**Responses to referee #1**

We would like to thank the referee for her/his comments and efforts in providing this review. Below, we repeat each comment by this referee (in blue font) followed by our response, and we indicate related changes made to a revised version of the manuscript. Page and line numbers stated are those from the original manuscript.

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:

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

**Authors' response:** Two additional sentences have been added.

**Changes to manuscript:** "Those studies were conducted at RH levels at or below 40 % with reported SOA mass yields ranging from 0.3 up to 9.0 %, indicating considerable variations. A robust feature of our associated gas–particle partitioning calculations covering the whole RH range, is the predicted enhancement of SOA yield at high RH (> 80 %) compared to low RH (dry) conditions, which is explained by the effect of particle water uptake and its impact on the equilibrium partitioning of all components."

2) 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.

**Authors' response:** The above sentence has been rephrased to clarify that some CLOUD data was used to fit model parameters. Other revisions in Sect. 2 also serve better clarification of this model–measurement comparison vs. tuning aspect.

**Changes to manuscript:** page 5, lines 11, rephrased:
"Selected data sets from CLOUD experiments, primarily those for seed-free ozone-initiated oxidation of isoprene, were also used to tune adjustable model parameters to match measurements taken at low and high relative humidity levels; see details described in Sect. 2."

3) 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−3 (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.

**Authors' response**: The above sentences have been rephrased to indicate that an average SOA mass density of 1.3 g $cm^{-3}$ was used. This average SOA density value was estimated from the measured elemental O:C and H:C values.

**Changes to manuscript;** page 6, lines 4 – 8, rephrased:
"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 spherical particles and using an average aerosol mass density of 1.3 g $cm^{-3}$ (Fuchs, 2017). The average organic aerosol mass density was calculated from average composition using a parameterization by Kuwata et al. (2012), which is based on the measured (by HR-ToF-AMS) elemental oxygen-to-carbon (O:C) and hydrogen-to-carbon (H:C) ratios.

4) 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?

**Authors' response**: We agree, this statement was not clear; we have modified it. The original sentence was meant to indicate that the final phase partitioning of a component is, in principle, irrelevant at the stage of input into the gas–particle partitioning model, since the model will use the total molar concentration in a unit volume of air to determine the equilibrium partitioning of the component – and this notion would work if a nearly complete set of components were used to compute the partitioning. However, because only a selection of surrogate compounds is used, knowing the approximate volatility of candidate components is useful for that initial selection process. We have rephrased the original sentence and expand on the volatility and functional groups (hygroscopicity) properties of importance in our approach.

**Changes to manuscript;** page 9, lines 2 – 5, rephrased:
"The use of a set of surrogate components typically means that the actual system of oxidation products is highly simplified in terms of number and chemical classes of components. Some components will partition mostly to the gas phase and others to a small or large extent to the condensed phase. From the perspective of the gas–particle partitioning physics common to the volatility basis set (VBS) as well as surrogate-based approaches, it is necessary and sufficient to cover different volatility classes by at least one surrogate species. In such a framework, it is then important to approximately match the volatility distribution of the surrogates contributing to the SOA mass, which is achieved by tuning surrogate yields to match observations (as far as the range of measured SOA concentrations allow). As such, knowing the pure-component volatilities of potential surrogate components matters; we exploit this by selecting a set of low-volatility and semi-volatile surrogate components that will likely contribute to the SOA mass under the given environmental conditions. In addition, higher volatility components, directly predicted by a gas-phase chemical mechanism, are part of our system and enable establishing a scalable link

between the yields of those products and the selected lower-volatility surrogate compounds. Aside from surrogate compound volatilities, it is also important to match approximately the distribution of functional groups and molecular sizes, such that the resulting SOA hygroscopicity is captured by the AIOMFAC model. This aspect is considered by tuning the surrogate yields to observations taken at substantially different RH levels."

5) 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 O3 oxidation of isoprene during the CLOUD experiments. The MCM model simulations should give this information.

**Authors' response**: The MCM model output suggests that about 30 % of the isoprene oxidation in the dark chamber was due to OH. The remaining approximately 70 % of the isoprene oxidation was due to $O_3$ for low-$NO_x$ conditions. This is an aspect that was studied by Fuchs (2017), both to confirm that the MCM model is capable of predicting the amounts of isoprene reacted in the continuous flow setup and to determine the main oxidants. Below we include Figure 3.9 from Fuchs (2017) showing modeled oxidant fractions.

