

RC1: ['Comment on acp-2021-901'](#), Anonymous Referee #1, 06 Dec 2021

Review of the manuscript “Global simulations of monoterpene-derived peroxy radical fates and the distributions of highly oxygenated organic molecules (HOM) and accretion products” by Xu et al.

This is overall a very interesting and well written global model study about peroxy radical autoxidation and the formation of Highly Oxygenated organic Molecules (HOM) from monoterpenes. The authors should be honored for that this is one of the first attempts to provide a global model assessment of the contribution of HOM from monoterpenes to the atmospheric SOA levels. The model sensitivity runs clearly demonstrate the large uncertainties that still exists about the HOM SOA production from monoterpenes. I think the manuscript is well worth to be published in atmospheric chemistry and physics after some relatively minor but essential revision.

General comment:

You perform a comprehensive set of global model sensitivity runs with different RO₂ autoxidation rates, RO₂+RO₂ termination rate coefficients and initial RO₂ branching ratios as listed in Table 1. But why do you not compare and try to constrain the mechanism uncertainties using existing observations from laboratory experiments? E.g. in the global chemistry transport model study by Weber et al. (2020) the mechanism was tested and compared against existing laboratory experiments and then after this used for global model simulations. Also it would be suitable to discuss your results a bit more in the context of existing atmospheric modelling studies about HOM formation such as Zhu et al. (2019), Roldin et al., (2019) and Weber et al. (2020). What are the major differences and similarities of the present mechanism and these other existing peroxy radical autoxidation and HOM formation mechanisms?

We thank the reviewer for their evaluation of our paper and suggestions for improving it.

We have based our mechanisms (e.g. rate coefficients and product branching) on the papers already compared to measurement data (e.g. Jokinen et al., PNAS, 2015; Berndt et al., ES&T, 2018; Pye et al., PNAS, 2019). That is, the mechanism is largely based on laboratory studies, and in this study we focus on the atmospheric implications of laboratory-constraint parameters in a global chemistry model, which is different from the studies referenced by the reviewer in this regard as we elaborate below.

Following the suggestion, we have evaluated the differences and similarities of our study with other existing studies like Zhu et al. (2019), Roldin et al., (2019) and Weber et al. (2020), and added some related discussions in the manuscript. From our perspective, despite different models used, most

reaction pathways and assumption details are quite similar among the studies, mainly because they rely on quite similar base mechanisms (e.g. MCM) and HOM-related laboratory experiments. However, some differences are also important to note.

The work of e.g. Roldin et al. (2019) and Weber et al. (2020) are not focused on implementation in an online global-scale simulation. In our study, the species are generally more lumped, in some cases based on existing GEOS-Chem species and some reactions are more simplified, but representative, for more efficient computation. Thus, this study allows the presentation of global-scale distributions, transport, and fates of HOM, which is a main additional feature compared to the previous studies. Additionally, some previous studies like Weber et al., (2020) treat HOM as gas-phase, while in this study we treat HOM as the total of both gas- and particle-phase compounds which allows for a more complete assessment of HOM contributions to the organic aerosol burden. The different treatments make the parameterizations of dry/wet deposition, the consideration of HOM condensation and chemical loss quite different among the studies.

The work of Zhu et al. (2019) also adds HOM formation reactions into global chemistry transport model and performs global-scale simulations, but it is based on the CESM model and focuses on nucleation. In their scheme, diacyl peroxide, pinic acid, pinanediol, and some oxidation products of pinanediol are defined as HOM, which is different from the consideration in this study. Their work considers the nucleation and transformation of HOM to SOA, while in this study gas- and particle-phase HOM are lumped together to analyze the HOM fates and distributions. Also, differences in the existing chemical schemes embedded in different global models should bring different results, even if the added mechanism is largely similar.

When I started to read the manuscript I thought that the modelled HOM concentrations you mention were gas-phase concentrations but on L238-239 it is indicated that it is the total gas+particle phase HOM concentrations you model. I think this should be clearly stated earlier in the manuscript. This assumption will of course also influence the dry and wet deposition losses of HOM and their chemical degradation. As I am sure that you are aware of, not all HOMs are ELVOCs and they will not partition irreversibly to the particle phase.

