We thank the reviewers for their encouraging and helpful comments on our manuscript. One major change we incorporated in our revised manuscript is to **remove discussion regarding sesquiterpene (BCARY) SOA**. This simplification is made because reactions of BCARY are highly uncertain and contribute little (< 1%) to OH-initiated BSOA, according to our results. Thus, this change has no impact on our main conclusions and simplifies the discussion.

Below, please find our point-to-point responses in black, the reviewers' comments in blue, and our edits to the manuscript in red.

Responses to reviewer #1

This manuscript describes a series of modeling experiments performed in CESM2 to test the importance of newly elucidated pathways in biogenic volatile organic compound (VOC) chemistry to the formation of secondary organic aerosol (SOA), and the resulting changes in that SOA under past and future climate scenarios. Specifically, the authors implement a number of new peroxy radical (RO2) reaction pathways in the model's chemical mechanism, some of which do not form SOA but compete with SOA-forming pathways (for isoprene) and some of which have SOA-forming capabilities of their own (isomerization and RO2 + RO2 chemistry, especially from monoterpenes). Using parameters from the literature for these new pathways, they authors find that monoterpene-RO2 isomerization is a hugely important pathway, accounting for nearly half of monoterpene-derived SOA. They also find that the effect on SOA of changes in biogenic VOC emissions from preindustrial to present to future conditions overwhelm the effects of changing chemistry (via temperature-dependent reaction rates and changing bimolecular RO2 reaction partners) and thermodynamics (gas-particle partitioning), and will likely cause increased in biogenic SOA in a warmer future climate.

The results of this study are certainly important and useful, and worthy of publication following some clarification as described below. I'm also very impressed by the clarity of the writing. The edits made to the model and mechanism are extensive, but I felt they were clearly enough laid out and walked through that I was never lost. The step-by step discussion of modeling results is excellent; in particular the paragraph on separating chemistry from emissions (L 551-565) does an exceptional job of explaining the experimental setup and highlighting the important results in a concise and clear manner. I think the finding that the change from PD to F is completely due to emissions -- and in fact that chemistry & thermodynamics would lead to a decrease in SOA with BVOC emissions held constant -- is an important one that should be highlighted in the abstract!

Thank you for the encouraging comments. We have added text to refer to impacts of chemistry and thermodynamics changes in our abstract as follow.

"Total biogenic SOA formed through OH oxidation decreases by 41% from PI to PD and increases by 113% from PD to F. This evolution from PI to F is largely driven by changes in biogenic VOC emissions, rather than shifts in chemistry or thermodynamic partitioning."

My main concern is that a lot of the mechanistically-specific conclusions (that monoterpene isomerization is hugely important to SOA formation; that RO2 + RO2 chemistry is not) seem based on the particular parameters the authors chose out of many highly uncertain ones, and this uncertainty is not satisfactorily expressed in the places where quantitative conclusions about the contributions of these pathways are noted. While some of these uncertainties are discussed in the methods section, they are then glossed over in places like the abstract and conclusions where headline numbers about the importance of isomerization, e.g., are reported. In particular, I *don't* think it's worth highlighting quantitatively in the abstract the very precise fraction of monoterpene SOA formed by isomerization (44-46%), which makes it look like the uncertainty range on this is tiny when in fact the parameterization that went into it is highly uncertain.

We have replaced the precise fraction of MTERP SOA formed by isomerization in our abstract with "nearly half". The modified sentence reads as follow.

"We find that in PD conditions, RO_2 isomerization accounts for nearly half of monoterpene SOA, while the contribution from RO_2 + RO_2 pathways is minor."

We agree with the reviewer that there are large uncertainties related to SOA formation. We tried to address this concern in our revised manuscript. Please find details below where we respond to the specific comments.

I write more detail below on the specific elements of uncertainty (or at least the specific parameters that seem highly uncertain) that come to mind, but overall I think the magnitudes of these compounding uncertainties in reaction rates, yields, and simplifying parameterizations (e.g. lumping of all terpenes and treating them like a-pinene) merit more discussion -- for example, how big a range could the isomerization fraction of monoterpene SOA actually span given the uncertainty on parameters like its rate, its SOA yield, the isomerize-able fraction (especially given the lumping of all terpenes into a-pinene), the low volatility and photorecalcitrance of its products? Not that you need to do more simulations testing all this -- just some back-of-the-envelope type analysis to temper the conclusions would be useful, I think.

Following the reviewers' suggestions, we have added more uncertainty discussion in our manuscript (both methodology and results sections). This includes discussion about (1) SOA formation through heterogeneous reaction; (2) lumping MTERPs into one species; (3) simplification of the isomerization mechanism and its SOA yields; (4) isomerization

branching ratio; (5) yields of RO_2 + RO_2 reactions and the volatility of the dimer products; (6) neglection of SOA formation through non-accretion products from the RO_2 + RO_2 reactions; (7) RO_2 reactions with NO_3, CH_3O_2, and CH_3CO_3; (8) ISOP-RO_2 + ISOP-RO_2 reactions; (9) SOA photolysis. Detailed of these discussions can be found in our point-to-point responses below. Our previous work also includes uncertainty discussion regarding (1) MTERP-RO_2 isomerization rates; (2) RO_2 + RO_2 reaction rates; (3) ISOP-RO_2 isomerization.

- L174-175 --> but ISOP makes SOA mostly through heterogeneous reactivity (IEPOX uptake being a reactive process), not volatility, so isn't that problematic? Not suggesting that you fully revise the isoprene SOA scheme here, but has there been any previous assessment you can point to here of the errors introduced by treating IEPOX SOA as a volatility-driven process, and/or can you speculate on how that would influence your findings about PI vs PD vs F for isoprene SOA?

The reviewer raises an interesting point. We agree that heterogeneous reaction is an important pathway for ISOP SOA formation (Marais et al., 2016; Paulot et al., 2009). However, we note that the split between gas-phase and aqueous-phase ISOP SOA formation (as constrained by lab experiments) is not well understood and represented in models. Most models have chosen to represent only one of these pathways. Our chemical mechanism follows the standard CAM6-Chem VBS configuration, considering only gas-phase reactions as in several other models (e.g., Bergman et al., 2022; Kirkevåg et al., 2018; Lou et al., 2020). Whereas the detailed SOA scheme in the GEOS-Chem model for example, exclusively represents aqueous phase isoprene SOA formation (Pai et al., 2020). Using gas-phase VBS potentially overemphasizes the sensitivity of SOA formation to volatility, which may particularly impact our estimates on future SOA. Also, this treatment mutes the impact of SO_2 emissions on ISOP SOA formation through perturbing aerosol acidity (Jo et al., 2021; Marais et al., 2016).

We clarify this uncertainty and how it may influence our results in the manuscript as follow.

In Section 2.2:

L179-186: “We note that our mechanism focuses on gas-phase reactions, whereas the SOA formation through heterogeneous chemistry is not considered as in baseline CAM6-Chem and many other models (e.g., Lou et al., 2020; Bergman et al., 2022; Kirkevåg et al., 2018). The aqueous-phase reactions are particularly important for isoprene SOA formation (Marais et al., 2016; Paulot et al., 2009). Ignoring these pathways may overemphasize sensitivity to volatility and overlook the impact of SO_2 emissions on SOA formation through perturbations in aerosol acidity (Jo et al., 2021; Marais et al., 2016).”

In Section 3.2:

L585-586-705: “In addition, our results may be oversensitive to volatility, due to the absence of aqueous phase isoprene SOA formation pathways.”

- L177-179 --> lumping of MTERP RO2s seems problematic given their very different structures; they'll likely have very different reaction pathways and balances between fragmentation vs functionalization. It's fine if the existing mechanism is tuned to get this right given the distribution of monoterpenes, but will that distribution change under preindustrial or future scenarios, and what influence would that have?

This difference in chemistry due to structures is certainly likely (e.g. SOA yields have been shown to be higher for limonene than other monoterpenes (Lee et al., 2006; Pye et al., 2010)) but is generally not fully constrained or represented in chemical mechanisms. This is true for baseline representations of SOA in 3D models, where yields are typically based on single monoterpene experiments. In particular, the VBS model framework in CESM2 is developed based on Hodzic et al. (2016), where the VBS parameters are fitted to wall-corrected chamber data performed in Caltech chambers (Zhang et al., 2014). The monoterpene yields are derived from α-pinene experiments, without considering other monoterpenes. Our additions to the biogenic SOA scheme follow this paradigm where we use available data and apply to all monoterpenes uniformly. Given that speciated parameters are not comprehensively available, we cannot speculate what influence this would have on our final results, but we now acknowledge this uncertainty in our manuscript:

L187-194: “Following the treatment in default MOZART-TS2, the RO_2 formed from the four MTERPs are lumped together in the modified VBS and assumed to have the same yields and reaction rates for the RO_2 reactions, due to a lack of comprehensive speciated data. We note that MTERP species have different structures and thus different distributions of reaction products. For example, LIMON has been found to have generally higher SOA yields than the other MTERPs (Lee et al., 2006; Pye et al., 2010). Therefore, the lumping treatment may bias the MTERP SOA burden and distributions.”

- L182-183 isn't that work by Pye et al just for a-pinene? Do these rates and yields hold across MTERPs, and if not, how much uncertainty is introduced from your treatment here?

Yes, the reviewer is correct. As in the above response, we apply the results of Pye et al. (2019), which is specifically for α-pinene, to the other MTERP species, due to the limited knowledge of the other MTERPs. The rates, yields, and branching ratio of the other MTERPs may be different from α-pinene. For example, Piletic and Kleindienst (2022) suggest that the branching ratio of RO_2 that can isomerize is similar for α-pinene and β-pinene but that for limonene is likely higher. The lumping assumption likely introduces substantial but poorly constrained uncertainty into our mechanism. We clarify this in our manuscript:

L216-222: “It is important to note that the branching ratio, SOA yields, and reaction rates are subjected to significant uncertainties, and we have applied the values from Pye et al. (2019) for α-pinene to all monoterpenes. This may introduce substantial uncertainty into our mechanism, given differences in the related parameters for other MTERPs. For example, Piletic and Kleindienst (2022) suggest that the branching ratio of RO_2 that can isomerize is similar for α-pinene and β-pinene but is likely higher for limonene. However, these uncertainties are generally poorly constrained. "

We further acknowledge this issue in Section 3.1.

L387-389: “Conversely, neglecting higher branching ratios and yields for limonene SOA may underestimate the importance of isomerization for total SOA formation from monoterpenes.”

Overall, we do not have information to quantitatively estimate the uncertainty. However, in the original submitted manuscript we included a brief discussion about reaction rates, according to Xu et al. (2019).

- L188-195 the isom pathway seems extremely poorly constrained and heavily oversimplified; is there any constraint on the high SOAG yields and subsequent SOA production from this pathway? Does that match any ambient or chamber observations? And is there any information at all informing the implementation of an equivalent rate and product yield for BCARY? I'm glad you acknowledge the uncertainties here, but later in the results section (e.g. L 313-321) it sounds like it's taken as fact, since you're describing the huge impact of isomerization-derived SOA there without any mention of the high uncertainty.

Thank you for this comment. Please find our responses below regarding the three aspects raised by the reviewer.

