1 Anonymous Referee #2

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1.1 General comments

In this manuscript, the authors have developed the global chemistry climate model ECHAM-HAMMOZ to include a more explicit coupling between the gas and particle phase models in order to describe the formation isoprene derived secondary organic aerosol (SOA). With their model, they predict that most of the iSOA is produced by IEPOX and Isop$(OOH)_2$. This ultimately leads to over predictions of iSOA in relatively pristine locations where models typically under predict SOA in general. There seems to be a growing tendency in the literature for models to capture ever increasing complexity in the chemical mechanisms because they are more capable of describing the wide variance of atmospheric conditions. For this reason, I believe this manuscript has a lot of value to interested readers. However, it is incumbent on the developers to describe in detail all the relevant additions to the mechanism and justify other aspects that were not considered. I feel that certain aspects of the chemical mechanism were not adequately characterized in this manuscript. For example, there was no discussion on HOx recycling in the mechanism (an important facet in low NOx regimes) or how specifically all the percentage yields in Figure 1 were obtained both of which affect oxidation state, product yields and branching ratios and therefore model results. For this reason, I would reconsider this publication after addressing the major and minor revisions detailed below.

Reply: We thank the referee for the positive comments and for the interest in additional details concerning the model chemical mechanism formulation. Indeed, the resulting yields are global, annual averages and Referee #1 criticized this point, as well. It seems, we did not formulate the text clear enough to be easily understandable. This, and all further specific comments, are addressed below.

1.2 Specific comments

1. The chemical mechanism as shown in Figure 1 contains many percentage yields. The authors described the reaction pathways and mentioned yields in the text on pages 6 and 7 although they either did not provide references or a brief discussion of how the yields were obtained. It may be stated in another reference but the crucial reaction yields shown in the figure need to be justified. For example, how was the 9 % gas phase yield of LISOPOOHOOH obtained or how was the 1 % gas phase yield of LC578OOH determined? It is these numbers which will directly affect SOA yields and it is therefore crucial to understand their uncertainties based on how they were derived. A discussion with pertinent references should be included on pages 6 and 7.

   Reply: The yields in Figure 1 and in the text are diagnosed after the one year simulation in 2012. This means that globally 9 % of isoprene carbon mass is converted into LISOPOOHOOH. After LISOPOOHOOH is produced in the gas phase, it partitions into the aerosol, which is a reversible process. Nevertheless, globally, the net yield of LISOPOOHOOH into the aerosol is 79 %. These numbers are derived from ECHAM-HAMMOZ reference simulation, thus the citation is "missing". Indeed, also Referee #1 asked about the yields. The text was adjusted to clarify these yields, as not fixed, but resulting on an global annual mean. Regionally, the yields vary according to chemical regime (radicals present) and the pre-existing aerosol for reactive uptake and partitioning.

2. HO_x recycling remains an issue in atmospheric chemistry models because HO_x levels are typically under predicted in areas of low NOx. [Archibald et al., "Impacts of HOx regeneration and recycling in the oxidation of isoprene: Consequences for the composition of past, present and future atmospheres", Geophys. Res. Letters, 2011, L05804.] Certain reactions will rapidly consume HO_x such as the formation of LISOPOOHOOH (2 OH and 2 HO_2 radicals typically consumed) while other reactions will recycle HO_x such as the ring closure reaction of the IsopOOH-(OH)2 radical to form IEPOX or intramolecular hydrogen shift reactions. The consumption of HO_x species has been expressed in the R1-R22 reactions but there seems to be no mention of HO_x species regeneration which affects the oxidative capacity of the atmosphere in regions of low NO_x. For example, reaction R3 will release OH radicals when IEPOX is produced but this is not specified in the reaction. A hydrogen shift reaction (not really discussed in any of the reactions as far as I can tell) may produce carbon centered radicals at hydroxyl sites that may react with O2 to yield a carbonyl compound and HO_2. These regenerated HO_x species are important and need to be accounted for and/or discussed in the paper in the section describing these reactions.

   Reply: The atmospheric chemical mechanism JAM3 includes reactions, which lead to HO_x recycling. Also some of the reactions described in the manuscript recycle OH and HO_2, but the radicals were not explicitly mentioned. This was adjusted, now radicals (OH, NO, HO_2) produced in reactions are given in the text. Moreover, JAM3 includes the 1,4H-shift of LC587O2 (precursor to LC587OOH), 1,6H-shift of LISOPOACO2 (lumped species ISOPAO2, ISOPOBO2), 1,5H-shift of ISOPBO2 and ISOPDO2, 1,6H-shift of LHC4ACCO3 (lumped species HC4ACO3, HC4CCO3). These H-shifts yield substantial OH either directly or via subsequent oxidation similarly as in the MOM mechanism (Lelieveld, Jos, et al. "Global tropospheric hydroxyl distribution, budget and reactivity." Atmospheric Chemistry and Physics 16.19 (2016): 12477.) and the LIM1 mechanism (Peeters, Jozef, et al. "Hydroxyl radical recycling in isoprene oxidation driven by hydrogen bonding and hydrogen tunneling: The upgraded LIM1 mechanism." The Journal of Physical Chemistry A 118.38 (2014): 8625-8643.).

