

On the potential use of highly oxygenated organic molecules (HOM) as indicators for ozone formation sensitivity

Jiangyi Zhang¹, Jian Zhao¹, Yuanyuan Luo¹, Valter Mickwitz¹, Douglas Worsnop^{1,2}, and Mikael Ehn¹

¹Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki, 00014, Finland

²Aerodyne Research Inc., Billerica, Massachusetts, 01821, United States

Correspondence: Jian Zhao (jian.zhao@helsinki.fi) and Jiangyi Zhang (jiangyi.zhang@helsinki.fi)

Response to Reviewer #2

General comments

The authors conducted chamber experiments to evaluate whether HOM can function as a real-time indicator of the O₃ production regime. They classified different types of HOM, and showed that the O₃ sensitivity can be estimated from the composition of HOM (nitrate-containing and non-nitrate compounds) in a single VOC system.

Overall, this manuscript is well written, and the results are useful to researchers working on the O₃ formation mechanism.

We thank the reviewer for taking the time to review our manuscript and for the positive and insightful comments. We will answer the specific comments point-by-point below. The reviewer's comments are in *blue*, and our answers are in *black* with updated content in *bold*.

Specific comments

Comment #1:

The authors used the ratios of non-nitrate HOM and nitrate-containing HOM as the indicating ratios. The reason for using HOM (not oxygenated VOC) is not clear to me. In general, HOM compounds have lower volatility than most OVOC compounds, and thus, they have more uncertainty factors, such as higher aerosol formation (for both ambient air and chamber experiments) and wall deposition (for chamber experiments). In this study, I guess the authors measured only gaseous HOM by CIMS, and thus, the production yield of HOM cannot be fully measured. The volatilities of HOM compounds varied widely, and thus, the fractions of HOM in a particulate phase or deposited on walls are different among compounds. The application of the OVOC/organic nitrate ratio as the indicating ratio seems more straightforward than the HOM ratio proposed in this manuscript. The reason for using HOM should be clearly stated.

(In a similar context, I do not understand why compounds with $O \leq 8$ are not included in this analysis. Compounds with $O > 8$ have lower volatility, and thus, aerosol formation or wall deposition would be expected to interfere with the estimation of the HOM production yields).

25 **Response:**

We thank the reviewer for this important comment, as it clearly indicates that we did not make this critical topic clear enough. The low volatility of HOM is very critical when we consider the features of potential indicating ratios. As we discussed e.g. in the Abstract line 15, Introduction line 106, and Conclusion line 334, the fast formation while very short lifetime makes HOM special and can be potentially used to track the instantaneous chemical regime of O_3 -related photochemistry in the atmosphere (i.e., as sort of a real-time indicator). However, if we use less oxygenated species in this study, e.g., HOM with $O < 8$ in Figure 3, these species will slowly but continuously evaporate off the wall after the previous experiment(s), interfering with their background measurements for the next experiment. Differently, the more oxidized HOM species decay faster and reach a relatively stable and lower level of background after the experiments. This is why we ended up with using these compounds. A similar argument stands for the real atmosphere, where HOM species condense similarly to the particle surfaces as they did onto the walls. Whereas, OVOC may linger in the air for hours to days, undergo multiple steps of oxidation and cycles before they are removed from the atmosphere. In this way, HOM is actually simpler than OVOC, thus more straightforward as especially a real-time indicator.

We only measured the gas-phase HOM, and in purpose. As explained in the next Comment (i.e. #2), we planned to run the experiments at low concentrations to prevent SOA formation, thus no condensation on particles. In addition, we are more interested in the effects of NO on the relative distribution of HOM, and how that relates to O_3 formation, instead of accurate HOM yield estimation. Overall, as the most oxygenated HOM species we selected had roughly comparable loss rates in the chamber (Fig. 3), the indicating ratios bear fewer uncertainties. We made modifications in section 3.2 to answer this comment as well as the comment #2 from reviewer #1.

Comment #2:

45 Is there the aerosol formation in this experimental system? If large fractions of the produced HOM are in a particulate phase, then, the interpretation of the derived indicating ratio becomes complicated. The information on aerosol formation in this experimental system is useful to readers.

Response:

There was no significant aerosol formation in our system, and the main loss of HOM was to the walls. Even if there had been aerosol formation, the nearly non-volatile behavior of the chosen HOM compounds would have caused a similar loss rate for all of them, thus not impacting the indicating ratios. We did connect a Differential Mobility Particle Sizer (DMPS), measuring particles larger than 10 nm, to our chamber briefly at the highest α -pinene injection (at 60 ppb) stage, and there was no sign

of particle formation. Also, if there was particle formation, the time series of HOM species may not be so steady at the end of each stage because of condensation (Zhao et al., 2023). We added a short discussion at the beginning of the section 3.3 to clarify this point: **It is worth noting that our experiments did not result in notable particle formation, and condensation to walls was always the dominant loss term for HOM. If aerosol formation had been significant, as has been observed in our chamber at higher oxidation rates (Zhao et al., 2023), HOM would first increase due to fast formation, and then decrease due to condensation sink.**

Comment #3:

60 The estimated threshold values of the indicating ratios are the key findings of this study, whereas the derivation of the thresholds is not explained in the main text. The derivation of these threshold values (shown in Lines 307-309) should be clearly explained.

Response:

Our key finding is the viability of using HOM ratios as real-time indicators, but we want to highlight that the estimated threshold values are limited only to our experimental system (α -pinene + O₃ + NO₂). We have now added a statement at the end of section 65 3.2 to make this more clear. The threshold values were not derived rigorously from a mathematical or chemical point of view. Instead, they were summarized from Figures 5, 6, A13, and A14, based on modeled EKMA curves and experimental points. The idea of giving those values is showing the possibility of using the absolute values of HOM ratios, but as also discussed in the response to reviewer #1, we have opted to avoid using the term “quantitatively” to avoid misinterpretation of these absolute numbers. We also changed the relevant sentence: **More specifically, based on modeled EKMA curves and steady state** 70 **HOM ratios (Fig. 5, 6, A13, and A14), regardless of...**

Technical comments

Comment #4:

Figure 5: “Measured” should be removed from the labels of the x and y axes, because the results of EKMA are also shown in this figure.

75 Response:

We have removed the "Measured" from labels (for Fig. 5–6 and A13–A14) and also did corresponding changes in the figure caption.

References

- 80 Zhao, J., Häkkinen, E., Graeffe, F., Krechmer, J. E., Canagaratna, M. R., Worsnop, D. R., Kangasluoma, J., and Ehn, M.: A combined gas- and particle-phase analysis of highly oxygenated organic molecules (HOMs) from α -pinene ozonolysis, *Atmospheric Chemistry and Physics*, 23, 3707–3730, <https://doi.org/10.5194/acp-23-3707-2023>, 2023.