molecules and its potential atmospheric relevance, Aerosol Sci. Technol., 53(9), 1040–1055, doi:10.1080/02786826.2019.1628177, 2019.

Nie, W., Yan, C., Huang, D. D., Wang, Z., Liu, Y., Qiao, X., Guo, Y., Tian, L., Zheng, P., Xu, Z., Li, Y., Xu, Z., Qi, X., Sun, P., Wang, J., Zheng, F., Li, X., Yin, R., Dallenbach, K. R., Bianchi, F., Petäjä, T., Zhang, Y., Wang, M., Schervish, M., Wang, S., Qiao, L., Wang, Q., Zhou, M., Wang, H., Yu, C., Yao, D., Guo, H., Ye, P., Lee, S., Li, Y. J., Liu, Y., Chi, X., Kerminen, V.-M., Ehn, M., Donahue, N. M., Wang, T., Huang, C., Kulmala, M., Worsnop, D., Jiang, J. and Ding, A.: Secondary organic aerosol formed by condensing anthropogenic vapours over China's megacities, Nat. Geosci., 15, 255–261, doi:10.1038/s41561-022-00922-5, 2022.

Wang, Z., Zhang, J., Zhang, L., Liang, Y. and Shi, Q.: Characterization of nitroaromatic compounds in atmospheric particulate matter from Beijing, Atmos. Environ., 246(October 2020), 118046, doi:10.1016/j.atmosenv.2020.118046, 2021.

Yan, C., Yin, R., Lu, Y., Dada, L., Yang, D., Fu, Y., Kontkanen, J., Deng, C., Garmash, O., Ruan, J., Baalbaki, R., Schervish, M., Cai, R., Bloss, M., Chan, T., Chen, T., Chen, Q., Chen, X., Chen, Y., Chu, B., Dällenbach, K., Foreback, B., He, X., Heikkinen, L., Jokinen, T., Junninen, H., Kangasluoma, J., Kokkonen, T., Kurppa, M., Lehtipalo, K., Li, H., Li, H., Li, X., Liu, Y., Ma, Q., Paasonen, P., Rantala, P., Pileci, R. E., Rusanen, A., Sarnela, N., Simonen, P., Wang, S., Wang, W., Wang, Y., Xue, M., Yang, G., Yao, L., Zhou, Y., Kujansuu, J., Petäjä, T., Nie, W., Ma, Y., Ge, M., He, H., Donahue, N. M., Worsnop, D. R., Veli-Matti Kerminen, Wang, L., Liu, Y., Zheng, J., Kulmala, M., Jiang, J. and Bianchi, F.: The Synergistic Role of Sulfuric Acid, Bases, and Oxidized

Organics Governing New-Particle Formation in Beijing, Geophys. Res. Lett., 48, 2020GL091944, doi:10.1029/2020gl091944, 2021.

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We are grateful to the helpful comments from this anonymous referee, and have carefully revised our manuscript accordingly. A point-to-point response to the comments, which are repeated in italic, is given below.

In addition to the reviewers' comments, we have noticed that an author has been added, who participated in the revision of the manuscript during the review process.

Reviewer #3's comments:

Lu et al applied a CI-Orbitrap to a field campaign in urban Shanghai. The motivation for the work is to offer higher mass resolving power for oxygenated (and nitrogenated) organic matter (OOM) in aerosol compared to previous works using CI-API-TOF. The CI reagent is the nitrate anion. They used positive matrix factorization to estimate the source contribution of the OOM that has 2 nitrogen groups identified on the analyte molecular composition. The paper offers interesting insight into nitrogen-containing aerosols and urban chemistry. I would suggest publication after the following comments are addressed.

Reply: We are very grateful to the positive viewing of our manuscript by Reviewer #3, and have now revised our manuscript accordingly.

Major comments:

1. *Line 127. The sensitivity of H2SO4 was used for all OOM analytes; the only justification given was that this has been "widely used" in other studies. Can the authors offer more compelling justification? The authors go on to say that H2SO4 has the highest sensitivity of all low-volatility vapors, which seems to contradict that H2SO4 is a good surrogate for sensitivity. They didn't disclose the range of sensitivity discrepancies between H2SO4 and OOM proxy compounds. The error margin of 50% is estimated based on error propagation from equation 2, which I find confusing considering that the error margin for the sensitivity estimate is not known... I suggest the authors to do one of two things:*

(1) Please cite at least one study that quantitatively demonstrates how different the sensitivities of authentic standards of OOM-like compounds are compared to H2SO4 and give that sensitivity error range separately. Clearly state the dependence of the sensitivity on relative humidity.