(1) About simplification

Indeed, we simplify the isomerization mechanism by Pye et al. (2019) to maintain computational efficiency and accommodate the complexity of the chemical mechanism in global models. In the original mechanism, the subsequent reactions of the first generation RO_2 and its products are also NO_x-dependent, with reactions with NO forming volatile compounds and competing with subsequent autooxidation. Our simplification loses this NO_x sensitivity and may overpredict SOA formation from isomerization under high-NO_x conditions. This bias can further influence our estimates in SOA trends from PI to PD and F. We clarify how the simplification is made compared to the Pye mechanism and the related uncertainty in the revised Section 2.2.

L200-214: “The 22% branching ratio is taken from the revised product yield of APINCO2 in the Table S1 of Pye et al. (2019), following the mechanism in Berndt et al. (2016) and Vereecken et al. (2007). The 50% SOA yield is calculated following Eq (S1) from Pye et al (2019) and their Table S2. To maintain computational efficiency and accommodate the complexity of the chemical mechanism in global models (consistent with the representation of other RO_2 pathways in the VBS), we collapse the multi-step autooxidation in Pye et al. (2019) into a single-step reaction, by only representing the first-generation branching point and the final SOA yield. In the original mechanism of Pye et al. (2019), the subsequent reactions of the first generation RO_2 and its products are also NO_x-dependent, with reactions with NO forming volatile compounds and competing with subsequent autooxidation. The SOA yield (50%) in our implementation is the maximum yield, assuming no subsequent competing bimolecular reactions. Therefore, our simplification does not fully represent the sensitivity of isomerization yields to NO_x, which may particularly result in overestimation of SOA formation from isomerization under high-NO_x conditions. This bias can influence our estimates of the SOA trends from the past to the future, as further discussed in Section 3.2.”

We further discuss this issue with other uncertainties regarding isomerization in Section 3.1.

L383-389: “We note that uncertainties in model parameters discussed in Section 2.2 and 2.3 could alter the estimated contribution of the isomerization pathway. In particular, the upper-limit 50% yield and applying the photo-recalcitrant fraction only to the lowest volatility bin (see Text S1) could over-emphasize isomerization. Conversely, neglecting higher branching ratios and yields for limonene SOA may underestimate the importance of isomerization for total SOA formation from monoterpenes.”

In addition, in Section 3.2, we mention this uncertainty due to simplification again after reporting the isomerization fSOA increase from 38% (PI) to 44% (PD) to 51% (F).

L579-585: “It is noted that the simplified representation of the isomerization process may overpredict SOA formed through this pathway under high-NO_x conditions (see Section 2.2 for details). Since the NO emissions peak in PD (Figure 7c and 7d), this high bias is likely to be more significant in PD than in PI and F, which may impact the continuous increasing trend in isomerization SOA contribution from PI to F and would further reduce the minimum predicted SOA in PD (see Figure 10a and the discussion below).”

(2) About constraints

Pye et al. (2019) validated their mechanism using chamber experiment data from the Secondary Organic Aerosol From Forest Emissions Experiment (SOAFFEE, see their Table 1). They found that they can reproduce the measured SOA yields, SOA O:C ratios, and volatility only after including the isomerization mechanism in the standard master chemical mechanism (MCM). Standard and regional CTM do not show similar agreement with observations.

Other than the above comparison, unfortunately, we did not find lab or field studies that can be used to constrain this pathway. Specifically, for our global modeling results, although isomerization has a large SOA yield, it decreases the SOA formed from the other pathways (Figure 5a). As a result, the total MTERP + OH SOA only increases by 20 to 30 %, which would be difficult to distinguish in the observed total organic aerosol.

In the revised manuscript, we highlight that more chamber experiments and ambient observations are needed to better constrain this pathway.

L227-228: "Overall, more chamber experiments and ambient observations are needed to better constrain the MTERP-RO_2 isomerization pathway."

(3) About BCARY

We agree with the reviewer that the isomerization (and the accretion reactions) of BCARY-RO_2 is highly uncertain and poorly studied. Also, according to our current results, BCARY only makes minor contribution to total SOA and the trends from PI to PD (Figures 5c and 10c). Therefore, we have decided to fully remove BCARY from our manuscript.

- Table 2 --> it appears that these added RO2 + RO2 reactions in Part 2 consume gas-phase RO2s that weren't part of the VBS scheme, which is contrary to how this mechanism's previous VBS chemistry seems to work, in that none of the reactions in Table 1 consume the gas-phase compounds implicated in the reactions (i.e. the reactions of precursors with OH still have the precursor and OH on the right side of the equation, so they effectively don't consume it, and the reactions of VBS compounds with HO2 & NO don't consume those either). Does the newly-added consumption of gas-phase RO2 in your scheme influence gas-phase chemical outcomes (I'm especially thinking of oxidant recycling) in places where this chemistry happens abundantly? I wouldn't be surprised, for example, if this consumption of RO2 in, say, the Amazon leads to somewhat lower HOx levels there...

Yes, the RO_2 + RO_2 reactions in Table 2, part 2 introduces extra loss for the RO_2 species in MOZART chemistry which are currently not represented in the gas-phase chemical mechanism (contrary to the pathways in part 3 for example which are already represented in the gas phase mechanism). Thus, across the gas-phase + VBS scheme, RO2s consumption and that of their bimolecular reaction partners is now fully represented. The impact on the global distributions of HO_x is shown below in Figure R1. Differences are relatively small and geographically variable. From BASE to NEW_fast, OH and HO_2 increase over the tropical forest regions (Figure R1a and R1c). This is potentially because the newly added consumption of RO_2 leads to less terminal loss of HO_2 through the RO_2 + HO_2 reaction. This impact is less evident in NEW_slow (which is the basis for all our PI to F results) because slower accretion reaction rates result in less RO_2 loss than in NEW_fast.

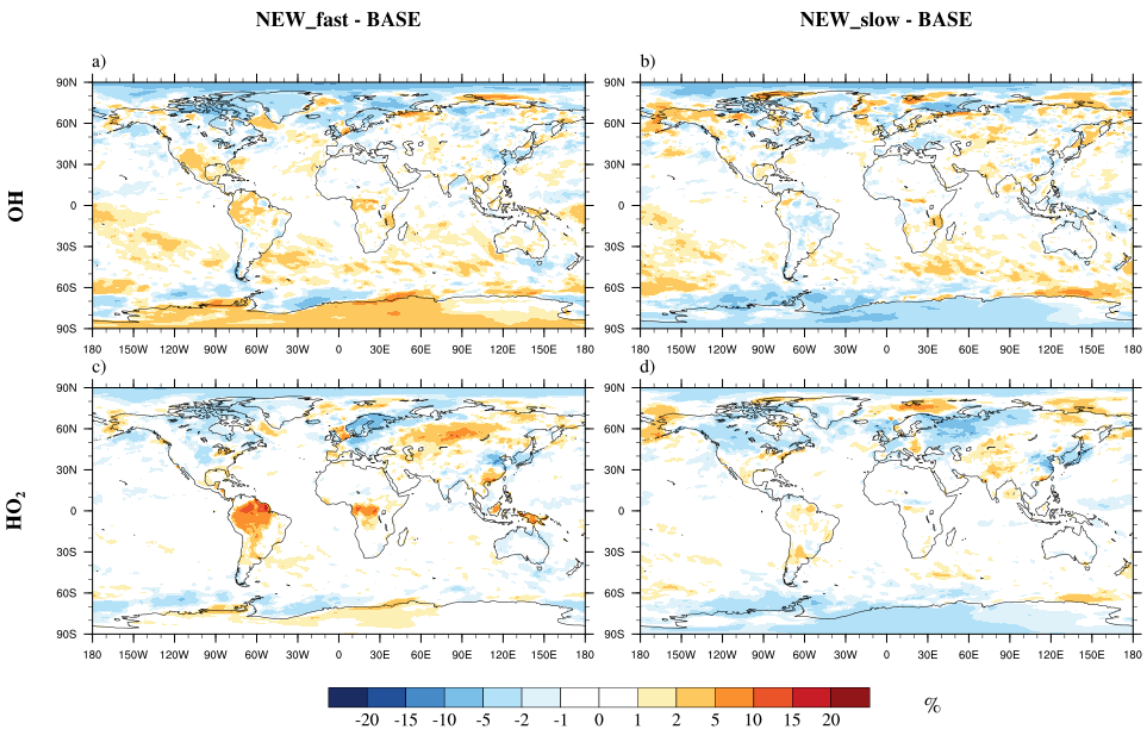

Figure R1. Global distributions of percentage changes in surface concentrations of OH (top row) and HO_2 (bottom row) from BASE to the new experiments. All percentage changes are calculated with respect to BASE.

- Also in Table 2 - Is it known that the reactions of MTERP/BCARY RO2's with CH3O2 and CH3CO3 make no SOA? (And ISOPRO2 + CH3O2/CH3CO3, for that matter, though that seems less likely anyway). And if that's known known experimentally, why is that assumed? Presumably these RO2-RO2 reactions could lead to a small fraction of accretion products (at least for the RO2 + CH3O2 reactions) -- the equivalent accretion products do show up as an appreciable chunk of the total in some locations in Mayhew et al (https://acp.copernicus.org/articles/25/17027/2025/, Fig 12, bottom, "sesquiterpenes + small VOCs" & "monoterpenes + small VOCs"). Even for the branching of these RO2 + RO2 reactions to non-accretion alkoxy radicals, some moderate-volatility products could be produced (especially for BCARY), for which volatilities could at least be estimated. Could you at least provide an estimate of what fraction of the mono-/sesquiterpenes go down these pathways to give the reader a sense of the uncertainty here?

Thank you for raising this point. We agree that these reactions may form SOA so our assumption may underpredict total SOA. We acknowledge Mayhew et al. (2025) in our manuscript. But we wanted to note that Mayhew et al. (2025) is not a direct comparison to our work. For one thing, they include VOC + O3 reactions, while we only focus on VOC + OH reactions. Also, they have explicit representations both first-generation RO_2 and RO_2

formed through downstream oxidation. So, some of the SOA from their monoterpene + small VOC accretion reactions may be already accounted by the empirical SOA yields from other RO_2 pathway (i.e., the double-counting issue mentioned by Mayhew et al. (2025)). Following the advice by Review #2, we also cite Kang et al. (2025). This is an experimental study showing that HOM-RO2 + RO2 may form HOM-RO, a branch of which can isomerize and propagate low-volatility HOM. In general, we think these processes, especially how much SOA is formed, are not well constrained. So, we decided to keep our current zero-SOAG assumption. The following discussion is added to Section 2.2:

L280-286: "Assuming these reactions do not form SOA may result in some underprediction in total MTERP SOA amount. Mayhew et al. (2025) reported that reactions with CH_3CO_3 can contribute to regional SOA formation by implementing accretion reactions generated by a chemical mechanism generator into a chemical transport model. A laboratory study also implies that highly oxygenated organic compounds (HOM) alkoxy radicals formed through HOM-RO_2 + RO_2 reactions may undergo isomerization and propagate low volatility HOM formation (Kang et al., 2025). However, these pathways are not well constrained."

