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

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Response to Reviewer #1

General comments

This work details on how HOM can function as an indicator for determining the sensitivity of O_3 formation. The authors have clearly communicated their approach, results, and the potential limitations of the study. In general, the manuscript is well-written and of good scientific quality. Therefore, I would recommend this manuscript for publication with the minor re-works and additions outlined below.

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:

How the photolysis rate of NO_2 was determined? Maybe a brief discussion (used expressions) can be included in the manuscript.

Response:

The photolysis rates of NO_2 were determined by varying the J_{NO_2} parameter in the model until the simulated O_3 and NO_x values agreed with the observations in the zero-VOC experiments (Fig. 1 and A2–A5). The values for J_{NO_2} could also be computed from the observed steady-state and input concentrations of NO_x/O_3 for each condition. We changed the text in the manuscript to more clearly reflect the method we used. We also added the a statement in the footnotes of Table A1 to describe

the expression from which J_{NO_2} could be numerically derived:

From steady-state (ss in subscript) balance of the O_3 concentration, we can write the following expression:

$$\frac{\mathbf{d[O_3]}}{\mathbf{dt}} = \mathbf{J_{NO_2}[NO_2]_{ss}} + \frac{\mathbf{[O_3]_{input} - [O_3]_{ss}}}{\tau} - \mathbf{k_{O_3,NO}[O_3]_{ss}[NO]_{ss}} = \mathbf{0}$$

where $\tau = \frac{2000\ \mathrm{L}}{55\ \mathrm{L\ min^{-1}}}$ is the residence time. O_3 has NO_2 photolysis ($\mathbf{J_{NO_2}[NO_2]_{ss}}$) and its input ($\frac{\mathbf{[O_3]_{input}}}{\tau}$) as sources, with reaction to NO ($-\mathbf{k_{O_3,NO}[O_3]_{ss}[NO]_{ss}}$) and flush-out ($\frac{-\mathbf{[O_3]_{ss}}}{\tau}$) as sinks. We can solve the equation to get NO_2 photolysis rate:

$$\mathbf{J_{NO_2}} = \frac{\mathbf{k_{O_3,NO}[O_3]_{ss}[NO]_{ss}} + \frac{\mathbf{[O_3]_{ss} - [O_3]_{input}}}{\tau}}{\mathbf{[NO_2]_{ss}}}$$

This expression can be used for each steady state to estimate $\mathbf{J_{NO_2}}$ in the corresponding experiment.

Comment #2:

It was not clear from the discussion (Section 2.3) and Table A2, whether wall losses have been accounted for or not. A discussion on these losses could be interesting to see the nature of the effect on indicating ratios.

Response:

Thanks for pointing this out, we should have mentioned that we considered RO_2 with a wall loss lifetime of 400 s (Peräkylä et al., 2020). We made corresponding modifications in Table A2. Wall loss remains a minor loss pathway for RO_2, though, as the lifetime with respect to bimolecular reactions tend to dominate. In contrast, for closed shell species used for the indicating ratios, wall losses are the dominant loss term, but these were not included in the model. We now clarified the discussion in section 3.2 to make it more clear, including statements on the choice of parameters used to calculate the indicating ratios. The choice of including only the most oxygenated, i.e., least volatile, species was done specifically in order to have very similar wall loss rates for the species, which in turn meant that the exact wall loss rates were not of any great significance.

Comment #3:

There can be a discussion on why IR1 holds a better potential than IR2 for indicating O_3 formation sensitivity.

Response:

As we discussed in lines 257-260, "...both indicating ratios are promising as indicators of O_3 formation sensitivity. However, in all time series, IR1 exhibited more pronounced changes compared to IR2 as we shifted the O_3 formation regimes." This highlights that IR1 may hold better potential for indicating O_3 formation sensitivity in the well-controlled chamber systems we investigated, since the nitrates are solely from RO_2+NO and the dimers solely from RO_2+RO_2. But HOM monomers can be from both of these reactions. On the other hand, in the real atmosphere, e.g., some polluted urban areas, where RO_2 mainly reacts with NO instead of another RO_2, we may not observe HOM dimers at all. In this case, IR2 would be better than IR1,

as discussed in more detail in section 3.5. Following the reviewer's suggestion, we added more discussion: **This highlights that in the well-controlled chamber systems we investigated, IR1 may hold better potential for indicating O_3 formation sensitivity in the absence of other perturbing factors. It can be explained by the fact that the nitrates are solely from RO_2+NO and the dimers solely from RO_2+RO_2. But HOM monomers can be from both of these reactions. On the other hand, in the real atmosphere, IR1 is expected to be much less robust, as discussed in more detail in section 3.5.**

Comment #4:

It is specified that this chamber study can estimate indicating ratios in determining O_3 formation sensitivity, both qualitatively as well as quantitatively. I suggest adding a table that shows the estimated and measured values of O_3 concentration as well as the indicating ratios, which will make it easier for the readers to refer to the values.

Response:

This is an important comment, and it seems that there is a misunderstanding towards our use of the term "quantitatively". We wanted to express that even the absolute values of the indicating ratios can determine either VOC- or NO_x-limited regimes in our experiments, and we already "quantitatively" gave the thresholds (i.e., IR1/IR2: <0.2/0.4, VOC-limited; >0.5/0.7, NO_x-limited). We now realize that it can be confusing and misleading to use "quantitatively", and we opted to remove this term completely from this context. Our point is already made clear by the fact that the absolute IR values alone were able to determine the sensitivity regime.

Technical comments

Comment #5:

Line 205: Despite showing a faster decay compared to $HOM_{ON,O\leq8}$, non-nitrate HOM monomers with fewer than 9 oxygen atoms ($HOM_{Mono,O\leq8}$) also showed overall slow decays (Fig. 3). – This sentence needs to be rewritten.

Response:

Additionally, non-nitrate HOM monomers with fewer than 9 oxygen atoms ($HOM_{Mono,O\leq8}$) also showed an overall slow decay (Fig. 3).

Comment #6:

After Table A1, the line 'The figures are shown....' should be deleted or completed.

Response:

Thanks for pointing out the redundant sentence, and it has been deleted.

References

Peräkylä, O., Riva, M., Heikkinen, L., Quéléver, L., Roldin, P., and Ehn, M.: Experimental investigation into the volatilities of highly oxygenated organic molecules (HOMs), Atmospheric Chemistry and Physics, 20, 649–669, https://doi.org/10.5194/acp-20-649-2020, 2020.