(2) put some authentic OOM surrogate standards in your mass spectrometer at different relative humidity and different m/z to quantitatively determine the range in errors from the sensitivity estimation alone. It is appropriate for CIMS instruments do this calibration prior to field measurements.

Reply: We now cite the corresponding literature (Ehn *et al.,* A large source of low-volatility secondary organic aerosol, *Nature*, 2014, 506, 476–479.) that has quantitatively demonstrated how different the sensitivities of authentic standards of OOM-like compounds are compared to H_2SO_4 and give that sensitivity error range separately in their METHODS section.

We have added the citations in our manuscript accordingly, which reads (L135-L139) "…which is widely used in previous studies (Ehn et al., 2014; Yan et al., 2021; Yao et al., 2018). Among the low volatility vapors, it had been demonstrated that nitrate ions exhibit highest charging efficiency toward H_2SO_4 (Ehn et al., 2014; Hyttinen et al., 2015, 2018; Riva et al., 2019b). The estimated concentrations of OOMs thus can be considered as the lower limits with an uncertainty of $\pm50\%$ according to error propagation (Ehn et al., 2014)."

2. *Line 249-255: The nighttime chemistry in Shanghai is fascinating due to the high NO levels at night, compared to a rural location where NO levels dropped to near zero after sunset (https://acp.copernicus.org/articles/16/7623/2016/acp-16-7623-2016.pdf). I suggest to state this clearly so the reader can have better context for the chemistry, e.g., in line 249 "Under the nighttime conditions observed in Shanghai (Table 1), it is estimated that monoterpenes primarily react with NO3, and the fate of nighttime RO2s is dominated by NO. Therefore, formation of..."*

Reply: The reviewer proposed a very good suggestion, a statement has been added, which reads (L268-L272) "Furthermore, under the nighttime conditions observed in urban Shanghai (Table 1), it is estimated that monoterpenes primarily react with NO_3, and the fate of nighttime RO_2s is dominated by NO, which is clear different from rural environment where NO levels likely drop to near zero after sunset (Romer et al., 2016) and RO_2s are likely terminated by NO_3-RO_2 cross-reactions (Bates et al., 2022). Therefore, formation of..."

3. *The authors should offer quantitative support for their suggested mechanism by doing a quick kinetic calculation based on IUPAC rates and the values in Table 1. In any case, with those concentrations of NO, I can estimate that NO reacts with something like >99% of the RO2s, consistent with the mechanism that the authors have discussed.*

Reply: To put the problem in context, we would like to do a quick kinetic calculation for the reactions between RO_2 and either HO_2 or NO. We use 8.5×10^{-12} cm^3 $molecules^{-1}$ s^{-1} for the RO_2 + NO rate constant and 2×10^{-11} cm^3 $molecules^{-1}$ s^{-1} for the RO_2 +HO_2 rate constant based on the Master Chemical Mechanism (Saunders *et al.*, 2003; Bianchi *et al.*, 2019). To the best of our knowledge, the HO_2 concentration is often on the order of 10 pptv (Holland *et al.*, 2003; Ren *et al.*, 2003), and several orders of magnitude lower than NO concentrations (*e.g.,* 2-3 ppb in this study). Therefore, it is typically expected that NO dominant the termination process of RO_2s.

4. *In an interesting contrast, Bates et al (ACP 2022, https://doi.org/10.5194/acp-22-1467-2022) did a model of the more rural location and found that nitrated RO2s were reacting primarily with HO2 and RO2. The result is that for the site studied in Bates et al, they might see more 2N-OOM with carbon number 20 (due to RO2+RO2 --> ROOR reaction, where each RO2 has one nitrate group) when in urban locations, the 2N-OOM may be more prevalent for carbon number 10 for the monoterpene + NO3 chemistry (where the 2N product is from the RO2+NO --> RONO2 reaction). This is worth adding to the discussion, as it highlights that mononitrates and dinitrates from this chemistry may be prevalent at multiple locations for different reasons.*

Reply: The reviewer provided a very interesting contrast, a statement has been added, which reads (L268-L272) "Furthermore, under the nighttime conditions observed in urban Shanghai (Table 1), it is estimated that monoterpenes primarily react with NO_3, and the fate of nighttime RO_2s is dominated by NO, which is clear different from rural environment where NO levels likely drop to near zero after sunset (Romer et al., 2016) and RO_2s are likely terminated by NO_3-RO_2 cross-reactions (Bates et al., 2022). Therefore, formation of..."

