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 #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

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