Replies to Interactive comments on "Isoprene derived secondary organic aerosol in a global aerosol chemistry climate model" by Scarlet Stadtler et al.

1 Anonymous Referee #1

Received and published: 27 November 2017

In the manuscript the authors describes a semi-explicit isoprene oxidation scheme and the explicit treatment of SOA formation from 6 isoprene oxidation products in the global chemistry climate model ECHAM-HAMMOZ. I find the method used to simulate isoprene SOA (iSOA) very novel and encouraging and I definitely think that this kind of explicit treatment of SOA formation from known oxidation products are necessary in order to improve the knowledge about SOA formation and anthropogenic impact (e.g. NOx) on SOA formation in the atmosphere. The manuscript is generally well written and clearly structured and I recommend that the manuscript should be accepted for publication after a minor revision where the authors carefully addressed my comments.

Reply: We thank the referee for the encouraging, introducing words and for the following, very useful comments and corrections. The main replies are listed below according to the comments.

1.1 General comments

I miss references in the main text to the supplement and the reactions R1-R22. This is needed for clarity.

Reply: The references to the chemical reactions in the main text were added. Moreover, according to the comments of Reviewer #2 the reaction equations were adjusted to show also radical turnover.

On Page 5, L9 and on several other places in the manuscript you refer to the isoprene oxidation products in Table 1 as low volatility compounds (LVOC) since their saturation vapor pressures (p_0*) at 298.15 K is below 0.01 Pa. I presume that you mean their pure-liquid saturation vapor pressures. Further, this is not the common p_0* limit for LVOC which e.g. according to Donaue et al., Faraday Discuss. 2013, 165, 91–104 is compounds with C* in the range of 10-0.5 to 10-3.5 μg m^{-3} which approximately correspond to a p_0* range of 4×10^{-6} to 4×10^{-9} Pa. Instead 0.01 Pa is somewhere on the limit between SVOC and IVOC. Thus, only LISOPOOHOOH in Table 1 can be referred to as LVOC at 298.15 K.

Reply: Indeed, the classification of the compounds according to Donahue et al. 2013 fits better to current literature and was adjusted thought the text. Especially, after running the sensitivity simulation using EVAPORATION instead of Nannoolal et al. 2008, the classification of

the four compounds as SVOC or LVOC was further complicated. Table 5 was extended and with the EVAPORATION values for $\log 10(C_0^*)$, for example, pushing LNISOOH ($\log 10(C_0^*) = 2.2$) to the group of IVOC and even LISOPOOHOOH gets close to be classified as an SVOC. This is further discussed in Section 3.3.

On Page 6-7 and in Figure 1 you refer to the yields of the iSOA precursors as if they were fixed yields. E.g. On Page 6, L9-10 you write that: "LISOPOOHOOH has the highest yield of the LVOC considered here, 9 % of isoprene end up as LISOPOOHOOH". First of all, what do you mean with this yield? Is it the molar or mass yield that is 9 %?

Secondly, how can these yields have a fixed value? If the gas-phase mechanism explicitly simulates the formation of the different iSOA precursors their yields should vary depending on the concentrations of NO, O_3, OH, NO3 etc. Maybe it is the global average yields derived with the model? If this is the case please state that.

Reply: The text was misleading, indeed there are no fixed yields in ECHAM-HAMMOZ, neither for gas-phase chemistry nor for SOA formation itself. The "annual, average mass yields" are now called like this and hopefully clearly understandable.

The section 2.1.2 is somewhat confusing when you discuss the SALSA-VBS system that apparently is not used in the present study but then in Figure 5 you still present results where you use the VBS method.

Reply: The comparison of ECHAM-HAMMOZ to the SALSA-VBS system was done in order to see how two very similar models can differ. The SALSA-VBS system seems to have similar limitations as AeroCom models in terms of SOA formation underestimation. This is the reason why this comparison was added. To clarify this, the introduction in Section 2.1.1 was extended to better guide the reader and reduce confusion.

On Page 10, L12-13 you write: "Loss processes for SOA in HAM-SALSA include sedimentation, deposition and wash out in the aerosol phase." But should it not be "Loss processes for SOA in HAM-SALSA include, apart from evaporation, sedimentation, deposition and wash out in the aerosol phase." I dont understand why/how the pH of the aerosol particles can differ by several order of magnitudes if the only inorganic species is ammonium bisulfate. I guess the pH is only calculated for the inorganic aqueous phase. Is the 4 order of magnitude difference in pH only related to the average RH at different locations? Please clarify this in the text on page 10 and also refer to the figure in the supplement.