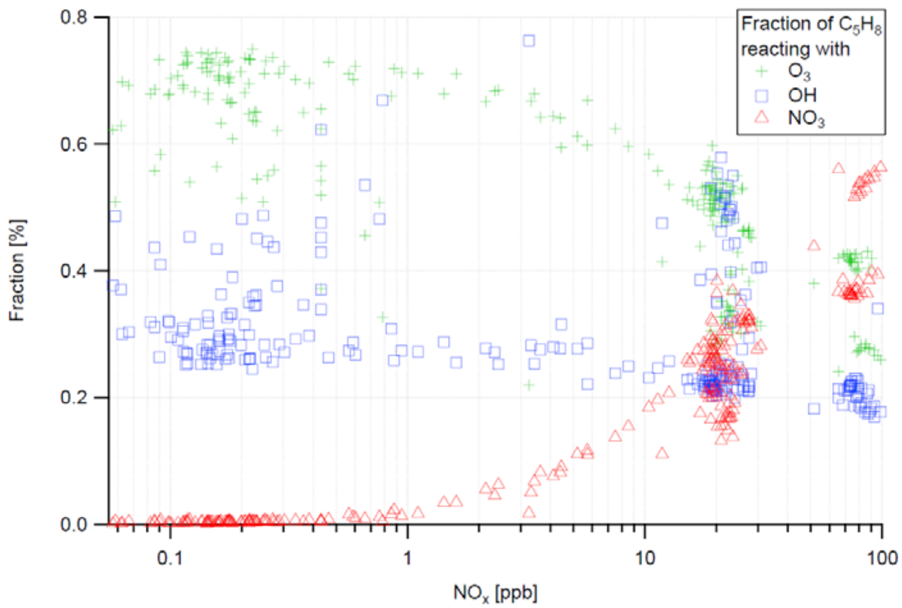

Figure 3.9: Modelled fractions of isoprene reacting with $O_3$, OH, or $NO_3$ in dependence of $NO_x$ concentration. The reaction of isoprene with OH stays overall constant while the reaction with $O_3$ decreases and the reaction with $NO_3$ increases with increasing $NO_x$ concentrations.

Figure 3.9 from the thesis by Claudia Fuchs (Fuchs, 2017).

**Changes to manuscript**; page 9, line 19, sentence added:
“Based on the MCM predictions, the reaction of isoprene by OH radicals is estimated to have accounted for approximately 30% of the isoprene oxidation while the remaining ~ 70% were due to oxidation by ozone (under dark, low-$NO_x$ conditions) (Fuchs, 2017; Section 3.5.3).”

6) 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.

**Authors’ response**: The fraction of the early generation products that go into forming the intermediate products (later generation products) is indicated by the scaling parameters in Table 1 (Page 16) of the manuscript.

7) 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 O3 and OH?

**Authors’ response:** The above sentenced has been rephrased.

**Changes to manuscript:** page 9, lines 16 – 17, rephrased:
“In order to validate the amounts of ozone, OH and “isoprene reacted” (i.e. the isoprene amount oxidized by $O_3$ or OH radicals) predicted by the MCM, conditions and measurements from …”

8) 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.”

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?
9) 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).

**Authors’ response:** As the early generation isoprene oxidation products simulated by MCM remain predominantly in the gas phase, they are insufficient to predict/replicate the SOA formation in comparison with CLOUD chamber observations. Higher generation products are indeed predicted by multi-generation MCM simulations and using all of those products may allow for a more detailed partitioning simulation. However, in this work, the molecular concentrations for all > 500 compounds that could be output by MCM for isoprene oxidation, have not been evaluated for the partitioning computations. This is due to limitations in the number of components the current AIOMFAC-based partitioning model can process for coupled gas–particle partitioning and liquid–liquid phase separation. Instead, using a set of surrogate components and associated scaling parameters was considered a more practical and reasonably detailed mode of modeling, especially given the easier tuning of scaling parameters to match experimental data for the purpose of calculations at various RH levels. See also the response to comment 4) above. We agree that improvements are possible in terms of number of simulated oxidation products directly used in partitioning computations. We note that independent work is ongoing to enable the AIOMFAC-based model to run with such more detailed MCM outputs with >100 compounds and to solve limitations in the number of surrogate compounds the AIOMFAC model can work with.