The reviewer is correct that not all HOMs are ELVOCs, and so gas-particle partitioning will be important to quantify in more refined model frameworks. Our approach assumes all HOM partition to existing organic aerosol mass, to provide insight into the upper-limit contribution to organic aerosol for HOM that form. We therefore treat HOM fate, in terms of dry/wet deposition, as though it were instantaneously organic aerosol. We now make this clearer in the model description.

The parameters from previous laboratory experiments were impart derived by fitting the disappearance of HOM from the gas-phase and the increase in organic aerosol, so the net partitioning of HOM to aerosol is partially represented by our choice of parameters. We further expect that most non-nitrate HOM with 7 or more O will be LVOC or ELVOC and thus largely partition to existing organic aerosol [Ehn et al] present at 1 ug/m³ or higher concentrations, which is commonly achieved. So, we certainly agree that some of the implied overestimates of organic aerosol predicted by assuming all HOM partition could well be that estimates of HOM volatility are significantly in error, which is a conclusion we mention more clearly now.

Specific comments

Abstract L31-34: "Within the bounds of formation kinetics and HOM photochemical lifetime constraints from laboratory studies, predicted HOM concentrations in MT-rich regions and seasons reach 10% or even exceed total organic aerosol as predicted by the standard GEOS-Chem model."

I had some problem to understand the meaning of this sentence. Can it be reformulated? I guess that the meaning is that, according to the model simulations, HOM from monoterpenes contribute to a SOA increase of between 10 % and up to more than 100% depending on the model assumptions.

Since the GEOS-Chem model version we use has an SOA formation scheme from MT, we assume that some of the SOA predicted includes already effects of HOM. Thus, replacing the existing SOA mechanism with one that explicitly treats HOM would not necessarily double current predictions – but could provide the explanation for all previously predicted MT SOA.

We have tightened the wording of the abstract and we have changed the above sentence to read: "Predicted HOM mass concentrations in MT-rich regions and seasons can exceed total organic aerosol mass concentrations, predicted by the standard version of GEOS-Chem depending on parameters used."

L166-168: "The fraction of first-generation MT-RO₂ able to undergo unimolecular H-shifts, and thus autoxidation (MT-bRO₂), is 20% from MT + OH and 3% from MT + O₃, in the base simulation (Table S3)."

Too me this sounds like a very low fraction of MT-bRO₂ formation from MT+O₃. The experimental results from Ehn et al., (2014) and Jokinen et al. (2015) for different monoterpenes and the detailed modelling of α-pinene + O₃ experiments at variable NO levels by Roldin et al. (2019) indicate that the HOM yields and HOM

SOA formation from MT + O₃ are substantially higher. I think this motivates a model sensitivity run with higher HOM production from MT+O₃ “HighProd” while keeping the default “LowProd” MT+OH fraction in the model. It would be interesting to compare the modelled diurnal trends from such a run with the existing HOM observations.

We report the fraction of first-generation MT-RO₂ able to undergo unimolecular H-shifts as a molar yield, which is ~ 1.5 to 2x smaller than the resulting HOM mass yield.

In addition, beta-pinene + O₃ isn't expected to lead to prompt C₁₀ HOM, but in GEOS-Chem alpha- and beta-pinene are lumped, and thus we take a lower overall fraction will probably avoid overestimate of MT-bRO₂ formation. Increasing the fraction would lead to higher HOM concentrations, and as we already show, within the current bounds allowed by laboratory studies, HOM concentrations can exceed total organic aerosol.

L180. “These MT-HOM-RO₂ undergo only bimolecular reactions with HO₂, RO₂, and NO₂, NO₃.”

I guess you mean NO and not NO₂ or?

Figure 1. “I do not see any specific HOM closed shell products formed from RO₂+RO₂ reactions in the schematic figure. Did you not consider C₁₀ HOM formation from RO₂+RO₂ reactions? Why do not HOM-RO₂ react with other RO₂ according to this scheme?”

