

Review of the manuscript acp-2021-251 “Modelling the gas–particle partitioning and water uptake of isoprene-derived secondary organic aerosol at high and low relative humidity” by Amaladhasan et al.

### **General comment:**

In the presented study, the authors perform model simulations of isoprene oxidation and secondary aerosol formation during a wide range of atmospheric relevant conditions (RH, temperature, seed aerosol type). The model system consist of the master chemical mechanism isoprene gas-phase chemistry and an equilibrium SOA partitioning model based on the AIOMFAC activity coefficient model for mixture non-ideality and the EVAPORATION model for pure compound liquid saturation vapor pressure estimates. The paper is in large parts well written, but it is not straightforward to understand all methods. Especially the SOA yield parameterization and SVOC partitioning will need some clarification and justifications. In addition, the atmospheric relevance of the present work can be highlighted more. After such improvements and careful considerations of my review comments, I think that the paper can be accepted for publication in Atmospheric Chemistry and Physics.

### **Specific comments:**

Last sentence in Abstract. Consider to add some conclusions about the results. What are the main findings from the present study?

Page 5, line 9 “The model predictions are compared to isoprene ozonolysis chamber experiments ...”.

Generally I think it is hard to differentiate between what results that are model fitting to the CLOUD experiment and which model results that actually are independently evaluate against the SOA mass concentration observations from CLOUD.

Page 6, lines 2-5: “The total organic mass concentration, resulting from the gas-phase and aqueous-phase oxidation chemistry under dynamic gas–particle partitioning, was derived from the SMPS measurements of the particle number–size distribution, assuming an average aerosol mass density of 1.3 g cm<sup>-3</sup> (Fuchs, 2017). The average aerosol mass density was calculated based on the HR-ToF-AMS-determined mass fractions by using a parameterization by Kuwata et al. (2011), which is based on the elemental oxygen-to-carbon ratio (O:C) and the hydrogen-to-carbon ratio (H:C).”

From this description, it is not clear to me if you used a SOA mass density of 1.3 or densities derived from the SOA elemental composition.

Page 9, lines 1-5: “Whether a component resides in the gas phase, the condensed phase or partitions significantly between both is, in principle, irrelevant at input, yet can be exploited to select mainly low-volatility and semi volatile components that substantially contribute to SOA mass under given environmental conditions.”

I don't understand what you want to say with this statement. How can this be irrelevant for SOA formation?

Page 9, lines 5-7 “A state-of-the-art chemical mechanism for gas phase reactions, the Master Chemical Mechanism (MCM), version 3.3.1 (Jenkin et al., 2015), available online: <http://mcm.leeds.ac.uk/MCM>, was used to account for the reactions of isoprene with ozone as well as OH radicals formed during the reaction process.”

I guess one purpose of using MCM is to estimate the fraction of isoprene that is oxidized by OH in the experiments. This will be very relevant for the SOA formation. I would like to see some information in the manuscript about the relative importance of OH vs O<sub>3</sub> oxidation of isoprene during the CLOUD experiments. The MCM model simulations should give this information.

Page 9, line 12-14: “The major stable products predicted by the MCM for the first/early generations of oxidation are compounds of low molecular mass with relatively low O:C ratios and high vapour pressures (VOC to IVOC class compounds).”

I suggest that you add numbers on how large fraction of the total modelled stable oxidation products that go via these intermediate early-generation oxidation products. Otherwise you wonder why you only selected these specific compounds.

Page 9, lines 16-18: In order to validate the amounts of ozone, OH and “isoprene reacted” predicted by the MCM, conditions and measurements from the CLOUD 10 and CLOUD 9 chamber experiments, reported by Fuchs (2017), were used for a comparison with observations, further discussed in the following.

Please consider to reformulate this sentence. It is not easy to understand what you mean with “isoprene reacted”. Do you mean amount of isoprene oxidized by O<sub>3</sub> and OH?