   DOMENICO? More needed here?

3. On page 6 of the manuscript (line 7) it states: "Not included is the H-shift of LISOPOOHO2 that yields much more volatile compounds than LISOPOOHOOH". I do not agree with the authors that the compounds produced would be 'much more volatile' and therefore

are not relevant to particle phase partitioning. If a 1,5-H-shift occurs in LISOPOOHO2, it would lead to a compound similar to LC578OOH except it would be heavier by one oxygen atom (i.e. a hydroxy-dihydroperoxy carbonyl derivative instead of the LC578OOH diol). Because LC578OOH partitions to the particle phase, so too would this newly produced compound derived from an H-atom shift. This product is indeed less volatile than LISOPOOHOOH, but it would be expected to partition into a particle phase thereby decreasing the influence of LISOPOOHOOH in the mechanism.

Reply: The sentence "If a 1,5-H-shift occurs in LISOPOOHO2, it would lead to a compound similar to LC578OOH except it would be heavier by one oxygen atom" motivated us to do two additional simulations taking into account the possible 1,5-H-shift in LISOPOOHO2. From D'Ambro et al. 2017 (DOI: 10.1021/acs.est.7b00460) Supplement Table S1 and Table S2 we took the idea of the possible product and the rate constant. The product of the 1,5-H-shift is a highly functionalized epoxide (SIMLES: CC(C(OO)C=O)(O1)C1O, Table S1). Introducing a new compound into the chemical mechanism requires a lot of adjustments in different parts of the code, especially when the molecule might be undergoing two processes, partitioning and reactive uptake. To keep it simple, two tests (3 month simulation, June, July and August 2012) were run: one introducing 1,5-H-shift in LISOPOOHO2 forming LIEPOX and a second one introducing 1,5-H-shift in LISOPOOHO2 forming LC578OOH. In both sensitivity simulations an unimolecular rate constant of 0.3 s^{-1} is used.

The results of both sensitivity simulations show reductions in iSOA burden, for the simulated time period (JJA), of 30 %. To discuss these additional results, we introduced a new Section called "Uncertainty in LISOPOOHOOH aerosol". The corresponding plots are shown in the Supplement 2, Figures S2 and S3.

4. The product branching ratios for the subsequent reactions of IsopO2 in Figure 1 seem fixed regardless of the environment. Is this the intended assumption? Because all the subsequent reactions of IsopO2 are bimolecular, the branching ratios (and therefore product yields) will depend on the relative concentrations of RO2, HO2 and NO radicals. The gas phase product yields will therefore not only be influenced by local isoprene concentrations but also on the relative concentrations of these radicals. A discussion of this effect should be included in the manuscript along with a justification as to why using these fixed values represents an average isoprene environment.

   Reply: The product branching ratios are not fixed and depend on the ambient radical concentrations. Instead, the yields here result from a global, average and indeed represent isoprene oxidation in ECHAM-HAMMOZ. ECHAM-HAMMOZ seems not to resolve high NO_x environments well, this might be caused by the coarse grid resolution of around 200×200 km. Further analysis of 3 hourly values in different grid boxes with high isoprene emissions and high NO_x showed, that NO_s suppression of iSOA precursors is resolved by the model, but lost once monthly and annual averages are considered.

5. The acronyms used to describe the chemical mechanism are not very clear. For instance, I cannot figure out what IsopOH is. I presume that IsopOOH is a hydroxy-hydroperoxy isoprene species (of which there are 8 isomers) so does that mean IsopOH is the diol? Chemical structures for all species listed in Table 1 and Figure 1 would be extremely useful.

   Reply: Indeed, the chemical structures would clarify the names. As ISOPOOH etc. are simplifications within Figure 1 and text, we added a table in the supplemental material 2 which contains all structures, SMILES codes, the names and corresponding names in MCM. MOZ includes many lumped species. Thus, all isomers are shown.

   After major revisions to the section describing the MOZ isoprene chemistry, we removed the minor pathway through the diol ISOPOH, therefore it does not appear in the new tables in Supplement 2.