Following the reviewer's suggestion, we estimate the fRO_2 for the MTERP/ISOP-RO2 reactions with CH3O2, CH3CO2. In total, these reactions contribute to 2-4% for total MTERP-RO2 fate and 4-5% for total ISOP-RO2 fate across all the experiments (i.e., NEW_fast, NEW_slow, PI, and F). The regional contribution is also small as can be seen from Figure 3e for MTERP-RO2.Therefore, should these reactions form SOA, the contribution to fSOA would remain minor. We further address this uncertainty related to MTERP-RO2 in Section 3.1.

L405-407: "Reactions with NO_3, CH_3O_2, and CH_3CO_3 only account for 2 - 4% of fRO_2. Thus, should any of these reactions form SOA, their contribution to the total MTERP SOA is likely to be minor."

For BCARY, as mentioned above, we have decided to fully remove it from our manuscript, due to the large uncertainty and its minor contribution to our results.

- Speaking of the branching to non-accretion products -- am I correct in interpreting the 0.04 SOAG0 yield from all the BCARYO2VBS + RO2 reactions as an attempt to represent just the accretion product, meaning that there's an assumed SOA yield of zero from non-accretion pathways? Again, this seems unlikely for the non-accretion pathways from sesquiterpenes and even monoterpenes, which leave you with more-oxygenated C10 and C15 compounds than you started with and could easily form compounds with low-enough volatility to contribute to SOA. Overall it seems this representation is likely to underestimate SOA from RO2 + RO2 pathways if it only accounts for accretion products, and with a fixed yield of 4%, despite mounting evidence that yields increase with molecular size (Berndt et al., 2018, DOI 10.1002/anie.201710989; Franzon, 2023, DOI 10.1021/acs.jpca.3c01890; Frandsen et al., 2025, DOI

10.1021/acsearthspacechem.4c00355). The justification for this fixed 4% number (L 222-224) needs to be stronger.

Yes, the reviewer is right that we only attempt to represent SOA formed through accretion products. We acknowledge this in our revised manuscript.

L271-273: "The SOA formed through non-accretion products from the RO_2 + RO_2 reactions is neglected, which likely underpredicts SOA formed through this pathway."

As mentioned above, we removed BCARY from our manuscript, due to its large uncertainty and little contribution to our results. Currently, we only represent the MTERP-RO_2 + RO_2 reactions (see revised Table 2, part 2) in our manuscript. But we keep the MTERPO2VBS + BCARYO2VBS reaction, as part of the MTERP-RO_2 reactions.

We agree with the reviewer that the yield of accretion products should ideally vary for different MTERP-RO_2 + RO_2 reactions, with higher yields expected for reactions involving larger and/or more oxygenated RO_2 species. However, we are not aware of a study providing quantitative estimates of the yields. We acknowledge these uncertainties and cite Berndt et al. (2018) and Franzon (2023) in our manuscript.

L269-271: "In addition, this fixed yield is likely an uncertain simplification, since the yields of accretion products are expected to be higher for reactions involving larger and/or more oxygenated RO_2 species (Berndt et al., 2018b; Franzon, 2023)."

In our previous Result Section (Section 3.1), we have acknowledged that the RO_2 + RO_2 SOA is likely underpredicted because the 4% yield is a lower limit. We further acknowledge the overlooked non-accretion products in the revised manuscript.

L392-395: "However, their contribution to total MTERP SOA is minor (8% in NEW_fast and 3% in NEW_slow). This is likely an underprediction, because only 4% of SOAG0 is formed through these reactions, and SOA formation through non-accretion products is neglected (as discussed in Section 2.2)."

- I assume "SOAG0" is a single compound with a fixed effective molar mass; if that's the case, surely the 0.04 molar yield of SOAG0 represents a fixed mass yield of this SOA compound from each of the RO2 + RO2 reactions, but that's not the same as saying that the reactions have the same dimer yields; a BCARYO2 + BCARYO2 dimer would have 30 carbons compared to a MTERPO2 + ISOPRO2 dimer's 15. So doesn't this method of fixing the yield at 0.04 SOAG0 skew the product formation, such that lighter precursors effectively have higher molar SOA yields? This is compounded by the fact that the C30 BCARYO2 + BCARYO2 dimer should be less volatile than the C15 MTERPO2 + ISOPRO2 dimer, and so should have a higher propensity to form SOA. You acknowledge this on L226-229, but it seems like it would be reasonable to estimate the volatilities of these dimers

and correctly apportion them into volatility bins rather than just putting them all in the same extremely-low-volatility bin together.

Before responding to the comment, we note again that we have decided to remove BCARY SOA from our manuscript, due to its large uncertainty and little contribution to our results. So, our responses here focus only on MTERP-RO_2 + RO_2 reactions as listed in Table 2, Part 2.

The reviewer raises a very good point - thank you for pointing this out! Yes, SOAG is a single compound, $C_{15}H_{38}O_2$, with molar mass of 250 g/mol. We agree with the reviewer that this turns the 0.04 molar yields into a fixed mass yield. This likely results in an underprediction of SOA formed through RO_2 + RO_2 reactions because the molar mass of the dimers, ranging from 302 g/mol ($C_{15}H_{26}O_6$ from MTERP-RO2 + ISOP-RO2) to 438 g/mol ($C_{25}H_{42}O_6$ from MTERP-RO2 + BCARY-RO2), is larger than that of SOAG0. To roughly estimate this, we calculated an adjusted RO_2 + RO_2 SOA with scaled molar mass offline and assuming no changes in gas-particle partitioning. If all the formed dimer products have the maximum molar mass of 438 g/mol, the MTERP SOA mass from accretion reactions will increase by 75.2%. As a result, in NEW_slow, the contribution from RO_2 + RO_2 reactions to fSOA will increase from 3.3% to 5.7%. In NEW_fast, it increases from 7.5% to 13.1%. Overall, this correction does not have a significant impact on our estimate, especially for the NEW_slow experiments, the mechanism we used to conduct PI and F experiments. This is because the 0.04 molar yield is small.

Our 0.04 molar yield is taken from Zhao et al. (2018), which is an experimental study based on α-pinene oxidation. According to their estimates, the saturation vapor pressure of the dimers ($C_{16\text{-}20}H_{22\text{-}34}O_{4\text{-}13}$) is likely below 0.01 μg m^{-3}, with the majority of dimers well below 10^{-4} μg m^{-3}. So, these dimers are likely to be even less volatile than SOAG0, whose volatility is 0.01 μg m^{-3}.

We acknowledge the issue regarding fixed molar yield and volatility in our manuscript:

L261-269: “Zhao et al. (2018) conducted experiments on α-pinene oxidation and reported a lower-limit dimer formation branching ratio of 4%. They also estimated that the volatility of these accretion products is well below 0.01 μg m^{-3}. Therefore, we assume all the RO_2 + RO_2 reactions form 4% of SOAG0. This 4% molar yield is also incorporated in the modeling study of Xu et al. (2022). However, it is noted that SOAG0 has a fixed molar mass of 250 g/mol, while the molar mass of the accretion products varies from 302 to 438 g/mol. Therefore, ideally, the molar yield should be scaled according to the molar mass ratio of the dimers to SOAG0, and our current fixed yield likely results in a modest underprediction of RO_2 + RO_2 SOA.”

- The overall sense here is that many compounding factors are making the SOA yield parameterizations from this RO2+RO2 chemistry hugely uncertain and likely a low

estimate, and as with the isomerization chemistry discussed above, I think that merits more mention of this uncertainty later on when large claims are made (e.g. L 575-576 in the conclusions that "The RO2 + RO2 reactions contribute moderately to the MTERP RO2 fate but make a minor contribution to the MTERP SOA formation" -- I think it's worth stating right in that sentence that this is perhaps only because the estimated SOA yields from RO2 + RO2 are quite low.

Thanks for this advice. We acknowledge the possible underprediction of RO_2 + RO_2 reactions in the Conclusion Section.

L673-675: "However, we note that the SOA contribution from RO_2 + RO_2 reactions is likely underestimated, due to the low and fixed yields applied to the reactions along with the absence of SOA formation from non-accretion products."

- L 224-225 it's unclear what's meant by "these two"

The related sentence is removed from our manuscript, since it is about BCARY chemistry.

- Table 3 - are the ISOP-RO2s not allowed to cross react with other ISOP-RO2s? Presumably this pathway could be important in some high-isoprene-emission locations, and would lead to a small yield of accretion products with sufficiently low volatility to contribute to SOA?

These reactions are not present in the detailed MOZART-TS2 scheme, and thus we did not include them in our mechanism. We agree that this is a possible reaction pathway and may contribute to RO_2 loss and SOA formation. However, the rate coefficients and yields of ISOP-RO_2 + ISOP-RO_2 reactions are highly uncertain (Wennberg et al., 2018). We are not aware of any studies reporting these parameters.

We briefly acknowledge these reaction pathways and their uncertainty in our manuscript.

L299-301: "In addition, we did not represent ISOP-RO_2 + ISOP-RO_2 reactions, which may potentially contribute to ISOP-RO_2 fate and SOA formation but are highly uncertain (Wennberg et al., 2018)."

- L 261-262 does the implementation of this photorecalcitrant fraction in just the lowest-volatility bin and not spread out across the bins -- which seems based in convenience rather than any physical or chemical characteristics of that volatility bin -- potentially bias your results toward overemphasizing the importance of the lowest volatility bin, which just

happens to be where you've put a lot of the new isomerization and RO2+RO2 SOA? How large could this effect be?

The implementation of photo-recalcitrant fraction is based entirely in convenience. Ideally, to explicitly represent photo-recalcitrant fraction, we would need to split each SOA species into two species, one susceptible to photolysis and the other not. This would add 92 new advected tracers and 92 non-advected tracers to our current configuration, which significantly increases the computation time, storage space for data archiving, and the difficulty to process model output. Since SOA photolysis is not the focus of our work, we simplified this process and aimed at just mimicking the photo-recalcitrant fraction by turning off the photolysis in the lowest volatility bin.

We agree with the reviewer that this simplification may impact the contribution of isomerization (and RO_2 + RO_2) to total SOA. To understand this uncertainty, we conducted a 1-yr experiment with NEW_slow chemical configuration in PD conditions while retaining photolysis loss for the lowest volatility bin. This experiment represents a condition where all SOA volatility bins are subject to the same photolysis rate (i.e. no recalcitrant fraction is considered, and OA photolysis loss is excessive). In this sensitivity experiment, SOA formed through isomerization and RO_2 + RO_2 reaction accounts for 38% and 2.6% of total MTERP + OH SOA. This is a little lower than our current estimates (44% and 3.3%, respectively) NEW_slow in PD (Figure 2b), however isomerization still dominates. This likely implies that the isomerization contribution to SOA in PI and F are slightly overpredicted (Figure 9b), and the SOA increase from PD to F due to isomerization has a minor high bias (Figure 10).

We acknowledge this uncertainty in our methodology and results in the manuscript. We also include Text S1 in the supplement to discuss the sensitivity experiment in detail.