Page 9, lines 20-21: “Additional components of semi-volatile and low-volatility nature formed via multi-generation oxidation, which are not fully considered by MCM, need to be included in the partitioning model as part of the isoprene system.”

1. I don't question that MCM do not predict all semi-volatile and low-volatility products that actually contributes to SOA mass, but have you actually tested to simulate the SOA formation from the isoprene oxidation products generated in MCM and compared the results with the observations in CLOUD?
2. I think this should be an easy test to do. I know that the MCM scheme for isoprene reacted with OH generate some semi- to low-volatility products that do contributes to SOA mass and yields comparable with experimental yields (see e.g. Xavier et al., *Atmos. Chem. Phys.*, 19, 13741–13758, 2019).
3. For pure isoprene + O<sub>3</sub> oxidation you probably do not form any semi- and low-volatility products that contribute to SOA mass formation but since you have secondary production of OH during the CLOUD experiments and in the model you should also form some low-volatility products from the MCM gas-phase chemistry scheme. On example is HMACROOH in Fig. 1 and 2.
4. When reading this I also ask the same question again: How large fraction of the reacted isoprene were via isoprene + OH?

Page 9, lines 23-28 “The selected surrogate components are shown in Fig. 1. Oxalic acid along with compounds such as 2-methyltetrol, 2-hydroxy-dihydroperoxide, 2-methylglyceric acid and a C5-alkene triol are among the main semi-volatile and low-volatility products that are expected to form after oxidation (by ozone and by OH) of the early generation compounds under low NO<sub>x</sub> conditions. The selected C10 hemiacetal dimer is a compound representing a whole class of potential dimer and oligomer compounds formed by accretion reactions from the above-mentioned five higher generation products.”

1. I miss a clear description about why these specific surrogate compounds were selected. At least add some proper references. You want to know how atmospheric relevant the selected SOA composition is.
2. I also miss information about the modelled and observed SOA elemental composition (O:C and H:C). Clearly these results exist and will provide at least some indication about how well the surrogate SOA species parameterization is able to represent the SOA properties e.g. hygroscopicity during the different CLOUD experiments.

Page 11, lines 19-21: “Surratt et al. (2010) proposed a chemical mechanism via the reactive intermediate epoxydiols (IEPOX) pathway leading to the formation of 2-methyltetrols and C5-alkene triols for the oxidation of isoprene by OH.”

The MCM chemistry represent formation of epoxydiols. Why did you not include IEPOX as an early generation precursor to 2-methyltetrols and C5-alkene triols? This would make the modelled SOA mass predictions more explicit.

Page 11, lines 24-25: “Multigeneration surrogate products from the MCM predicted yields of early-generation products are used to ensure that no carbon mass is unaccounted for.”

I don't understand this sentence completely. Do you mean that all (100 %) of all isoprene - oxidation pathways will go via the 6 selected early-generation oxidation products in Fig. 1 and hence, no carbon mass is unaccounted for?

Page 13, lines 17-19 “Molar yields of MCM-predicted products used in the model for the CLOUD 10 (seedfree) case were different based on the individual concentration of components present at the time when the chamber stabilized for the seed-free experiment.”

This sentence I do not understand. Please clarify what you mean.

Page 13, lines 27-30: “Details of the MCM box model approach in Fuchs (2017) are as follows: the box model used inputs for the isoprene concentration, ozone concentration, condensation sink (from SMPS data), inorganic seed concentration, rainout rate constant (quantifies the rate of formation of cloud droplets and the associated mass loss in the cloud), dilution rate constant, aerosol wall loss rate constant, RH, reaction rate constants of isoprene with the OH and O<sub>3</sub> oxidants, the hygroscopic growth factors ...”

Is this also the approach you used? With isoprene and ozone concentration, do you mean the steady state concentrations in the chamber or the concentrations in the inflow?