10) For pure isoprene + O3 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.

When reading this I also ask the same question again: How large fraction of the reacted isoprene were via isoprene + OH?

**Authors' response:** See the response to comment 5) above.

11) 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 NOx 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."

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.

**Authors' response:** Several of the selected surrogate compounds were based on SOA-relevant species suggested by Couvidat and Seigneur (2011): 2-methyltetrol, 2-hydroxy-dihydroperoxide, 2-methylglyceric acid; the semi-volatile component oxalic acid from the work by Carlton et al. (2009) and the $C_5$-alkene triol species as well as the $C_{10}$ hemiacetal dimer based on the work by Surratt et al. (2010). The production of the two latter surrogates is based on an aqueous (aerosol) phase reaction pathway following gas–particle partitioning of IEPOX. Associated sentences have been revised.

**Changes to manuscript;** sentences from page 9, lines 23–28 revised to:
"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 $C_5$-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-$NO_x$ conditions. Oxalic acid formation in the aqueous phase is shown in Carlton et al. (2009); the compounds 2-methyltetrol, 2-hydroxy-dihydroperoxide, 2-methylglyceric acid are suggested as surrogate compounds by Couvidat and Seigneur (2011). The $C_5$-alkene triol and the $C_{10}$ hemiacetal dimer are selected as surrogates based on partitioning of IEPOX to aerosols followed by aqueous-phase reactions described by Surratt et al. (2010). The selected $C_{10}$ 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."

12) I also miss information about the modelled and observed SOA elemental composition (O:C and H:C). Clearly these results exists 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.

**Authors' response:** Fuchs (2017) reports average SOA elemental compositions based on measured desorption profiles from a FIGAERO-CIMS instrument. For the seed-free case (and low-$NO_x$ conditions) the determined average O:C for SOA ranged from 0.62 – 0.67 at low RH (~35 % RH) and up to 0.69 at high RH (~85 % RH), i.e. indicating only a small change in average O:C between low and high RH conditions (Fuchs, 2017) (Section 3.6.1, p. 79 in that work). The measured average H:C ratios were about 1.48 to 1.50. Our modelled SOA is of higher average O:C and H:C ratios. At 278 K, for 140 µg $m^{-3}$ of reacted isoprene (a typical value for comparison with the CLOUD experiments, see Fig. 3), the predicted SOA has the following properties: at 35 % RH, 1.77 µg $m^{-3}$ SOA, O:C of 0.843 and H:C of 2.26; at 85 % RH, 3.14 µg $m^{-3}$ SOA, O:C of 0.844 and H:C of 2.18. The values at RH levels in between are similar. The lower-volatility surrogate species used with the model have individual H:C ≥ 2.0; e.g., the $C_{10}$-dimer has a H:C ratio of 2.2 and O:C ratio of 0.7. While this comparison suggests substantial differences between measured and modelled average elemental organic aerosol composition, it remains unclear how different the associated SOA water uptake behavior is. We note that we do not have direct hygroscopicity measurements, such as growth factors, to compare to. The O:C ratio of the surrogates are shown in Fig. 2. The above paragraph is added to the revised manuscript.

**Changes to manuscript:** at the end of Sect. 3.1.1 we add the following statements in the revised version: Fuchs (2017) report average SOA elemental compositions for the CLOUD experiments based on measured desorption profiles from a FIGAERO-CIMS instrument. For the seed-free case (and low-$NO_x$ conditions) the determined average O:C for SOA ranged from 0.62 – 0.67 at low RH (~35 % RH) and up to 0.69 at high RH (~85 % RH), i.e., indicating only a small change in average O:C between low and high RH conditions (Fuchs, 2017) (Section 3.6.1 in that work). The measured average H:C ratios were about 1.48 to 1.50. Our modelled SOA is of higher average O:C and H:C ratios. At 278 K, for 140 µg $m^{-3}$ of reacted isoprene (a typical value for comparison with the CLOUD experiments, see Fig. 3), the predicted SOA has the following properties: at 35 % RH, 1.77 µg $m^{-3}$ SOA, O:C of 0.843 and H:C of 2.26; at 85 % RH, 3.14 µg $m^{-3}$ SOA, O:C of 0.844 and H:C of 2.18. The values at RH levels in between are similar. The lower-volatility surrogate species used with the model have individual H:C ≥ 2.0; e.g., the $C_{10}$-dimer has a H:C ratio of 2.2 and O:C ratio of 0.7. While this comparison suggests substantial differences between measured and modelled average elemental organic aerosol composition, it remains unclear how different the associated SOA water uptake behavior is.