"Text S1. Discussion regarding photolysis

We turn off the photolysis of SOA in the lowest volatility bin to mimic the photo-recalcitrant fraction as observed in previous laboratory studies (O'Brien and Kroll, 2019; Sun and Smith, 2024; Zawadowicz et al., 2020). This is a simplification based entirely in convenience and computational cost (specifying a photo-recalcitrant fraction for each SOA species would add 92 advected tracers, and 92 non-advected tracers to the configuration).

The simplification may overemphasize the isomerization and RO_2 + RO_2 reactions, which form SOA solely in the lowest volatility bin (Table 2, part 1 and part 2). To understand this uncertainty, we conducted a 1-year experiment with NEW_slow chemical configuration in PD conditions while retaining photolysis loss for the lowest volatility bin. This experiment represents a condition where all SOA volatility bins are subject to the same photolysis rate (i.e. no recalcitrant fraction is considered, and OA photolysis loss is excessive). In this sensitivity experiment, SOA formed through isomerization and RO_2 + RO_2

reaction accounts for 38% and 2.6% of the total MTERP + OH SOA. This is slightly lower than our current estimates (44% and 3.3%, respectively) from NEW_slow in PD (Figure 2b), however isomerization still dominates. This implies that the isomerization contribution to SOA in PI and F are also slightly overpredicted (Figure 9b), and the SOA increase from PD to F due to isomerization has a minor high bias (Figure 10a)."

L318-321: "However, this simplification may overemphasize the isomerization and RO_2 + RO_2 reactions, which form SOA solely in the lowest volatility bin (Table 2, part 1 and part 2). We conduct a sensitivity experiment to address this uncertainty (see details in Text S1)."

L383-389: "We note that uncertainties in model parameters discussed in Section 2.2 and 2.3 could alter the estimated contribution of the isomerization pathway. In particular, the upper-limit 50% yield and applying the photo-recalcitrant fraction only to the lowest volatility bin (see Text S1) could over-emphasize isomerization. Conversely, neglecting higher branching ratios and yields for limonene SOA may underestimate the importance of isomerization for total SOA formation from monoterpenes."

L624-628: "However, the increase from isomerization may be slightly overpredicted due to turning off the photolysis of SOA from the lowest volatility bin (see also Text S1). Indeed, we notice that the MTERP SOA lifetime due to photolytic loss is longer in F than PD (Table S1), likely because a large fraction of MTERP SOA is formed through isomerization in F but not photolyzed."

- L 284 "reduced future anthropogenic emissions" of what? A priori it seems directly counter to the high CO2 stated in the previous sentence. Reduced emissions of NOx? How is that compatible with increased CO2 that likely comes from fossil fuel combustion?

Here, we meant reduced emissions in air pollutants, including both aerosols (e.g., black carbon) and reactive gases (e.g., NO_x and SO_2). CO_2 emissions and air pollutions are not correlated in SSP predictions. SSP5 is a scenario driven by fossil-fueled development, resulting in high level of CO_2 in the future. Meanwhile, it has strong pollution control, associated with fast development of pollution control technology and enforcement of environmental laws (Rao et al., 2017). This leads to less emissions in anthropogenic air pollutants. We clarify this in the revised manuscript:

L341-343: "This is also a strong pollution control scenario, which reduces future anthropogenic emissions of aerosols and reactive gases compared to PD levels (Rao et al., 2017)."

- L 403-406 - the introduction of new ISOPRO2 reactions that compete with the SOA-forming pathways and decrease overall isoprene-derived SOA brings up an important

point: were the original SOA yields from ISOPRO2's HO2 and NO pathways based exclusively on chamber experimental results, or were they at all tuned in order to match ambient observations of isoprene-derived SOA? Because if it's the latter, then adding new pathways that compete with those old ones means you should artificially bump up the SOA yields to compensate; otherwise, you're now biased low on isoprene SOA formation relative to the previous tuning. If it's the former, keeping those old SOA yields should be okay -- but you're really only getting the decrease because you've assumed zero SOA formation from the newly added isomerization and RO2 + RO2 pathways for isoprene, which is likely not correct (e.g. Berndt et al 2025 for SOA formation from isomerization, Mayhew et al 2025 for the contribution of isoprene RO2 + isoprene RO2 accretion products to SOA).

The SOA yields we use are derived from chamber experiments with adjustments to wall loss (Hodzic et al., 2016). They were not tuned to ambient measurements. Thus, there is no inconsistency introduced by this competition. We agree with the reviewer that the resulting decrease is partly because we assume isomerization do not form SOA and we ignore the ISOP-RO_2 + ISOP-RO_2 reactions. In response to comments above, this is now acknowledged in the text.

Responses to reviewer #2

This manuscript investigates the role of expanded biogenic RO_2 chemistry in secondary organic aerosol (SOA) formation using CESM2.2, with a particular focus on monoterpene RO_2 isomerization and RO_2 + RO_2 accretion pathways under pre-industrial, present-day, and future conditions. The study addresses an important and timely problem: current global models generally represent biogenic SOA formation using highly simplified chemistry, while recent laboratory and modeling studies indicate that autoxidation and accretion chemistry may substantially affect SOA formation and its response to changing climate and anthropogenic emissions. The implementation of these pathways in a global chemistry–climate model, together with the comparison across PI, PD, and F conditions, has the potential to provide useful insight into the drivers of biogenic SOA burden and its future evolution.

Overall, I find the manuscript scientifically interesting and potentially suitable for publication. I consider this study a strong and potentially valuable contribution to the field. However, the manuscript currently lacks important methodological detail, and several aspects of the model formulation and interpretation require further clarification and discussion before the main conclusions can be fully evaluated. I therefore recommend publication after the authors address the points below.

1. Lines 182-187: The implementation "MTERPO2VBS → 0.5 SOAG0" simplifies the downstream chemistry described in Pye et al. (2019). In the original mechanism (their Fig. 1 and SI Fig. S2), the fate of first-generation $C_{10}H_{17}O_7$-RO_2 is NOx-dependent: reaction with HO_2 produces very low-volatility hydroperoxides ($C^* \approx 7.3 \times 10^{-3}$ μg m^{-3} for the major products), while reaction with NO yields a mix of organic nitrates with $C^* \approx 0.1–0.4$ μg m^{-3} and alkoxy radicals (~87.5%) that largely decompose to more volatile fragments. Collapsing these pathways into a single 50% SOAG0 yield loses the NOx sensitivity of post-isomerization HOM-RO_2 termination and product volatility, and may overestimate SOA formation under relatively high-NO conditions. This is particularly relevant given that one of the paper's central results concerns the PI→PD→F trend in isomerization-derived SOA, and the NO-related chemical environment differs substantially across these periods, with anthropogenic NO emissions peaking at PD. The reported increase in the isomerization contribution from 38% (PI) to 44% (PD) to 51% (F) could therefore be sensitive to this simplification.

I recommend that the authors expand Section 2.2 to explicitly explain this simplification, including which pathways from Pye et al. (2019) are lumped together, why the 50% value was chosen as representative, and how this differs from the original mechanism. Specific references to the source of each parameter — for example, Pye et al. (2019) SI Table S1 for the 22% APINCO2 branching and SI Table S2 for the 0.5 branching ratio — would help readers verify the linkage. A qualitative discussion of how this simplification might bias the PI→PD→F trend would also strengthen the paper.

We appreciate the reviewer for this instructive and helpful comment. We agree that our simplification loses some of the NO_x sensitivity and may overestimate SOA production from MTERP isomerization under high NO_x conditions. We have clarified this uncertainty in the revised Section 2.2. Following the reviewer's suggestion, we also elucidate how the simplification is made compared to the Pye mechanism, and how we derive the parameters from Pye et al. (2019).

L200-214: "The 22% branching ratio is taken from the revised product yield of APINCO2 in the Table S1 of Pye et al. (2019), following the mechanism in Berndt et al. (2016) and Vereecken et al. (2007). The 50% SOA yield is calculated following Eq (S1) from Pye et al (2019) and their Table S2. To maintain computational efficiency and accommodate the complexity of the chemical mechanism in global models (consistent with the representation of other RO_2 pathways in the VBS), we collapse the multi-step autooxidation in Pye et al. (2019) into a single-step reaction, by only representing the first-generation branching point and the final SOA yield. In the original mechanism of Pye et al. (2019), the subsequent reactions of the first generation RO_2 and its products are also NO_x-dependent, with reactions with NO forming volatile compounds and competing with subsequent autooxidation. The SOA yield (50%) in our implementation is the maximum yield, assuming no subsequent competing bimolecular reactions. Therefore, our simplification does not fully represent the sensitivity of isomerization yields to NO_x, which may particularly result in overestimation of SOA formation from isomerization under high-NO_x conditions. This bias can influence our estimates of the SOA trends from the past to the future, as further discussed in Section 3.2."

We further discuss this issue with other uncertainties regarding isomerization in Section 3.1.

L383-389: "We note that uncertainties in model parameters discussed in Section 2.2 and 2.3 could alter the estimated contribution of the isomerization pathway. In particular, the upper-limit 50% yield and applying the photo-recalcitrant fraction only to the lowest volatility bin (see Text S1) could over-emphasize isomerization. Conversely, neglecting higher branching ratios and yields for limonene SOA may underestimate the importance of isomerization for total SOA formation from monoterpenes."

In addition, in Section 3.2, we mention this uncertainty due to simplification again after reporting the isomerization fSOA increase from 38% (PI) to 44% (PD) to 51% (F).

L579-585: "It is noted that the simplified representation of the isomerization process may overpredict SOA formed through this pathway under high-NO_x conditions (see Section 2.2 for details). Since the NO emissions peak in PD (Figure 7c and 7d), this high bias is likely to be more significant in PD than in PI and F, which may impact the continuous increasing trend in isomerization SOA contribution from PI to F and would further reduce the minimum predicted SOA in PD (see Figure 10a and the discussion below)."

2. Lines 234-236: The reactions of MTERP-RO_2 with NO_3, CH_3O_2, and CH_3CO_3 are incorporated in the modified VBS as additional loss pathways that do not produce SOAG. Given that the VBS treatment represents SOA-forming potential through effective yields assigned to first-generation RO_2 pathways, it is unclear why these additional channels are assumed to have no downstream SOA-forming potential. In particular, recent work by Kang et al. (2025) provides experimental evidence that highly oxygenated alkoxy radicals formed during α-pinene oxidation can undergo isomerization with a branching ratio of approximately 50%, regenerating RO_2 and propagating HOM formation. Thus, treating these additional MTERP-RO_2 loss pathways as zero-SOAG channels may neglect potentially relevant alkoxy–peroxy contributions to SOA formation.

I recommend that the authors clarify the rationale for treating the reactions in Table 2 part 3 as zero-SOAG pathways. Because the relative importance of these pathways may vary across PI, PD, and F chemical environments, a brief qualitative discussion of the resulting uncertainty in the reported SOA trends would be helpful.

Thank you for the suggestion. We agree that these reactions may form SOA so our assumption may underpredict total SOA. We now acknowledge Kang et al. (2025) in our manuscript. But we note that Kang et al. (2025) is not specifically for reactions with CH_3O_2 and CH_3CO_3. Also, their work about HOM-RO and HOM-RO_2 is more likely to be downstream reactions, which is not directly related to our mechanism that is based on first generation RO_2. We also cite Mayhew et al. (2025) following Reviewer #1's suggestion. They found that MTERP + small VOCs, mainly CH3CO3, can be regionally important to form accretion products in aerosol phase. However, we note that they also include VOC + O3 reactions, and they may have double-counting issue, since their accretion reactions may be considered by the empirical SOA yields from other RO_2 pathways.