Reply: Page 10, L12-13: yes, the evaporation sink is missing in this sentence, it was adjusted accordingly.
The second part of the comment: The aerosol pH calculation is done with strong assumptions and we admit it is a crude estimate for testing the model. We do take into account water taken up by all compounds, but we assume that they don't affect the activity of hydrogen ion and thus pH (the negative logarithm of the hydrogen ion activity). Which means that the difference is related to the average RH at different locations. The text on page 10 was adjusted and the Figure in S2 referenced.

I miss labeling (e.g. a, b, c) of the panels in all figure and the figure text to figure 2 need to describe what the two panels actually display.

Reply: Labeling of all panels in all figures was added and the figure text of Figure 2 extended.

In the results section on Page 14 and maybe on some other places you use the terms "quite big" and "quite high". Try to avoid using these vague statements and instead write concrete numbers (e.g. contributes to 30 % of the SOA mass instead of contributes to quite big amounts of the SOA mass).

Reply: The vague statements were specified throughout the manuscript.

On Page 14, L10 you state that LSOPOOHOOH-SOA is extremely low volatile but it is not. At least not at 298.15 K (see the comment concerning LVOC above).

Reply: Indeed, the wording is misleading, we wanted to express it is the most low volatile among the compounds in MOZ. The text was changed accordingly.

Concerning the uncertainty of the estimated saturation vapor pressures (Section 3.3). I think it is good that you discuss the uncertainties related to the functional group contribution methods used to estimate the pure liquid saturation vapor pressures.

In publication by Kurtn et al., J. Phys. Chem. A 2016, 120, 2569–2582 it is stated that: "Unfortunately, the basis data sets of existing group contribution based empirical parametrizations for determining saturation vapor pressures of organic molecules (e.g., SIMPOL, or the widely used and generally successful Nannoolal et al. approach) do not contain complex polyhydroperoxides (or multiply substituted peroxy acids), and the parametrizations may therefore not be reliable for HOMs." LSOPOOHOOH can be considered as a HOM with two hydroperoxide functional groups.

Thus, according to the results from Kurtn et al., 2016 it may have been more appropriate to use the EVAPORATION method which also is provided via UManSysProp (Topping et al., 2016). With EVAPORATION/Nannoolal I get a p_0* (298.15 K) of 10-5 Pa, e.g. 38 times higher than the value you used at 298.15 K. In fact according to EVAPORATION LSOPOOHOOH is not a LVOC but a SVOC (C* $\approx$ 1 μg m^{-3}) at 298.15 K.

Reply: An additional simulation using EVAPORATION instead of Nannoolal et al. was run, evaluated and integrated into the uncertainty discussion. The iSOA budget is influenced by the saturation vapor pressures calculated using EVAPORATION. Annual iSOA production for 2012 is reduced by 12.8 %, the burden is reduced by 16.7 %. A detailed Table was added showing the impact on each iSOA precursor. Nevertheless, this study mainly focuses on surface concentrations, there the $10-20$ % reduction is not visible. The main conclusion, the importance of LIEPOX and LISOPOOHOOH in ECHAM-HAMMOZ does not change.

1.2 Technical corrections

Write out that ISOP(OOH)2 refers to dihydroxy dihydroperoxide in the abstract

Reply: Changed.

Page 4, L16: Change from "... and its evaluation it is referred ..." to e.g. "... and its evaluation the reader is referred ..."

Reply: Changed.

Page 4, L33: Change from "The semi-explicit isoprene oxidation with 147 reactions constitutes a major of these reactions in JAM3." e.g. to: "Thus, the 147 reactions in the semi-explicit isoprene oxidation scheme constitute a substantial fraction of these reactions in JAM3."

Reply: Changed.

Page 5, L20: Change from "For simplicity there are ..." to "For simplicity they are ..."

Reply: Changed.

On Page 15, L24: I think it should be "lifetime" and not "life time". Try to reformulate the wording "huge wet deposition loss".

Reply: "life time" was changed to "lifetime". The huge wet deposition loss was deleted and we added some sentences on the wet deposition loss clarifying the rather short lifetime of iSOA in ECHAM-HAMMOZ.

On Page 17, L3: Remove "is" after iSOA and remove one "motivated" on L5.

Reply: Removed.

On Page 17, L14: What do you mean with VBS classes 0, 1 and 10? If it is C^* in $\mu g\,m^{-3}$ non of these species are LVOC at 298.15 K according to e.g. Donahue et al., 2013.

Reply: The naming of the VBS classes was misleading and was adjusted. Now they are called: VBSnonvol (former VBS0), VBS0 (former VBS1), VBS1 (former VBS10). The class VBSnonvol is for non volatile oxidation products, which condense and do not evaporate. VBS0 and VBS1 refer to compounds with $\log 10(C^*) = 0$ and $\log 10(C^*) = 1$ respectively. VBS0 and VBS1 are classified as SVOC, according to the Donahue et al. definition. The whole Section 3.2.1 was corrected, to clarify the comparison.