Thanks for catching these issues. “NO₂” should be “NO”, and is now corrected. MT-HOM-RO₂ do react with other RO₂ in this scheme, but the green arrow is missing. We assume these reactions lead mostly to accretion products or fragmentation products. We have corrected the figure. In the current scheme, RO₂+RO₂ reactions can lead to HOM, specifically when Mta-RO₂ react with other RO₂, a small fraction is assumed to produce MTb-RO₂, which can undergo autoxidation. This is analogous to the suggestion of Kurtén et al JPC 2015 (see manuscript) that alkoxy driven ring opening of a-pinene radicals can lead to autoxidation.

L287-289: “For HOM measurements, molecular formulas of compounds contain 10 carbon atoms and greater than or equal to 7 oxygen atoms were selected as HOM for comparisons.”

Are the closed shell HOM products with 7 or more O atoms not primarily expected to be products from MT+O₃? I thought that the MT+OH oxidation primarily are expected to results in closed shell HOM products with 6 or possibly 7 O atoms. In the manuscript you do not call the ROOR dimers HOM but accretion products. Did

you not compare modelled and observed HOM (accretion products) with >10 C atoms? This would maybe provide some constraints on the importance of ROOR for the atmospheric SOA production.

MT + OH has been observed to produce HOM with 7 or more O, though mostly 7 is what the kinetic modeling suggests (see Bernd et al Nat Com 2016 and Pye et al PNAS 2019). We do not include products with 6 or less O as HOM. We also aim to only track HOM with 10 C atoms, or associated accretion products of C10-RO2. These choices are partly based on improving the validity of our assumption that most HOM we track would be low or extremely low volatility. Therefore, we only consider C10 compounds in the observations to which we compare.

Table 4 and L427-429: “Interestingly, even for a small branching to accretion products, MT-RO2 derived accretion products are a substantially larger fate than HOM, suggesting either that the rates and branching are too high or that the chemical loss pathways of associated products are not well represented.” This, seems a bit strange. I think this should motivates some sort of box-model tests and evaluation of the present mechanism against existing HOM dimer (C18-C20) gas-phase observations from laboratory smog chamber experiments. Does this imply that most RO2s that undergo autoxidation are lost by RO2+RO2 reactions leading to ROOR before they become HOM-RO2 in the present mechanism? The model do seem to overestimate the Isoprene concentrations in Centreville and Amazon quite a bit according to Figure S8. Can this result in overestimated RO2 +RO2 cross reactions and ROOR formation?

We agree with the reviewer that the importance of RO2 + RO2 as a fate for MT-RO2 in wide regions is likely unexpected but that is in large part because laboratory studies have found MT-RO2 + RO2 rate coefficients to be much larger than what is traditionally included in GEOS-Chem mechanisms. Indeed, a key point of our paper is that these new rate constants have a large change in what the fate of RO2 is, which Berndt et al (see main manuscript for reference) already pointed out using a different model incorporating the Berndt et al rate constant measurements. There is disagreement as to what the appropriate RO2 + RO2 rate constant is for an average MT-RO2 + other-RO2, and Isoprene-RO2 plays a major role, but both sets of new rate constants are significantly larger than what GEOS-Chem used in the past, so our finding of the importance of RO2 + RO2 as a fate is not dependent on which set of rate constants are used.

There is even larger disagreement and thus uncertainty as to the product branching of the RO2+RO2, in terms of accretion products vs radical propagation or termination. We illustrate the very large differences in predicted accretion products using the 4% branching vs 100% branching for MT-HOM-RO2. We agree that further refining these values, which we have

taken from comparisons to laboratory oxidation studies (flow tube not smog chamber studies Zhao et al PNAS 2019 and Berndt et al EST 2018) will be crucial for simulating SOA through an explicit HOM-RO2 mechanism.

A second contributing factor to uncertainty about RO2 + RO2 as an important fate is whether models such as GEOS-Chem accurately predict NO concentrations in remote forest boundary layers. The geographical extent of regions with RO2+RO2 as a dominant fate might not be as large as shown here if soil NOx emissions or NOx recycling mechanisms are not sufficient. However, that will require field measurements of NOx to constrain the models on this aspect.