In general, we think these processes, especially how much SOA is formed, are not well constrained. Thus, we keep our current zero-SOAG assumption and add the following discussion to Section 2.2:

L280-286: "Assuming these reactions do not form SOA may result in some underprediction in total MTERP SOA amount. Mayhew et al. (2025) reported that reactions with CH_3CO_3 can contribute to regional SOA formation by implementing accretion reactions generated by a chemical mechanism generator into a chemical transport model. A laboratory study also implies that highly oxygenated organic compounds (HOM) alkoxy radicals formed through HOM-RO_2 + RO_2 reactions may undergo isomerization and propagate low volatility HOM formation (Kang et al., 2025). However, these pathways are not well constrained."

In addition, we estimate the fRO_2 for the MTERP-RO2 reactions with NO3, CH3O2, and CH3CO2. In total, these reactions contribute to 2-4% for total MTERP-RO2 fate across all the experiments (i.e., NEW_fast, NEW_slow, PI, and F). The regional contribution is also small as can be seen from Figure 3e for MTERP-RO2. Therefore, should these reactions form SOA, the contribution to fSOA would still be minor. We further address this uncertainty related to MTERP-RO2 in Section 3.1.

L405-407: “Reactions with NO_3, CH_3O_2, and CH_3CO_3 only account for 2 - 4% of fRO_2. Thus, should any of these reactions form SOA, their contribution to the total MTERP SOA is likely to be minor.”

3. Lines 255–270: To mimic the photo-recalcitrant fraction observed in laboratory studies, the authors turn off the photolysis of SOA in the lowest volatility bin (SOAG0). However, this choice ties photo-recalcitrance to volatility, whereas laboratory studies typically report photo-recalcitrant fractions based on bulk or precursor-specific SOA behavior rather than volatility-resolved measurements (e.g., O'Brien and Kroll, 2019; Zawadowicz et al., 2020). Highly oxidized, low-volatility products formed via autoxidation can contain photolabile functional groups, including carbonyls and hydroperoxides, suggesting that the relationship between volatility and photo-recalcitrance is not straightforward.

This choice may also have implications for the reported PI→PD→F trend. Because the contribution of isomerization, which feeds directly into SOAG0, increases from 38% in PI to 44% in PD and 51% in F, a growing fraction of MTERP SOA is produced through a pathway assigned zero photolytic loss. This treatment could contribute to the simulated future increase in isomerization-derived SOA. I recommend that the authors clarify the physical rationale for tying photo-recalcitrance to volatility and discuss qualitatively how this assumption might affect the reported PI→PD→F trend.

The implementation of photo-recalcitrant fraction is based entirely in convenience. Ideally, to explicitly represent photo-recalcitrant fraction, we would need to split each SOA species into two species, one susceptible to photolysis and the other not. This would add 92 new advected tracers and 92 non-advected tracers to our current configuration, which significantly increases the computation time, storage space for data archiving, and the difficulty to process model output. Since SOA photolysis is not the focus of our work, we simplified this process and aimed at just mimicking the photo-recalcitrant fraction by turning off the photolysis in the lowest volatility bin.

We agree with the reviewer that this simplification may impact the contribution of isomerization (and $RO_2 + RO_2$) to total SOA. To understand this uncertainty, we conducted a 1-yr experiment with NEW_slow chemical configuration in PD conditions while retaining photolysis loss for the lowest volatility bin. This experiment represents a condition where all SOA volatility bins are subject to the same photolysis rate (i.e. no recalcitrant fraction is considered, and OA photolysis loss is excessive). In this sensitivity experiment, SOA formed through isomerization and $RO_2 + RO_2$ reaction accounts for 38% and 2.6% of total MTERP + OH SOA. This is a little lower than our current estimates (44% and 3.3%, respectively) NEW_slow in PD (Figure 2b), however isomerization still dominates. This likely implies that the isomerization contribution to SOA in PI and F are slightly overpredicted (Figure 9b), and the SOA increase from PD to F due to isomerization has a minor high bias (Figure 10).

We acknowledge this uncertainty in our methodology and results in the manuscript. We also include Text S1 in the supplement to discuss the sensitivity experiment in detail.

"Text S1. Discussion regarding photolysis

We turn off the photolysis of SOA in the lowest volatility bin to mimic the photo-recalcitrant fraction as observed in previous laboratory studies (O'Brien and Kroll, 2019; Sun and Smith, 2024; Zawadowicz et al., 2020). This is a simplification based entirely in convenience and computational cost (specifying a photo-recalcitrant fraction for each SOA species would add 92 advected tracers, and 92 non-advected tracers to the configuration).

The simplification may overemphasize the isomerization and RO_2 + RO_2 reactions, which form SOA solely in the lowest volatility bin (Table 2, part 1 and part 2). To understand this uncertainty, we conducted a 1-year experiment with NEW_slow chemical configuration in PD conditions while retaining photolysis loss for the lowest volatility bin. This experiment represents a condition where all SOA volatility bins are subject to the same photolysis rate (i.e. no recalcitrant fraction is considered, and OA photolysis loss is excessive). In this sensitivity experiment, SOA formed through isomerization and RO_2 + RO_2 reaction accounts for 38% and 2.6% of the total MTERP + OH SOA. This is slightly lower than our current estimates (44% and 3.3%, respectively) from NEW_slow in PD (Figure 2b), however isomerization still dominates. This implies that the isomerization contribution to SOA in PI and F are also slightly overpredicted (Figure 9b), and the SOA increase from PD to F due to isomerization has a minor high bias (Figure 10a)."

L318-321: "However, this simplification may overemphasize the isomerization and RO_2 + RO_2 reactions, which form SOA solely in the lowest volatility bin (Table 2, part 1 and part 2). We conduct a sensitivity experiment to address this uncertainty (see details in Text S1)."

L383-389: "We note that uncertainties in model parameters discussed in Section 2.2 and 2.3 could alter the estimated contribution of the isomerization pathway. In particular, the upper-limit 50% yield and applying the photo-recalcitrant fraction only to the lowest volatility bin (see Text S1) could over-emphasize isomerization. Conversely, neglecting higher branching ratios and yields for limonene SOA may underestimate the importance of isomerization for total SOA formation from monoterpenes."

L624-628: "However, the increase from isomerization may be slightly overpredicted due to turning off the photolysis of SOA from the lowest volatility bin (see also Text S1). Indeed, we notice that the MTERP SOA lifetime due to photolytic loss is longer in F than PD (Table S1), likely because a large fraction of MTERP SOA is formed through isomerization in F but not photolyzed."

4. Lines 271–291: The description of the simulation setup, particularly for the PI and F experiments, lacks sufficient detail to fully evaluate and reproduce the results. In the current form, it is unclear how the authors set up the CESM simulations. Several key choices should be clarified:

- CESM component configuration: It is not specified whether the simulations use an atmosphere–land configuration with prescribed SST and sea ice, such as an F-compset, or a fully coupled configuration, such as a B-compset. The reference to SST data for each period suggests that prescribed-ocean boundary conditions may have been used, but this should be stated explicitly. This distinction is important for interpreting the reported temperature changes, such as the +5.9 K increase from PD to F, as either an internally generated coupled climate response or an atmospheric response constrained by prescribed boundary conditions.

We use the atmosphere-land configuration (i.e., the F-compset) for all the simulations. In the submitted manuscript, we mentioned that these experiments are conducted with CAM6-Chem (Section 2.4), and CAM6-Chem is the atmosphere component of CESM2.2, which is coupled with the CESM2 land component (Section 2.1). We further clarify that we use prescribed SST and sea ice in our revised manuscript:

L328-329: "We conduct three sets of CAM6-Chem experiments with prescribed sea surface temperature (SST) and sea ice."

- Source and temporal treatment of SST and sea-ice forcing: If SST and sea ice were prescribed, please identify the source of the PI, PD, and F fields and explain how they were constructed, for example, whether they were taken from a parent CESM2/CMIP6 coupled simulation under SSP5-8.5 and whether climatological or time-varying boundary conditions were applied. The sources and temporal treatment of CO_2, anthropogenic and natural emissions, and land-use forcing should also be specified.

Thanks for this suggestion. We added Text S2 in the supplement to provide details regarding these fields (also see below). We note that due to the availability of existing input files, some of these data are climatological average, while some are single year conditions. This may result in some inconsistency, but the influence on results is likely small because data from within a decade tend to be more consistent than those from different climate conditions. All experiments were conducted with free-running configuration, meaning that the meteorology is not constrained by external meteorological datasets.

"Text S2. Experimental settings for PI, PD, and F

Our experiments for the pre-industrial (PI), present-day (PD), and future (F) conditions utilize sea surface temperature (SST), sea ice, CO_2 concentrations, anthropogenic and natural emissions of aerosols and reactive gases, and land use data representing 1850, 2010, and 2100 conditions, respectively. SST and sea ice for PI and PD

originate from Hadley Centre sea ice and SST dataset (Hurrell et al., 2008). PI uses data for 1850, which is constructed by SST and sea ice climatology from 1870 to 1889. PD uses 2010 climatology, which is averaged from 2005 to 2015. The future SST and sea ice are generated from a fully coupled CESM2 experiment that was conducted under SSP5-8.5 trajectory and uses data from 2100 single year. The CO_2 concentrations for PI and PD conditions are taken from Meinshausen et al. (2017), with PI represented by the 1850 climatology (averaged from 1845 to 1855) and PD represented by the 2010 climatology (averaged from 2006 to 2014). Future CO_2 concentrations follow the SSP5 pathway from Riahi et al. (2017), using the projected values for the year 2100. Anthropogenic emissions of aerosols and reactive gases for PI and PD originate from the Community Emissions Data System (Hoesly et al., 2018), while the biomass burning emissions for PI and PD are constructed by van Marle et al. (2017). The future anthropogenic and biomass burning emissions are projected following the SSP5 pathway (Gidden et al., 2019). PI, PD, and F experiments are conducted with climatological emissions for 1850 (averaged from 1850 to 1859), 2010 (averaged from 2006 to 2014), and 2100 (averaged from 2091 to 2100), respectively. Emissions of biogenic volatile organic compounds (BVOCs) are calculated online through the Model of Emissions of Gases and Aerosols from Nature (MEGAN2) parameterization (see Section 2.1). The BVOC emissions are impacted by vegetation types determined by land use. The land use conditions for PI, PD, and F are taken from the dataset of Land-Use Harmonization 2 project (Hurtt et al., 2020) for single year 1850, 2010, and 2100, respectively. All the prescribed input data are in one-year length and used cyclically throughout the model integration. We note that the temporal treatments for these input datasets differ, due to the availability of existing input files. The influence on results is likely small because data from within a decade tend to be more consistent than those from different climate conditions."

We also add the following sentence in the main text.

L338-339: "Detailed settings for the PI, PD, and F conditions are provided in Text S2."

- Please also clarify whether the 10-year simulations represent repeated time-slice forcing or transient integrations.

