

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 #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 H₂SO₄ 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 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).”

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 NO₃, and the fate of nighttime RO₂s 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 RO₂s are likely terminated by NO₃-RO₂ 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 RO₂ and either HO₂ or NO. We use $8.5 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ for the RO₂ + NO rate constant and $2 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ for the RO₂ + HO₂ rate constant based on the Master Chemical Mechanism (Saunders *et al.*, 2003; Bianchi *et al.*, 2019). To the best of our knowledge, the HO₂ 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 RO₂s.

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 NO₃, and the fate of nighttime RO₂s 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 RO₂s are likely terminated by NO₃-RO₂ 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, [O₃]/[NO₃] 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 NO₃ are about 60,000-140,000 times faster than that between monoterpenes and O₃ at 293K (MCMv3.1) as mentioned in the manuscript, NO₃-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 NO₃ 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 RO₂ 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...” NO_x (NO+NO₂) is ambiguous, and will not matter much if all of the NO_x is NO₂. Same comment on line 294, 299, 303 etc. The authors should re-do this analysis with NO not NO_x.*

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 RO₂ 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 RO₂ and NO (Bianchi et al., 2019). The oxygenation levels of 2N-OOM_{Alk} 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) 'HO_x 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.