Page 15, lines 23-25: “In our simple model, the scaling parameters (branching ratios) are adjustable and are determined iteratively by model–measurement comparison. After the gas–particle partitioning model was used to calculate the equilibrium SOA mass concentration formed at varying levels of reacted isoprene, covering the range observed in the CLOUD chamber experiments,”

1. Ok, so in a way you produce a 5-species SOA yield parameterization which match the observed SOA mass, or?
2. I don't understand this completely. Was this not the same experiments which you used to fit the branching ratios? I have hard to differentiate between what actually was statistic fitting of the branching ratios and what is standalone modelling without tuning.
3. Which input parameters did you use to constrain the branching ratios and how was it done in practice. I guess you can find many different combinations of the beta parameters that give more or less the same SOA yield curves.

Page 24, line 1: “However, in the absence of OH radicals and light in the CLOUD experiments ...”

But OH was formed during the ozonolysis of isoprene.

Page 24, lines 4-6: “For consistency, the same molar yields were used for all seeded cases considered since the differences among the experimental conditions during the seeded experiments were relatively minor (yet different compared to seed-free).”

I don't understand completely. Did you use the same molar yields for the early products as in the seed-free case or different yields? I thought that a novelty with the model approach was that you base the yield calculations of the near-explicit MCM chemistry.

If you do not allow the early generation yields to vary according to the MCM chemistry I don't see the point in calculating the beta parameters based on the specific selected MCM compounds. Can you please clarify this?

Page 24, lines 8-14: “Hence, the gas–particle partitioning model was modified to account for RH-dependent SOA and water partitioning in the presence of an aqueous phase of variable inorganic seed concentration. We note that the measured steady-state flow chamber aerosol mass concentration is affected by the dynamic interplay between the different vapour and particle loss mechanisms: wall-loss, loss by chamber outflow, and the aerosol condensation sink. The latter depends on the particle size distribution and therefore also on humidity-dependent water uptake by seed particles and organic partitioning.”

1. It is unclear to me what you actually mean with this. How was the model modified? Did you change the beta values?
2. You note the importance of the dynamics interplay between the vapor on the walls and the condensation onto the particles, but do you consider it somehow in the model?

Page 24, lines 30-21: “. Occasionally, the formed clouds led to some precipitation in the chamber, which may have led to subsequent loss of organic aerosol mass and number concentration (reducing the condensation sink).”

Yes but was not steady state reach in-between the precipitation events? Can you provide some experimental data (e.g. from the SMPS) that justify the suggested decreasing condensation sink? If steady state is not reached, it must be hard to constrain an equilibrium model based on the observations.

Figure 6. Is the increasing SOA mass as a function of the inorganic seed aerosol a result of increased condensation sink, changed chemistry or both? Can you differentiate between these effects?

Page 27, line 14: “Observations by Kleindienst et al. (2007), using an ammonium sulfate seed ( $0.05 \mu\text{g m}^{-3}$ )” This is a very low concentration of AS seed. Is the value correct?

Page 28, lines 16-17: “SOA yield values observed in the chamber vary from 0.3 % to 1.4 % (uncorrected), while the model predicted values are in the range of 0.8 % to 1.4 % for the same SOA mass concentration range (Fig. 8b).”

Can you explain the difference between the modelled and observed yields at low SA seed concentrations? How would the dynamics i.e. condensation sink affect the results?

Page 29, lines 19-20: “That is, we are not accounting for possible changes in gas-phase or particle-phase chemical reaction pathways due to changes in RH, aqueous phase ionic strength and/or acidity.” and maybe even more important the dynamic e.g. condensation vs wall losses of condensable vapors or?

Page 36, lines 13-15: “Tools like the AIOMFAC-based phase separation model coupled with chemical kinetics and flow simulations could be used in the future to better constrain the effect of non-ideality and aerosol water content on the overall chamber dynamics and related interpretation of measurement data.”

I fully agree with you.