14) 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.

**Authors' response:** One of the reasons for not including IEPOX as additional early generation precursor is because the AIOMFAC model is limited in the functional groups it can account for and epoxy groups are not covered. Furthermore, the IEPOX uptake to aerosols is not covered by MCM, so there would still be a gap between predicted IEPOX (by MCM) and formation of the 2-methyltetrols and $C_5$-alkene triol surrogate compounds (requiring a scaling parameter). As stated on page 11, lines 14 – 17, we aimed for a rather simple surrogate system, for the stated reasons, which implies accepting gaps in the chemical pathways leading to the set of selected surrogate compounds.

15) 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?

**Authors’ response:** We agree that this sentence was unclear. It refers to how the mass concentrations of higher generation surrogate products were linked to the early generation products directly predicted by MCM. Our approach ensures that the carbon mass present in higher generation surrogate compounds (based on set branching ratios) is accordingly deducted from early generation products that were assumed to act as parent compounds for the higher generation products. Since this is described in more detail in Sect. 2.3.4, we have deleted this unclear sentence in the revised version.

**Changes to manuscript:** sentence deleted.

16) Page 13, lines 17-19 “Molar yields of MCM-predicted products used in the model for the CLOUD 10 (seed-free) 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.

**Authors’ response:** We have revised this sentence.

**Changes to manuscript**; page 13, lines 17 – 19, sentence revised to:
“We note that the molar yields of individual MCM-predicted products differed between the simulations of CLOUD 9 and CLOUD 10 cases due to differences in experimental conditions. This is accounted for by means of different sets of input concentration data for the gas–particle partitioning calculations of seeded or seed-free cases when compared to the CLOUD experiments.

17) 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 O3 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?

**Authors’ response:** The approach we used is based on the same MCM simulation setup for the gas phase chemistry, but with a simplified treatment of wall-loss correction. We did not use the volatility basis set box model for this work since the partitioning is computed with our thermodynamic equilibrium model accounting for non-ideal mixing. This is mentioned later in the same paragraph. Regarding the isoprene and ozone concentrations, we mean the concentrations in the chamber inflow.

**Changes to manuscript:** first part of sentence revised to “Details of the MCM box model approach in Fuchs (2017) are as follows: the box model used inputs for the isoprene and ozone inflow concentrations, condensation sink (from SMPS data), inorganic seed concentration, …”

21) 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,”.

Ok, so in a way you produce a 5-species SOA yield parameterization which match the observed SOA mass, or?

**Authors’ response:** Yes, it is a form of a yield parameterization. However, as written in the sentences following the cited statement, our parameterization of the branching ratios involves a simultaneous fit to data from both low and high RH conditions in the experiments, which is different from the approach taken in traditional parameterizations, such as with a (1-D) volatility basis set fitted to dry conditions data only.

**Changes to manuscript:** (page 16, line 1) sentence added before “Reasonably good agreement…”: “The consideration of observed SOA mass concentrations formed at several levels of reacted isoprene as well as low and high RH levels makes our scaling parameter determination distinct from the approach taken in more traditional SOA yield parameterizations, such as fitting of a (1-D) VBS to dry conditions data only.”

22) 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.

**Authors’ response:** This section (Sect. 2.3.4) and the specific lines (page 15, lines 20 – 28) describe how the branching ratios were determined based on CLOUD chamber data for seed-free experiments (CLOUD 10) under low-$NO_x$ conditions. Hence this is about the fitting approach not standalone modeling. Results from modeling different conditions (including the whole RH range) based on the determined branching ratios are discussed in section 3. In section 3, we also compare and discuss cases where the branching ratios were scaled (e.g. in case of the seeded CLOUD experiments), for reasons described there (Sect. 3.2.1).

23) 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.