The input data are single year forcing or one-year climatology. They are used cyclically for the 11-year experiments. Therefore, it represents repeated time-slice forcing. We note this in our manuscript.

L352-354: "The model is integrated for 11 years in a free-running configuration and using cyclically repeated one-year input data. Therefore, the simulated results represent repeated time-slice forcing."

5. Lines 281–285: The future analysis is based solely on SSP5-8.5, which combines very strong warming and CO_2 increases with declining anthropogenic air pollutant emissions. Because both temperature-driven BVOC emission changes and changes in NO emissions strongly influence the simulated SOA response, the choice of future scenario is important for interpreting the reported PD→F changes. Please clarify the rationale for selecting SSP5-8.5 as the only future scenario.

We chose SSP5-8.5 because it is the considered as the most extreme scenario, thus providing the most contrast with PD and PI in the changes of temperature and CO_2 level. While NO_x emissions change substantially from PD to F following this scenario, we note that our BSOA results are, in fact, not very sensitive to this change. If we use another future scenario, it is very likely that the future SOA burden would quantitatively differ, but the overall trajectory and response is robust. In the revised manuscript, we explain the reason for choosing SSP5-8.5 and acknowledge that using different future scenarios may lead different results. Following reviewer 3's suggestion, we also acknowledge that SSP5-8.5 is debated to be implausible. Our modifications to the manuscript are as follow:

L343-347: "We chose SSP5 because it is considered as the most severe scenario, providing the strongest contrast to PD and PI in temperature and CO_2 level. However, it is noted that SSP5 is an extreme case and debated to be implausible (Hausfather and Peters, 2020). Thus, the magnitude (though not the sign) of our PD to F results may be significantly different if considering another future scenario."

L645-647: "Also, the PD-to-F changes largely depend on the selected future scenario. Using an alternative scenario with different NO emissions, temperature, and/or CO_2 level can lead to substantially different results."

6. Figures 6, 11, and 12: The dotted regions are described as statistically significant at the 0.05 level, but the statistical testing procedure is not provided. Please specify the test used, the sample basis for the test (e.g., annual means from the 10-year simulations), and any other information needed to interpret the dotted regions.

We used Welch's t-test. The sample basis is the annual means from the 10-year simulations (n = 10). We have added this clarification to the figure captions.

Figure 6 caption:

"… Dotted regions on the middle and right panels are where the changes are significant to the 0.05 levels, based on Welch's t-test using yearly annual means from the 10-yr experiments. …"

Figure 11 caption:

"… Dotted regions are where the changes are significant to the 0.05 levels, based on Welch's t-test using yearly annual means from the 10-yr experiments. …"

7. Lines 317–318 and 332–334: Xu et al. (2022) is the most directly comparable prior global modeling study of monoterpene-derived RO_2 autoxidation and RO_2 + RO_2 chemistry, yet the comparison in Section 3.1 is limited to brief qualitative statements. Given that the present work follows Xu et al. in testing fast and slow RO_2 + RO_2 reaction-rate combinations, a more quantitative comparison of the globally averaged MTERP-RO_2 fate partitioning between the two studies, where the diagnostics are comparable, would substantially strengthen the paper.

Unfortunately, it is challenging to conduct quantitative comparisons with Xu et al. (2022). Xu et al. (2022) represents multi-phase oxidation of MTERP by both OH and O_3, while we focus on the first-generation oxidation initiated by OH. Their analysis about RO_2 fate focuses more on HOM-RO_2, instead of the first generation RO_2, which is not comparable with our fRO_2. Also, they compare their fast- and slow-rate experiments by evaluating HOM organic nitrates (HOM-ON), HOM non-organic nitrate (HOM-non-ON), and organic aerosol mass with observations at three surface sites. We do not simulate equivalent HOM-ON or HOM-non-ON and thus cannot make similar comparison. They do not represent HOM gas-particle partitioning in their study. So, we limit our comparisons with Xu et al. (2022) as it is.

8. Section 3.2: The attribution of PI→PD and PD→F changes in SOA burden focuses on BVOC emissions, RO_2 fate, and gas–particle partitioning, but changes in SOA removal and lifetime may also be important. This is particularly relevant because SOA photolysis is modified in this study and because wet scavenging may change substantially under different climate conditions. I recommend that the authors provide a quantitative SOA loss budget for PI, PD, and F, separating at least photolytic loss, wet deposition, and dry deposition, together with any other relevant modeled losses. Corresponding changes in SOA lifetime would help support the attribution of the reported burden trends. If possible, these diagnostics should be provided separately for MTERP SOA, ISOP SOA, and total BVOC + OH SOA.

Thank you for this helpful suggestion. We calculate the burden, loss budget, and lifetime for ISOP, MTERP, and total SOA in Table S1. The lifetime due to the wet deposition does vary from PI to F. In particular, it plays a role in the total SOA burden decrease from PI to PD, though has little impact on the PD to F evolution. We also see a clear increase in the lifetime due to photolytic loss from PI to F for MTERP SOA and thus total SOA. This is likely related to our treatment of photolysis – there is no photolysis on the lowest volatility bin, but a large fraction of MTERP SOA is formed through isomerization and RO2+RO2 reactions in this bin. We added Table S1 and discussion related to this in our manuscript.

L624-628: “However, the increase from isomerization may be slightly overpredicted due to turning off the photolysis of SOA from the lowest volatility bin (see also Text S1). Indeed, we notice that the MTERP SOA lifetime due to photolytic loss is longer in F than PD (Table S1), likely because a large fraction of MTERP SOA is formed through isomerization in F but not photolyzed.”

L636-638: “Wet removal is another critical factor that can impact the evolution of SOA burden. We find that SOA lifetime due to wet deposition varies from PI to F, contributing, in particular, to the simulated burden decrease from PI to PD (Table S1).”

L658-660: “Overall, about half of the simulated decrease in total biogenic SOA from PI to PD is due to chemistry, thermodynamics, and wet deposition (24% from PI_PDB to PD compared to 41% from PI to PD; Figure 10c and Table S1).”

Table S1. SOA burden and loss budget for PI_PDB, PI, PD, F, and F_PDB. Unit for the loss budget is Tg/yr. The numbers in parentheses are lifetime that corresponds with each loss term (unit: day).

	Burden (Tg)	Photolytic loss	Wet deposition	Dry deposition
ISOP SOA				
PI_PDB	0.28	14.6 (7.0)	9.4 (10.9)	0.6 (170.3)
PI	0.32	16.7 (7.0)	11.6 (10.1)	0.7 (166.9)
PD	0.20	10.2 (7.2)	8.9 (8.2)	0.7 (104.3)
F	0.23	11.5 (7.3)	9.9 (8.5)	0.6 (139.9)
F_PDB	0.14	6.6 (7.7)	5.8 (8.8)	0.4 (127.8)
MTERP SOA				
PI_PDB	0.21	4.6 (16.7)	13.8 (5.6)	2.0 (38.3)
PI	0.24	5.0 (17.5)	15.7 (5.6)	2.0 (43.8)
PD	0.20	3.6 (20.3)	14.4 (5.1)	2.0 (36.5)
F	0.60	9.1 (24.1)	35.9 (6.1)	4.4 (49.8)
F_PDB	0.20	3.0 (24.3)	13.0 (5.6)	1.8 (40.6)
Total SOA				
PI_PDB	0.49	19.2 (9.3)	23.3 (7.7)	2.7 (66.2)
PI	0.56	21.6 (9.5)	27.2 (7.5)	2.8 (73.0)
PD	0.40	13.8 (10.6)	23.3 (6.3)	2.7 (54.1)

F	0.83	20.6 (14.7)	45.8 (6.6)	5.0 (60.6)
F_PDB	0.34	9.6 (12.9)	18.8 (6.6)	2.2 (56.4)

9. The manuscript attributes part of the PD→F change in SOA burden to temperature-driven changes in gas–particle partitioning, but the thermodynamic parameters governing this response are not specified. I recommend that the authors (1) report the enthalpy of vaporization (ΔH_vap) values used for each volatility bin and the basis for these choices, and (2) briefly discuss how the assumed ΔH_vap influences the gas–particle partitioning response in the PD→F simulation and the interpretation of the reported +113% SOA increase.

The enthalpy of vaporization (ΔH_vap) is unchanged from the standard CESM2: 153, 142, 131, 120, and 109 kJ mol^{-1} for SOA volatility bins with C^* of 0.01, 0.1, 1, 10, and 100 μg/m^3, respectively (Epstein et al., 2010; Hodzic et al., 2016). This is on the higher end of values typically assumed in 3D models (e.g., a uniform 42 kJ mol^{-1} in GEOS-Chem (Pye et al., 2010)). Larger ΔH_vap indicates a higher sensitivity of gas-particle partitioning to temperature change. If using a smaller ΔH_vap, the evaporation of SOA from PD to F due to temperature increase will be weaker, leading to an even larger increase in total SOA. We report the values for ΔH_vap and discuss its potential impacts on the PD to F trends in our manuscript as follow.

L144-146: "The enthalpy of vaporization (ΔH_{vap}) for the five bins is 153, 142, 131, 120, and 109 kJ mol^{-1} (Epstein et al., 2010; Hodzoc et al., 2016), respectively."

L619-622: "We note that the assumed ΔH_{vap} values in CAM6-Chem lead to strong evaporation in response to temperature increase. If a smaller ΔH_{vap} were used, the overall increase in SOA would be greater due to weaker changes in gas-particle partitioning."

Responses to reviewer #3

This manuscript incorporates an expanded biogenic RO_2 chemical mechanism into CESM2 to investigate the atmospheric fate of biogenic RO_2 and its role in biogenic SOA formation across pre-industrial, present-day, and future climate scenarios. Although uncertainties remain regarding the parameterizations of RO_2 isomerization and RO_2 + RO_2 accretion, there is significant scientific interest in how the detailed biogenic RO_2 chemistry can improve our understanding of the biogenic SOA burden and its temperature-driven evolution in a warming climate. The results highlight the critical role of monoterpene RO_2 isomerization in biogenic SOA formation, which accounts for nearly half of monoterpene SOA. Furthermore, the model suggests an increase in biogenic SOA under the SSP5-8.5 scenario, driven primarily by elevated biogenic VOC emissions. Overall, this manuscript is well-written and within the scope of ACP. I recommend it for publication after the authors address the comments below.

1. Table 1: The table indicates that APIN, BPIN, LIMON, and MYRC are assigned identical SOA yield in the model. However, previous studies have demonstrated that the SOA yield of LIMON is generally higher than that of other terpenes (Pye et al., 2010). I recommend that the authors clarify the rationale for this uniform treatment, as applying a single yield across these distinct species may lead to an underestimation of terpene-derived SOA.