6. In the chemical mechanism, there is no mention of dinitrate formation which is likely to occur in high NO_x environments.[see Piletic et al. "Barrierless Reactions with Loose Transition States Govern the Yields and Lifetimes of Organic Nitrates Derived from Isoprene", J. Phys. Chem. A, 2017, 8306 and Jenkin et al. The MCM v3.3.1 degradation scheme for isoprene, Atmos. Chem. Phys., 2015, 11433.] These species are highly oxidized and relatively heavy and therefore may affect the SOA yield in high NO_x regime.

   Reply: JAM3 includes organic nitrates from isoprene (LNISOOH, which is considered as iSOA precursor, LISOPNO3OOH, LISOPNO3NO3 (dinitrate from isoprene), LISOPNO3O2 etc., see tables S3 and S4 in Supplement 2). They are not considered as iSOA precursors here, because their saturation vapor pressure p_0^* at 298.15 K is not lower than 0.01 Pa, when the group contribution method by Nannoolal et al. (2008) is used. Nevertheless, they might affect the SOA yield, but this is not tested within this study, because the large amount of computational resources needed for each new SOA-tracer, which is defined 11 times (1 gas-phase tracer + 10 SALSA aerosol bin tracers).

1.3 Technical comments

1. On page 3 line 21, remove "the" for In the light of

   Reply: Corrected.

2. On page 5 line 14, replace "., it is referred to the " with ", the reader is referred to the "

   Reply: Corrected.

3. On page 5 line 17, replace "Also the O3 initiated reactions pathways are included in MOZ, but none of the products was low volatile enough." with "The O3 initiated reaction pathways are included in MOZ, but the products are too volatile to contribute to SOA."

   Reply: Corrected.

4. On page 9 line 17, add a comma between the words "dependence" and "sensitivity".

   Reply: Added.

5. On page 9 line 25, replace "'...processes to only the aerosol sized that are relevant..." with "...processes to include only the aerosol sizes that are..."

   Reply: Corrected.

6. On page 9 line 30, replace "Here this model..." with "Here, the model..."

   Reply: Corrected.

7. On page 12 line 24, replace "... especially LISOPOOHOOH molar mass of 168.14 g/mol is very large." with "...especially due to LISOPOOHOOH which has a molar mass of 168.14 g/mol that is very large."

   Reply: Corrected.

8. On page 14 line 2, replace "... 2-methyltetrols in the order of ng/m3 are measured in..." with " 2-methyltetrols are present in ng/m3 concentrations in the..."

   Reply: Corrected.

9. On page 14 lines 9 and 18, the sentences are poorly expressed and need to be rewritten (i.e. "On the LISOPOOHOOH-SOA plot..." and "Hodzic et al")

   Reply: The sentences were rewritten.

10. On page 14 line 33, the sentence should read "24 % of isoprene ends up as IEPOX, 9 % as LISOPOOHOOH, ..." where every 'in' is replaced with 'as'

    Reply: Corrected.

11. On page 15 line 7, it should read ”The majority of precursors are destroyed chemically ...”

    Reply: Corrected.

12. On page 15 line 19, replace ”... AeroCom mean value, because iSOA...” with ”... AeroCom mean value because the iSOA...”

    Reply: Corrected.

13. On page 17 line 5, remove ”motivated” (word duplicated)

    Reply: Corrected.

14. On page 17 line 21, replace ”in contrary as can be seen in Figure 5 iSOA...” with ”On the contrary as can be seen in Figure 5, iSOA...”

    Reply: Corrected.

15. On page 20 line 14, replace ”...of the various different organic ” with ”for the different organic compounds...”

    Reply: Corrected.

16. On page 20 line 17, replace ”...using for all of them 30 kJ/mol.” with ”using 30 kJ/mol as the ΔH_{vap}.”

    Reply: Corrected.

17. On page 21 line 11, replace the word ’at’ with ’for’ at the end of the line.

    Reply: Corrected.

18. On page 21 line 14, switch the order of ”holds also” to ”also holds”.

    Reply: Corrected.

19. On page 22 line 20, remove the word ’atmospheric’ (redundant).

    Reply: Removed.

20. On page 22 line 21, add the word ’the’ before AMS at the end of the line.

    Reply: Added.

21. On page 25 line 3, replace the word ’pure’ with ’purely’.

    Reply: Corrected.

22. On page 25 line 8, the sentence either needs to be split up or more clearly stated.

    Reply: The sentence was split and clarified.

23. On page 26 line 12, add the word ’the’ between ’has most’

    Reply: Added.

24. On page 26 line 16, add the word ’by’ between ’followed OH’

    Reply: Added.

25. On page 26 line 17, the sentence should read ”... NO_x dependent pathways...”

    Reply: Corrected.