**Authors’ response:** We used a manual model fitting approach, in which the gas–particle partitioning model was run using the MCM-predicted early generation product concentrations and with a guess for the branching ratios to predict the amount of SOA formed in comparison with measured SOA mass concentrations from the seed-free CLOUD experiments. This process was iterated over several times with manual adjustments to the branching ratios to determine a suitable fit of the modelled SOA curve with the measured SOA data at 35 % and 85 % RH simultaneously (described in last paragraph of page 15 and top of page 16) Yes, it is the case that various other combinations of the scaling parameters (i.e. branching ratios) can result in approximately the same SOA yield curves; although attempting to match the observed RH-dependence constrains the options compared to fitting only to data at one particular RH. Our determined parameter set listed in Table 1 is therefore not unique. We clarify this in the revised text.

**Changes to manuscript:** (page 16, line 2) sentence revised: “We note that our set of determined scaling parameters (i.e. the branching ratios) is not unique; other combinations of scaling parameters may provide similar agreement with the observations. The determined scaling parameters for the surrogate species are provided in Table 1.”

24) 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.

**Authors’ response:** Yes, 30% of isoprene reaction pathway was with OH, so this sentence has been rephrased.

**Changes to manuscript:** Page 24 line 1 “However, in the absence of light in the CLOUD experiments, the rates of aqueous SOA formation pathways are limited to dark processes and are likely only of minor importance.”

25) 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?

**Authors’ response:** The phrasing of this sentence was not clear; we have revised it. We used MCM to predict the yields. The point here is about the use of the same molar yields (predicted by MCM) for the early generation products in the case of the various seeded experiments (listed in Table S2). Those yields were different from those for the seed-free simulations.

**Changes to manuscript:** (Page 24, lines 4-6), sentence rephrased to:
“The MCM-predicted molar yields of the early generation products for the conditions of the seeded experiments were different from those for the seed-free ones. In contrast, the predicted molar yields of the various seeded experiments were similar; therefore, for consistency and ease of comparison among different model calculations for seeded cases, a single set of molar yields was used (listed in Table S2).”

26) 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.”

It is unclear to me what you actually mean with this. How was the model modified? Did you change the beta values?

**Authors' response:**
Sentence rephrased. “Modified” was perhaps unclear wording. We meant that the model allows for the influence of an aqueous inorganic (seed) phase and partitioning to this phase or an organic-rich phase, where present.

**Changes to manuscript:** (Page 24, line 8) sentence rephrased to:
“Hence, the gas–particle partitioning model was run in a mode which allows for liquid–liquid phase separation as well as non-ideal organic–inorganic mixing in each particle phase, i.e. for RH-dependent partitioning of water, SOA, and inorganic seed either into a single mixed phase or into two distinct particle phases.”

27) 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?

**Authors' response:** The gas–particle partitioning model considers the impact of this dynamic interplay only indirectly by means of an introduced adjustment of the determined scaling parameters (branching ratios β) by a factor of 0.55 for the seeded cases. This is further described in Sect. 3.2.1 on the following page in the manuscript. We added a sentence to the revised manuscript.

**Changes to manuscript** (Page 24, line 13) sentence added at end of paragraph:
“Such effects are only indirectly accounted for in the equilibrium gas–particle partitioning calculations by means of scaling the branching ratios for the higher generation surrogates (by a factor of 0.55) in the seed-containing cases; see details in Sect. 3.2.1.”

28) 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.

**Authors' response:** For model–measurement comparisons, we only selected time periods when steady state or near-steady conditions were reached in the chamber experiments, i.e. excluding times during and shortly after cloud/precipitation formation in the chamber. Below, we included Fig. 3.2 from the thesis by Fuchs (2017), which shows the SMPS-measured dried aerosol size distribution for a time period spanning several hours, and including three cloud formation events, during the CLOUD 9 experiments. As explained in Fuchs (2017, page 65) the initial decrease in particle number concentration occurs primarily due to dilution in the chamber (seed particles were only added at the beginning). Our statements in this paragraph of the manuscript (page 24, lines 32 to page 25 line 5) provide one aspect of explaining why the MCM-simulated molar yields of early generation species and the resulting SOA mass concentration may deviate from the measurements after such events: increase in the relative importance of wall losses, not considered by the MCM simulations. On the contrary, at least prior to the first cloud formation event, the presence of seed particles would be expected to lower the importance of organic vapour wall losses compared to the seed-free cases (CLOUD 10 experiments). Therefore, while changes in the vapour wall-loss behavior between the two series of CLOUD experiments are likely contributing to the discrepancy, our quantitative understanding remains incomplete.
To this end, we will add a statement to the pertaining paragraph in the revised manuscript.