A related point raised by the reviewer in a few comments is on the accuracy of BVOC emissions inventories, both of MT and especially isoprene in this context of RO2+RO2 because as noted, the dominant RO2 reacting with MT-RO2 is often isoprene-RO2. The validation of these is beyond the scope of this paper but will certainly be a key factor in improving predictions of SOA.

L533-539 “We scale the predicted HOM concentrations in the lowest model level by the ratio of observed to predicted monoterpene concentrations in order to account for potential biases in the monoterpene emissions (Figure S8). For SOAS and GoAmazon, we use the hourly average measured monoterpene data to compare with the hourly GEOS-Chem predictions, while for the BAEEC campaign at SMEAR II station, we use the campaign average of measured monoterpene concentrations.”

First, I do not understand this approach completely. You also state that the particulate HOM potentially represent the integral of multiple days of formation. Thus, most HOM PM will not be formed at the station but upwind the station where the monoterpene concentrations will be different.

Second, does not the absolute BVOCs concentrations and RO2 pool also influence the fate of the MT-bRO2, MT-cRO2 and HOM-RO2 concentrations and the relative fraction of C10 HOM and HOM accretion products (ROOR)? I think that the relatively large differences/uncertainties in the observed and modelled BVOC concentrations could be mentioned as an additional source of error in the absolute HOM SOA formation. Maybe the uncertainties in the absolute BVOC emissions are even greater than the HOM SOA yields? I suggest that you extend the discussion about these uncertainties in the paper.

We have found that using the default MEGAN emissions does not accurately reproduce the observed concentrations of BVOC precursors like isoprene and monoterpenes as shown in Figure S8, which will certainly influence the comparison to HOM concentrations. We assume that the modeled HOM concentration bias is linearly proportional to the bias of modeled

monoterpenes, and we use the ratio of observed to predicted monoterpene concentrations to “correct” the predicted HOM concentrations. We agree this correction is limited in accuracy because observed HOM (in the particle phase) may be transported to the site rather than formed locally, but essentially we are assuming that the monoterpene emission and chemistry model bias extends to the upwind locations.

This issue highlights the BVOC emission and concentration uncertainty that brings additional sources of error in the HOM formation simulation. The simulated BVOC concentration at and near the observation site in GEOS-Chem may be quite different from observations, and thus the RO₂ concentrations and complex interactions within the RO₂ pool may also be quite different. Our scaling here can only serve as a simplified way to reduce the concentration bias when most HOM are formed locally, but when upwind transport prevails, it is much less useful. Comparisons of simulated HOM concentrations and related nucleation mode particles to observations will be sensitive to the accuracy of BVOC emissions, not just the chemistry.

Figure 9. I did not find a definition of the R_{mt} scaling factor used to generate the results in Fig. 9 in the manuscript. I think it would be good to also provide the reader with some information about the modelled and observed absolute HOM-ON and HOM-non-ON C₁₀ concentrations at each station e.g., in the form of a table.

Please see the previous comment about the scaling factor and its applicability. We hesitate to add more to this paper which already has a significant number of tables and figures, and the observations of HOM-ON and HOM-non-ON have been described before in the literature in the referenced papers.

This would then provide some information about the total uncertainties in the surface layer HOM SOA concentrations. It is not clear to me which altitude above the ground that the observed and modelled HOM concentrations and MT, NO and O₃ concentrations in Fig. S8 are taken from. The observed NO concentrations seem to be close to the detection limit of conventional NO monitors and I also wonder why the observed and modelled NO concentrations do not go down to 0 in the nighttime at some of the stations. Can you please add a short discussion about this in the SI?

For comparison to observations, we sample the model within the closest lat/lon grid at the lowest model level (typically having a mid-point of about ~60 m above ground). We agree the NO concentrations are likely close or below the detection limits of conventional monitors, but if NO is actually lower than measured, it does not affect our conclusions. The elevated NO at nighttime in the Amazon location can be due to several reasons, such as

continued NO emissions and low/titrated O₃, detection limit issues in both NO and O₃ instruments, among other possibilities.

