

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 NO₃ radicals with the boundary layer height before calculating the correlation coefficients in Figure 4a 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 NO₃ 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 H₂SO₄ (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 $\pm 50\%$ 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 $nC \leq 10$, 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).