Yes, the four MTERPs are assumed to have same SOA yields. As mentioned in the caption of Table 1, this is the default treatment by CAM6-Chem MOZART-TS2. We follow this approach in our mechanism to avoid introduce additional tracers and reactions for each MTERP and thus minimize computational cost. Further, comprehensive and consistent data for all monoterpene species yields is not available to accurately implement a fully speciated scheme. We agree with the reviewer that this may lead to underprediction in MTERP SOA burden and biases in SOA distributions, which influences our estimates in the changes from PI to F. We have acknowledged this uncertainty and cited Pye et al. (2010) in our manuscript:

L187-194: "Following the treatment in default MOZART-TS2, the RO_2 formed from the four MTERPs are lumped together in the modified VBS and assumed to have the same yields and reaction rates for the RO_2 reactions, due to a lack of comprehensive speciated data. We note that MTERP species have different structures and thus different distributions of reaction products. For example, LIMON has been found to have generally higher SOA yields than the other MTERPs (Lee et al., 2006; Pye et al., 2010). Therefore, the lumping treatment may bias the MTERP SOA burden and distributions."

2. Line 171: The manuscript states that OH-initiated pathways account for 59% of total biogenic SOA in CAM6-chem. This high overall fraction is likely driven by isoprene, whose SOA formation is predominantly OH-initiated. In contrast, for terpene-derived SOA, the

contribution from ozonolysis is crucial (Hallquist et al., 2009). Please clarify how the absence of ozonolysis-derived RO_2 might affect the simulations of terpene-derived RO_2 and subsequent SOA formation.

As shown in Figure 6a and 6d, the OH initiated MTERP SOA and ISOP SOA burden in BASE is 0.151 Tg and 0.235 Tg, respectively. The MTERP oxidation makes considerable contribution (39%) to total biogenic SOA formed through OH-initiated oxidation, though ISOP oxidation indeed contributes more.

As described in Section 2.2, we have included RO_2 formed through terpene ozonolysis and subsequent oxidation for MTERP-RO_2 + RO_2 reactions. These RO_2 species are denoted as TP2-RO_2 (see Table 2, part 2 for details). The fRO_2 and fSOA of these reactions are summed up with other accretion reactions in Table 2, part 2 in our following analysis.

As we do not simulate ozonolysis-initiated SOA in this study (by design), we cannot comment further on this contribution.

3. Line 174-175: The majority of isoprene-derived SOA forms from the heterogeneous reactions, such as the heterogeneous uptake of IEPOX (Marais et al., 2016). By omitting these heterogeneous processes, the model may have biases in the atmospheric fate of ISOP-RO_2. I recommend that the authors clarify how the absence of these pathways might impact ISOP-RO_2 and isoprene-derived SOA.

The reviewer raises an interesting point. We agree that heterogeneous reaction is an important pathway for ISOP SOA formation (Marais et al., 2016; Paulot et al., 2009). However, we note that the split between gas-phase and aqueous-phase ISOP SOA formation (as constrained by lab experiments) is not well understood and represented in models. Most models have chosen to represent only one of these pathways. Our chemical mechanism follows the standard CAM6-Chem VBS configuration, considering only gas-phase reactions as in several other models (e.g., Bergman et al., 2022; Kirkevåg et al., 2018; Lou et al., 2020). Whereas the detailed SOA scheme in the GEOS-Chem model for example, exclusively represents aqueous phase isoprene SOA formation (Pai et al., 2020). Using gas-phase VBS potentially overemphasizes the sensitivity of SOA formation to volatility, which may particularly impact our estimates on future SOA. Also, this treatment mutes the impact of SO_2 emissions on ISOP SOA formation through perturbing aerosol acidity (Jo et al., 2021; Marais et al., 2016).

We clarify this uncertainty and how it may influence our results in the manuscript as follow.

In Section 2.2:

L179-186: “We note that our mechanism focuses on gas-phase reactions, whereas the SOA formation through heterogeneous chemistry is not considered as in baseline CAM6-Chem and many other models (e.g., Lou et al., 2020; Bergman et al., 2022; Kirkevåg et al., 2018). The aqueous-phase reactions are particularly important for isoprene SOA formation (Marais et al., 2016; Paulot et al., 2009). Ignoring these pathways may overemphasize sensitivity to volatility and overlook the impact of SO_2 emissions on SOA formation through perturbations in aerosol acidity (Jo et al., 2021; Marais et al., 2016).”

In Section 3.2:

L585-586: “In addition, our results may be oversensitive to volatility, due to the absence of aqueous phase isoprene SOA formation pathways.”

4. Line 263: Although turning off the photolysis of SOA in the lowest volatility bin may reproduce the observed photo-recalcitrant fraction in laboratory experiments, this approach may lead to an overestimation in the SOA formed from RO_2 isomerization, given that this specific reaction exclusively forms SOAG0. I recommend that the authors discuss the potential for this overestimation and its implications, particularly regarding projected future changes in the biogenic SOA burden.

The implementation of photo-recalcitrant fraction is based entirely in convenience. Ideally, to explicitly represent photo-recalcitrant fraction, we would need to split each SOA species into two species, one susceptible to photolysis and the other not. This would add 92 new advected tracers and 92 non-advected tracers to our current configuration, which significantly increases the computation time, storage space for data archiving, and the difficulty to process model output. Since SOA photolysis is not the focus of our work, we simplified this process and aimed at just mimicking the photo-recalcitrant fraction by turning off the photolysis in the lowest volatility bin.

We agree with the reviewer that this simplification may impact the contribution of isomerization (and RO_2 + RO_2) to total SOA. To understand this uncertainty, we conducted a 1-yr experiment with NEW_slow chemical configuration in PD conditions while retaining photolysis loss for the lowest volatility bin. This experiment represents a condition where all SOA volatility bins are subject to the same photolysis rate (i.e. no recalcitrant fraction is considered, and OA photolysis loss is excessive). In this sensitivity experiment, SOA formed through isomerization and RO_2 + RO_2 reaction accounts for 38% and 2.6% of total MTERP + OH SOA. This is a little lower than our current estimates (44% and 3.3%, respectively) NEW_slow in PD (Figure 2b), however isomerization still dominates. This likely implies that the isomerization contribution to SOA in PI and F are slightly overpredicted (Figure 9b), and the SOA increase from PD to F due to isomerization has a minor high bias (Figure 10).

We acknowledge this uncertainty in our methodology and results in the manuscript. We also include Text S1 in the supplement to discuss the sensitivity experiment in detail.

"Text S1. Discussion regarding photolysis

We turn off the photolysis of SOA in the lowest volatility bin to mimic the photo-recalcitrant fraction as observed in previous laboratory studies (O'Brien and Kroll, 2019; Sun and Smith, 2024; Zawadowicz et al., 2020). This is a simplification based entirely in convenience and computational cost (specifying a photo-recalcitrant fraction for each SOA species would add 92 advected tracers, and 92 non-advected tracers to the configuration).

The simplification may overemphasize the isomerization and RO_2 + RO_2 reactions, which form SOA solely in the lowest volatility bin (Table 2, part 1 and part 2). To understand this uncertainty, we conducted a 1-year experiment with NEW_slow chemical configuration in PD conditions while retaining photolysis loss for the lowest volatility bin. This experiment represents a condition where all SOA volatility bins are subject to the same photolysis rate (i.e. no recalcitrant fraction is considered, and OA photolysis loss is excessive). In this sensitivity experiment, SOA formed through isomerization and RO_2 + RO_2 reaction accounts for 38% and 2.6% of the total MTERP + OH SOA. This is slightly lower than our current estimates (44% and 3.3%, respectively) from NEW_slow in PD (Figure 2b), however isomerization still dominates. This implies that the isomerization contribution to SOA in PI and F are also slightly overpredicted (Figure 9b), and the SOA increase from PD to F due to isomerization has a minor high bias (Figure 10a)."

L318-321: "However, this simplification may overemphasize the isomerization and RO_2 + RO_2 reactions, which form SOA solely in the lowest volatility bin (Table 2, part 1 and part 2). We conduct a sensitivity experiment to address this uncertainty (see details in Text S1)."

L383-389: "We note that uncertainties in model parameters discussed in Section 2.2 and 2.3 could alter the estimated contribution of the isomerization pathway. In particular, the upper-limit 50% yield and applying the photo-recalcitrant fraction only to the lowest volatility bin (see Text S1) could over-emphasize isomerization. Conversely, neglecting higher branching ratios and yields for limonene SOA may underestimate the importance of isomerization for total SOA formation from monoterpenes."

L624-628: "However, the increase from isomerization may be slightly overpredicted due to turning off the photolysis of SOA from the lowest volatility bin (see also Text S1). Indeed, we notice that the MTERP SOA lifetime due to photolytic loss is longer in F than PD (Table S1), likely because a large fraction of MTERP SOA is formed through isomerization in F but not photolyzed."

5. Line 278-280: The manuscript currently lacks sufficient detail in the setup of the pre-industrial (PI) and future (F) experiments. The authors should provide a more comprehensive description of these scenarios, particularly clarifying the prescribed or online-calculated inventories used for anthropogenic, open biomass burning, and biogenic emissions across the PI, present-day (PD), and F experiments.

Thanks for this suggestion. We added Text S2 in the supplement to provide details regarding these fields (also see below). We note that due to the availability of existing input files, some of these data are climatological average, while some are single year conditions. This may result in some inconsistency, but the influence on results is likely small because data from within a decade tend to be more consistent than those from different climate conditions. All experiments were conducted with free-running configuration, meaning that the meteorology is not constrained by external meteorological datasets.

"Text S2. Experimental settings for PI, PD, and F

Our experiments for the pre-industrial (PI), present-day (PD), and future (F) conditions utilize sea surface temperature (SST), sea ice, CO_2 concentrations, anthropogenic and natural emissions of aerosols and reactive gases, and land use data representing 1850, 2010, and 2100 conditions, respectively. SST and sea ice for PI and PD originate from Hadley Centre sea ice and SST dataset (Hurrell et al., 2008). PI uses data for 1850, which is constructed by SST and sea ice climatology from 1870 to 1889. PD uses 2010 climatology, which is averaged from 2005 to 2015. The future SST and sea ice are generated from a fully coupled CESM2 experiment that was conducted under SSP5-8.5 trajectory and uses data from 2100 single year. The CO_2 concentrations for PI and PD conditions are taken from Meinshausen et al. (2017), with PI represented by the 1850 climatology (averaged from 1845 to 1855) and PD represented by the 2010 climatology (averaged from 2006 to 2014). Future CO_2 concentrations follow the SSP5 pathway from Riahi et al. (2017), using the projected values for the year 2100. Anthropogenic emissions of aerosols and reactive gases for PI and PD originate from the Community Emissions Data System (Hoesly et al., 2018), while the biomass burning emissions for PI and PD are constructed by van Marle et al. (2017). The future anthropogenic and biomass burning emissions are projected following the SSP5 pathway (Gidden et al., 2019). PI, PD, and F experiments are conducted with climatological emissions for 1850 (averaged from 1850 to 1859), 2010 (averaged from 2006 to 2014), and 2100 (averaged from 2091 to 2100), respectively. Emissions of biogenic volatile organic compounds (BVOCs) are calculated online through the Model of Emissions of Gases and Aerosols from Nature (MEGAN2) parameterization (see Section 2.1). The BVOC emissions are impacted by vegetation types determined by land use. The land use conditions for PI, PD, and F are taken from the dataset of Land-Use Harmonization 2 project (Hurtt et al., 2020) for single year 1850, 2010, and 2100, respectively. All the prescribed input data are in one-year length and used cyclically throughout the model integration. We note that the temporal treatments for these input datasets differ, due to the availability of existing input files. The influence on results is

likely small because data from within a decade tend to be more consistent than those from different climate conditions."