**Changes to manuscript** (Page 25, line 5) sentence added at end of paragraph:
"On the contrary, the presence of seed particles would be expected to lower the importance of organic vapour wall losses compared to the seed-free cases (CLOUD 10 experiments). However, the application of the equilibrium partitioning model with scaling parameters tuned by CLOUD 10 observations led to over-predicted SOA mass concentrations. Therefore, while changes in the wall-loss behavior between the two series of CLOUD experiments are likely contributing to the resulting discrepancy, our quantitative understanding remains incomplete."

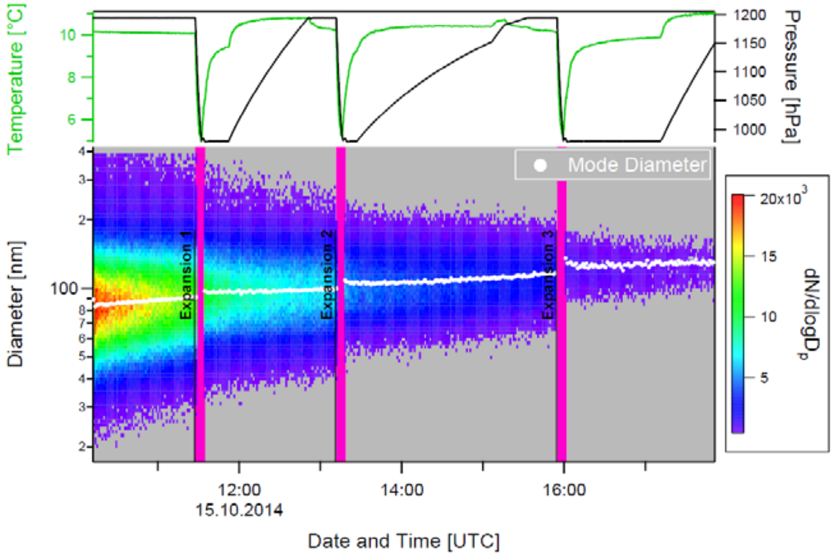

Figure 3.2: Time series of temperature, pressure and dried aerosol size distribution of a typical experiment measured with an SMPS. The drop in pressure and temperature (upper panel) indicates an adiabatic expansion causing a cloud formation (pink areas in the SMPS size distribution, lower panel, demonstrate the presence of a cloud). Grey areas represent sub-saturated conditions (RH ~90 %). The white dots illustrate the mode diameter indicating the growth of the dry aerosol particles. The beginning of each expansion is demonstrated by the vertical lines. The data gaps during the cloud periods are due to flow issues in the SMPS.

Figure 3.2 from the thesis by Claudia Fuchs (Fuchs, 2017), showing (dried) aerosol size distribution data for a time period and conditions during the seeded CLOUD 9 experiments.

29) 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?

**Authors' response:** In the experiments, the increasing SOA mass concentration is possibly due to a combination of effects, which cannot be easily differentiated from the data alone: hygroscopicity effects leading to enhanced partitioning to the condensed phase due to higher absorbing aerosol mass are likely the dominant effect (considering the related model predictions); however, there may have been changes in aqueous-phase chemistry and some changes in the condensation sink affecting the resulting SOA mass concentration. The gas–particle partitioning model does not include any changes due to chemistry or condensation sink at different seed concentrations. Therefore, the predicted increasing

SOA mass concentration as a function of inorganic seed mass concentration is due to the increased absorbing mass concentration of the mixed organic–inorganic aerosol particles as shown by the model curves in Fig. 6a. The absorbing aerosol mass is increased by a combination of effects: higher seed mass concentration also leads to higher aerosol water content at 85 % RH and this leads to enhanced partitioning of semi-volatile organic (surrogate) compounds to the particles (into a mixed phase), which in turn enhances aerosol water content and absorbing mass. This is the mechanism that the model captures, which is in reasonable agreement with the observed SOA enhancement at constant amounts of reacted isoprene. Such effects are discussed in more detail in section 3.2.4. Note that if the AIOMFAC-based model is run with the inorganic seed and SOA not allowed to mix (forced complete phase separation), there would be no increase in predicted SOA mass concentration with ammonium bisulfate mass concentration. That is, the model curves would be horizontal lines in Fig. 6a at the level predicted for zero seed mass concentration.