5. *Lines 256-259: This discussion is a bit confusing. Can the authors pick one monoterpene and give the result of the quantitative assessment of reactivity? E.g., for 22.8 ppb of ozone and 1.3 ppt of NO3, X% of monoterpene reacts with NO3 and Y% of reacts with ozone? Also Table 1 shows that the polluted nighttime case is 6.2 ppt, it would be worth calculating for both clean and polluted nighttime cases.*

Reply: Due to the technical issues, the isomers of different monoterpenes could not be distinguished by CI-orbitrap (as well as other CI-MS). Therefore, we only roughly provided the range of reaction rates between three monoterpenes (i.e., alpha-pinene, beta-pinene and limonene) and oxidants. From Table 1, $[O_3]$/$[NO_3]$ ratios were about 4400 and 40000 for the polluted nighttime case (PL_{night}) and the clean nighttime case (CL_{night}), respectively. Since the reaction rate between monoterpenes (i.e., alpha-pinene, beta-pinene and limonene) and NO_3 are about 60,000-140,000 times faster than that between monoterpenes and O_3 at 293K (MCMv3.1) as mentioned in the manuscript, NO_3-initiated oxidation process posed significant impacts on 2N-OOM_{MT} formation during nighttime for both cases.

6. *Line 262: I think the Figure S8 offers clearer evidence to support the NO3-related claims of the paper, whereas some of the other figures (e.g., Fig. 4) do not tell a clear story, as evidenced by Reviewer 2's comments. It might be worth to bring S8 to the main text and to offer a correlation factor R2 analysis for these two data products?*

Reply: We now include the correlation factor for the data of Figure S8 in the manuscript according to this reviewer's comment and have revised our manuscript accordingly in L284-L285, which reads "…which tracked the NO_3 concentrations well (Figure S9, R=0.46) and peaked at around 19:00-23:00…".

7. *General comment is that the nitrogen compounds from aromatics should also consider the nitroaromatics.*

Reply: In fact, we could identify a number of nitrated phenols. However, these nitrated phenol molecules are characterized by remarkably high concentrations and high volatility (Dang *et al.*, 2019; Cheng *et al.*, 2021) but negligible contribution to SOA via condensation (Wang *et al.*, 2021). On the other hand, the formation of nitrated phenol from aromatics is unlikely to pass through RO_2 process as other N-containing OOMs based on the Master Chemical Mechanism. These reasons led us to finally exclude them in this study.
We also note that in some review and research articles on OOMs/HOMs, the authors also tend to exclude these nitroaromatics (Bianchi *et al.*, 2019; Yan *et al.*, 2021; Nie *et al.*, 2022).

Minor comments:

1. *Line 44. What does "under different atmosphere" mean?*

Reply: Field measurements cited here were conducted in different regions of the world with different atmospheric conditions. We now describe it more clearly and include the data points in *Ng et al.* (2017) as well as those from other parts of the world based on the Reviewer #1's comments, and have revised our manuscript accordingly, which reads (L46-L50) "Field measurements also observed that up to 77 % of molecules in organic aerosol (OA) contain nitrate functional groups under different atmospheric conditions (Ditto et al., 2020; Kenagy et al., 2021; Kiendler-Scharr et al., 2016; Lee et al., 2016; Lee Ng et al., 2017; Lin et al., 2021; Rollins et al., 2013; Xu et al., 2015; Ye et al., 2021; Yu et al., 2019)."

2. *Page 4, when citing mass resolving power please also note the mass that this number is calculated at. Each m/z in the spectrum has a different mass resolving power associated Powered by TCPDF (www.tcpdf.org) with it. For example, 12000 m/dm at m/z 400.*

Reply: We now describe it more clearly and have revised our manuscript accordingly in L75-L77,

which reads "a CI-APi-TOF with highest mass resolution of 12,000 ($m/\Delta m$, in full width at half maximum) at m/z=200 Th and above, can hardly identify the molecular compositions of 2N-OOMs unambiguously", and in L87, which reads "… in ultra-high mass resolving power ($m/\Delta m > 100,000$ at m/z=200-500 Th) …".

3. *The authors use both "mass resolving power" and "mass resolution" throughout to refer to the same entity, it would be more correct and consistent to just use "mass resolving power."*

Reply: We now revised our manuscript accordingly in L75, L79, L82, L84, L87 and L113.