We also add the following sentence in the main text.

L338-339: "Detailed settings for the PI, PD, and F conditions are provided in Text S2."

6. Line 285: The authors utilize the SSP5-8.5 scenario to project the future evolution of biogenic RO_2 and SOA. However, a recent study suggests this extremely high fossil-fuel emission pathway is increasingly viewed as implausible (Hausfather and Peters, 2020). It would be more appropriate for the authors to explicitly regard their SSP5-8.5 results as an upper-bound sensitivity test. Furthermore, I recommend that the authors consider including an additional simulation under a more moderate pathway (such as SSP2-4.5) to provide a more realistic projection of future biogenic SOA burdens.

Thanks for this suggestion. We chose SSP5-8.5 because it is the considered as the most extreme scenario, thus providing the most contrast with PD and PI in the changes of temperature and CO_2 level. In our revised manuscript, we mention this and acknowledge that SSP5-8.5 is debated to be implausible. We also acknowledge that our results depend on our choices of future scenario, and the results can be different if switching to another scenario. Please find our modifications below.

L343-347: "We chose SSP5 because it is considered as the most severe scenario, providing the strongest contrast to PD and PI in temperature and CO_2 level. However, it is noted that SSP5 is an extreme case and debated to be implausible (Hausfather and Peters, 2020). Thus, the magnitude (though not the sign) of our PD to F results may be significantly different if considering another future scenario."

L645-647: "Also, the PD-to-F changes largely depend on the selected future scenario. Using an alternative scenario with different NO emissions, temperature, and/or CO_2 level can lead to substantially different results."

We agree that showing results from a moderate future scenario would be very interesting. However, we do not have computational resources to do an extra 11-yr simulation. Also, including another future experiment would make our manuscript too lengthy and not easy to read. Therefore, we respectfully decline the reviewer's suggestion to conduct an addition future experiment.

7. Line 290: Please specify the exact simulation periods for the PI, PD, and F experiments.

The experiments were conducted with free-running configuration, meaning that the meteorology is fully prognostically calculated by the model and is not constrained by

external meteorology dataset. The 11-year experiments are conducted with repeated 1-year input data, representing PI (1850), PD (2010), and F (2100) conditions (see above response above and Text S2). Therefore, there is no specific time period for the experiments. We have clarified that our experiments use free-running configuration and repeated forcing in the revised manuscript.

L352-354: "The model is integrated for 11 years in a free-running configuration and using cyclically repeated one-year input data. Therefore, the simulated results represent repeated time-slice forcing."

8. Line 424: The text notes that the NEW simulations predict a decrease relative to the BASE scenario over tropical forest regions. However, the underlying drivers for this change are not discussed. I recommend that the authors add a brief explanation of this regional decrease.

The total SOA decrease over tropical forests from BASE to the NEW experiments are dominated by the strong decrease in ISOP SOA (Figure 6d-f). As discussed in the paragraph above (L403-406 in the previous manuscript), this is because the newly implemented ISOP-RO_2 reactions introduces extra losses of ISOP-RO_2 that compete with the RO_2 + HO_2 and RO_2 + NO reactions but do not form SOA. In addition, the increase in total SOA over regions out of the tropical forest is dominated by MTERP SOA increase (Figure 6a-c). The changes in global distributions of MTERP SOA has also been discussed earlier in the manuscript. We briefly mention the role of ISOP SOA and MTERP SOA in the changes in global total SOA in the revised manuscript:

L495-497: "Globally, the NEW experiments predict a decrease from BASE over the tropical forest regions (Figure 6g-i), which is dominated by ISOP SOA (Figure 6d-f), and an increase over the rest of the world due to changes in MTERP SOA (Figure 6a-c)."

9. Line 425-428: As acknowledged in the text, the simulation results are highly dependent on the parameterizations for the biogenic RO_2 chemical mechanism, which is highly uncertain. It would strengthen the manuscript to provide a summary of the SOA yields, reaction rate constants, and branching ratios from various laboratory studies, and then to evaluate the extent to which the uncertainties in these specific parameters impact the modeled biogenic RO_2 and SOA.

The RO_2 chemistry is highly uncertain and has not been comprehensively explored. Also, many existing studies do not provide quantitative estimates of these parameters. Therefore, it is challenging to systematically provide a range for them.

In the submitted manuscript, we provided quantitative discussion regarding MTERP-RO_2 isomerization rates and RO_2 + RO_2 reaction rates. We also discuss uncertainty regarding ISOP-RO_2 isomerization.

Following the reviewers' suggestions, we have added more uncertainty discussion in our manuscript (both methodology and results sections). This includes discussion about (1) SOA formation through heterogeneous reaction; (2) lumping MTERPs into one species; (3) simplification of the isomerization mechanism and its SOA yields; (4) isomerization branching ratio; (5) yields of RO_2 + RO_2 reactions and the volatility of the dimer products; (6) neglection of SOA formation through non-accretion products from the RO_2 + RO_2 reactions; (7) RO_2 reactions with NO_3, CH_3O_2, and CH_3CO_3; (8) ISOP-RO_2 + ISOP-RO_2 reactions; (9) SOA photolysis. Detailed of these discussions can be found in our point-to-point responses to Reviewer #1 and in the track-change version of the revised manuscript.

10. Line 467-469: It would be beneficial to clarify the range of estimated future BVOC emissions in the selected scenario, and then evaluate the extent to which the uncertainties in these future BVOC emission estimates might affect the projected biogenic SOA burden.

We agree with the reviewer that it would be helpful to show a potential range for future BVOC emissions. However, this is difficult because the emissions change with various factors, including models, climate scenarios, how emissions are parameterized (MEGAN or other schemes) in the model, model biogeochemical configurations and tuning parameters, the selection of land use map, etc. In our submitted manuscript we reference Cao et al. (2021) who compared isoprene emission for the SSP scenarios across several CMIP models – these values represent a range rather than an uncertainty. As far as we know, there has not been a study systematically exploring a range of potential emissions of future scenarios and thus no such estimate exists.

11. Line 471-476: I recommend adding a figure for the global distributions of changes in the VOC emissions from anthropogenic and biomass burning sources from PI to PD and from PD to F in the supplementary, which would better support the authors' discussion about the shifts in OH and HO_2 concentrations.

We added the historical and future changes of toluene emissions from anthropogenic and biomass burning sources in Figure S3. The changes in the other anthropogenic and biomass burning VOC species follow the same trends as toluene.

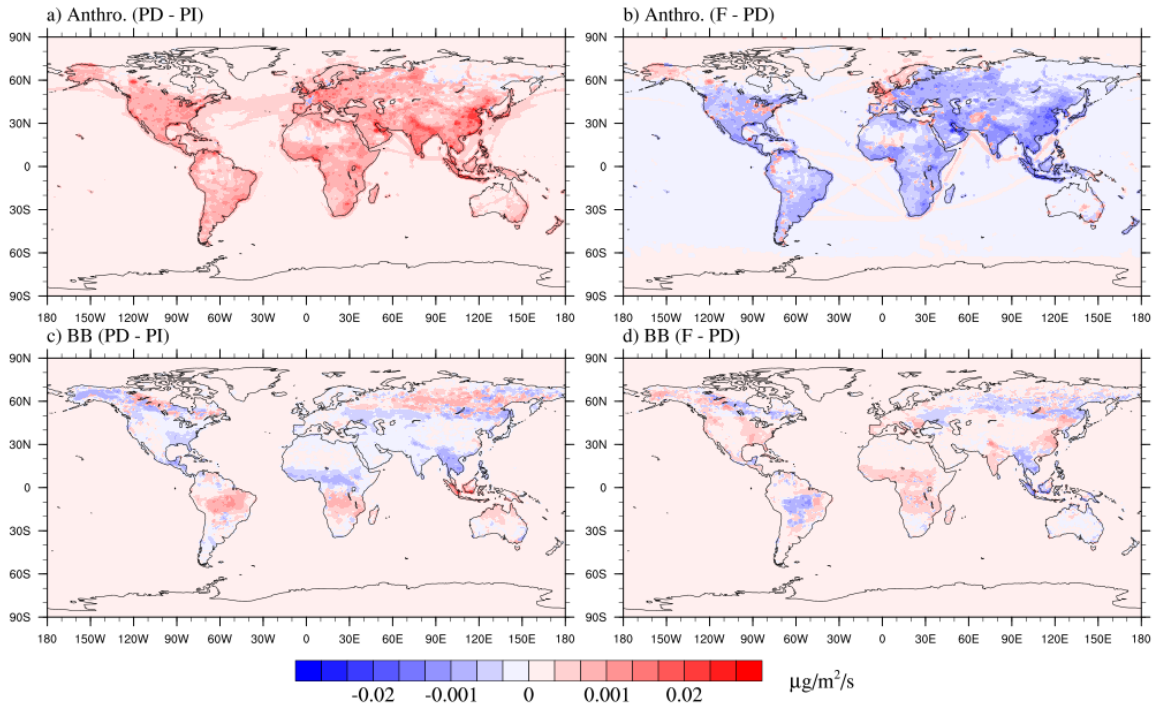

Figure S3. Historical (left panel) and future (right panel) changes of toluene emissions from anthropogenic (Anthro.) and biomass burning (BB) sources. The other anthropogenic and biomass burning VOC species follow the same trends.

We also added the following statements in Section 3.2:

L553-556: "The oxidant changes can also be impacted by changes in VOC emissions from anthropogenic and biomass burning sources (Figure S3). The trends in anthropogenic VOC emissions are generally opposite to the changes in BVOC emissions, likely counteracting some of the impacts of BVOC emissions on oxidant changes."

12. Figures 11 and 12: Please clarify in the figure captions how the differences are calculated (e.g., whether they represent PD minus PI and F minus PD, respectively).

We have modified the figure captions as follow.

"Figure 11. Changes in annual mean SOA column concentrations from PI to PD, calculated as PD minus PI, …

Figure 12. Same as Figure 11, except for changes from PD to F, calculated as F minus PD."

13. Line 537-539: The manuscript currently attributes the increase in SOA from RO_2 isomerization solely to the reduced evaporation of low volatility products. However, the increase is likely driven not only by this volatility effect, but also because the higher temperature kinetically favors the RO_2 isomerization pathways themselves, as illustrated in Figure 1. I recommend that the authors explicitly highlight that by incorporating detailed biogenic RO_2 chemistry, the modeled biogenic SOA formation becomes more sensitive to temperature changes than estimated by previous simplified schemes.

Thank you for pointing this out. We mention that the acceleration of isomerization may contribute to the increase in isomerization SOA in the revised manuscript. However, we note that the isomerization is so fast compared to the bimolecular reactions that it is already nearly saturated in PD, and the fRO_2 increase from PD to F is small (from 19% to 20%). Therefore, the impact of temperature on isomerization SOA increase is likely minor.

L628-631: "The increase in SOA formed through the isomerization pathway may also be related to the favoring of this pathway under the extreme warming in SSP5. However, such impact is likely limited, since isomerization is already nearly saturated in PD and the fRO_2 increase from PD to F is minor (Figure 9a)."

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