30) Page 27, line 14: "Observations by Kleindienst et al. (2007), using an ammonium sulfate seed (0.05 µg m-3)" This is a very low concentration of AS seed. Is the value correct?

**Authors' response:** Yes, this value seems low. We checked again and 0.05 µg $m^{-3}$ of AS seed is indeed the value stated in paragraph [8] of Kleindienst et al. (2007). It may have been so low because their intended use of AS seed was simply to promote aerosol formation.

31) 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?

**Authors' response:** At low sulfuric acid seed concentrations in the experiments, the losses of isoprene oxidation products to the chamber walls may compete substantially with condensation to aerosol particles, which would at least partially explain the observed lower SOA mass concentrations compared to those from our model predictions. At higher seed mass concentrations, such wall-loss effects are expected to be smaller. Figure 8 indicates that the model–measurement agreement for SOA mass concentration and yield improves with increasing seed concentration. This interpretation is further supported by additional unpublished sensitivity analyses using the box model simulations from Fuchs (2017; their Chapter 3) as starting point.

**Changes to manuscript** (Page 28, line 17) sentence added at end of the paragraph:
"At low sulfuric acid seed concentrations in the experiments, the losses of isoprene oxidation products to the chamber walls may compete substantially with condensation to aerosol particles, which would at least partially explain the observed lower SOA mass concentrations compared to those from our model predictions. At higher seed mass concentrations, such wall-loss effects are expected to be smaller. Figure 8 indicates that the model–measurement agreement for SOA mass concentration and yield improves with increasing seed concentration.

32) Page 31, 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?

**Authors' response:** Yes, in addition we are also not accounting for changes in reaction pathway due to wall-loss of condensable vapors at different RH levels. The wall-loss effects likely explain discrepancies at very low seed concentrations. However, note that the discussion on those lines is concerning the predicted SOA mass yield enhancement effects by the partitioning model in a general sense (not a specific chamber experiment context). Therefore, we think that it would be confusing to mention dynamic condensation and wall loss at that point.

33) 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.

**Authors' response:** Thank you for your comments and queries.

## References

Carlton, A., Wiedinmyer, C., and Kroll, J.: A review of Secondary Organic Aerosol (SOA) formation from isoprene, Atmospheric Chemistry and Physics, 9, 4987-5005, 2009.

Couvidat, F., and Seigneur, C.: Modeling secondary organic aerosol formation from isoprene oxidation under dry and humid conditions, Atmospheric Chemistry and Physics, 11, 893-909, 2011.

Fuchs, C.: Investigation of the role of $SO_2$ and isoprene in aqueous phase secondary aerosol formation, Dissertation ETH Zurich 2017 No. 24157, 177 pages, 2017.

Jenkin, M. E., Young, J. C., and Rickard, A. R.: The MCM v3.3.1 degradation scheme for isoprene, Atmos. Chem. Phys., 15, 11433-11459, 10.5194/acp-15-11433-2015, 2015.

Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., Jaoui, M., and Edney, E. O.: Ozone-isoprene reaction: Re-examination of the formation of secondary organic aerosol, Geophysical Research Letters, 34, 2007.

Kuwata, M., Zorn, S. R., and Martin, S. T.: Using Elemental Ratios to Predict the Density of Organic Material Composed of Carbon, Hydrogen, and Oxygen, Environmental Science & Technology, 46, 787-794, 10.1021/es202525q, 2012.

Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M. N., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, PNAS, 107, 6640-6645, 10.1073/pnas.0911114107, 2010.

Xavier, C., Rusanen, A., Zhou, P., Dean, C., Pichelstorfer, L., Roldin, P., and Boy, M.: Aerosol mass yields of selected biogenic volatile organic compounds – a theoretical study with nearly explicit gas-phase chemistry, Atmos. Chem. Phys., 19, 13741-13758, 10.5194/acp-19-13741-2019, 2019.