4. *Line 290: Please change to "...known that NO is also critical in determining the fate of RO2..." NOx (NO+NO2) is ambiguous, and will not matter much if all of the NOx is NO2. Same comment on line 294, 299, 303 etc. The authors should re-do this analysis with NO not NOx.*

Reply: In combination with the ninth major comment of reviewer #2, we now explore the effects of NO as well as the total NO_x concentrations on the average oxygenation levels of 2N-OOMs in this part, and have revised the Figure 7 as well as the corresponding paragraph accordingly, which reads (L313-L327) "It is known that NO is also critical in determining the fate of RO_2 radical during the oxidation, forming RO radicals or organonitrates. Formation of RO radicals and organonitrates will have opposite effects on the oxidation state of the termination products since the former will significantly increase the oxygenation state of carbon through initiating propagation reactions before termination. We thus explore the effects of NO as well as the total NO_x concentrations on the average oxygenation levels of 2N-OOMs from different precursors during the whole campaign (Figure 7). Consistent with previous studies in polluted urban environment (Qiao et al., 2021; Yan et al., 2021), the detected 2N-OOMs were also of low oxygenation with nO_{eff} of 3.9-5.4 (25-75% percentile) compared to those measured in forest or in laboratory studies (Berndt et al., 2016; Ehn et al., 2014; Jokinen et al., 2014; Rissanen et al., 2014; Yan et al., 2016). nO_{eff} of 2N-OOM$_{Aro}$ and 2N-OOM$_{MT}$ increased with the decrease of NO/NO_x concentrations. This is likely due to the prevailing of NO termination reactions because the maximum autoxidation rate constant of alkylbenzenes with long-chain substituents (e.g., isopropyl-benzene, ethyl-benzene) and monoterpene are comparable to the bimolecular reaction rate between RO_2 and NO (Bianchi et al., 2019). The oxygenation levels of 2N-OOM$_{Ali}$ appears to be insensitive to the pollution levels and NO/NO_x concentrations, which should be further investigated in future studies."

The extension of analysis on this issue does not lead to changes in our conclusions.

Reference

Bianchi, F. *et al.* (2019) 'Highly Oxygenated Molecules (HOM) from Gas-Phase Autoxidation Involving Organic Peroxy Radicals: A Key Contributor to Atmospheric Aerosol', *Chemical Reviews*, 119, pp. 3472–3509. doi: 10.1021/acs.chemrev.8b00395.

Cheng, X. *et al.* (2021) 'Secondary Production of Gaseous Nitrated Phenols in Polluted Urban

Environments', *Environmental Science and Technology*, 55(8), pp. 4410–4419. doi: 10.1021/acs.est.0c07988.

Dang, C. *et al.* (2019) 'The effect of structure and isomerism on the vapor pressures of organic molecules and its potential atmospheric relevance', *Aerosol Science and Technology*. Taylor & Francis, 53(9), pp. 1040–1055. doi: 10.1080/02786826.2019.1628177.

Holland, F. *et al.* (2003) 'Measurements of OH and HO2 radical concentrations and photolysis frequencies during BERLIOZ', *Journal of Geophysical Research: Atmospheres*, 108(4). doi: 10.1029/2001jd001393.

Nie, W. *et al.* (2022) 'Secondary organic aerosol formed by condensing anthropogenic vapours over China's megacities', *Nature Geoscience*. Springer US, 15, pp. 255–261. doi: 10.1038/s41561-022-00922-5.

Ren, X. *et al.* (2003) 'HOx concentrations and OH reactivity observations in New York City during PMTACS-NY2001', *Atmospheric Environment*, 37(26), pp. 3627–3637. doi: 10.1016/S1352-2310(03)00460-6.

Saunders, S. M. *et al.* (2003) 'Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): Tropospheric degradation of non-aromatic volatile organic compounds', *Atmospheric Chemistry and Physics*, 3(1), pp. 161–180. doi: 10.5194/acp-3-161-2003.

Wang, Z. *et al.* (2021) 'Characterization of nitroaromatic compounds in atmospheric particulate matter from Beijing', *Atmospheric Environment*. Elsevier Ltd, 246(October 2020), p. 118046. doi: 10.1016/j.atmosenv.2020.118046.

Yan, C. *et al.* (2021) 'The Synergistic Role of Sulfuric Acid, Bases, and Oxidized Organics Governing New-Particle Formation in Beijing', *Geophysical Research Letters*, 48, p. 2020GL091944. doi: 10.1029/2020gl091944.