SI, "MT-RO₂ reactions with NO/NO₃"

"Yet for MT-aRO₂, a 5% branching of MT-bRO₂ formation was added. This is because in polluted regions, the formation of HOM may well be facilitated by certain NO reactions through the alkoxy channel"

I agree that such pathways probably are important to consider but what do you base this assumption on? Did you consider some experimental observations or other existing mechanism that have been evaluated and constrained this pathway to HOM production in the presence of NO? The near explicit Peroxy Radical Autoxidation Mechanism (PRAM, Roldin et al., 2019), which was constrained using α -pinene ozonolysis experiments at variable NO concentrations, also take into account such RO₂ + NO \rightarrow RO and RO + O₂ \rightarrow bRO₂ formation pathways.

For the most part we chose the 5% branching based on the possibility that RO₂ + RO₂ is the source of HOM from ozonolysis as previously proposed by Kurtén et al JPC 2015. Other than that, it is mostly uncertain. Given that in large regions the RO₂ + RO₂ fate is more important than the RO₂ + NO fate, we leave it as such, but we now mention the branching from Roldin et al, 2019 as suggested by the reviewer.

We now also reference the other publications suggested by the reviewer:

Öström et al. Atmos. Chem. Phys., 17, 8887–8901, 2017

Zhu, Nat. Commun., 10, 423, <https://doi.org/10.1038/s41467-019-08407-7>, 2019.

McFiggans et al, Nature, 565, 587–593, <https://doi.org/10.1038/s41586-018-0871-y>, 2019

Roldin, et al. Nat. Commun., 10, 1–15, <https://doi.org/10.1038/s41467-019-12338-8>, 2019

Weber et al. Atmos. Chem. Phys., 20, 10889–10910, 2020

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RC2: ['Comment on acp-2021-901'](#), Anonymous Referee #2, 19 Dec 2021

General Comments

In this study, autoxidation reactions and the resulting highly oxidized organic molecules (HOM) and accretion (ROOR) products derived from monoterpene oxidation were incorporated into the GEOS-Chem model, with wet and dry deposition and photolysis being sinks for HOMs and ROOR products. Sensitivity studies were conducted for a range of reaction rate constants and branching ratios taken from recent lab studies to explore the competition between MT-RO₂ isomerization and bimolecular reactions with RO₂, HO₂, NO, and NO₃, and their impact on the fates of monoterpene-derived organic peroxy radicals (MT-RO₂). Model predictions of MT-RO₂ fates or HOM concentrations are presented for annually averaged global distributions in the planetary boundary layer and vertical and diurnal profiles in the Southeast US and Amazon. When possible, the results are compared to results from field campaigns in an effort to constrain the input values used in the model.

I think this is an interesting and important study, and provides useful insights into the likely role of autoxidation in the atmospheric chemistry of monoterpenes and the potential contribution of HOM and ROOR products to secondary organic aerosol formation. It also points out the sorts of future studies that are needed to improve confidence in the model predictions, a valuable contribution. The work seems technically and scientifically sound, the sensitivity studies explore an appropriate set of conditions, and the discussion of the observed model trends is thorough and reasonable. The manuscript is also well written. I have no Specific Comments and only a few Technical Comments, and so think the manuscript can be published in ACP with only very minor edits.

We thank the reviewer for their time evaluating our manuscript and their technical comments to improve it.

Specific Comments

None.

Technical Comments

We have made each change or addition as suggested by the reviewer below

1. Line 52–53: I suggest defining SVOC, LVOC, and ELVOC.
2. Line 97: “Hydrogen” should be “hydrogen”.
3. Line 124: Add link.

4. Line 162: "Pinene" should be "pinene".
5. Line 280: "Ozone" should be "Oxidant".
6. Line 288: "contain" should be "containing".
7. Line 289: Delete "atom".
8. Line 442: "concentrations" should be "concentration".
9. Lines 648–652: Something missing in the sentence. Perhaps Line 651 should read "...predicted by the model indicate a comprehensive...".

Citation: <https://doi.org/10.5194/acp-2021-901-RC2>