

Reply on Referee #1

This paper describes the 3D-atmospheric model MESSy for a comprehensive evaluation of the impact of aqueous-phase chemistry on SOA in a CAABA/MECCA box model platform. The authors need to clarify the fundamental assumption and the limitation of the model. This manuscript may be suitable to be published in ACP after major revision by considering the comments as listed below.

Thank you very much for the helpful comments, text and figure corrections!

1. The authors should clarify the criteria of the SOA model. It is unclear that the SOA model of this paper is subjective to aqueous droplet or any aerosol including SOA aerosol without aqueous phase. For the organic and inorganic mix, it is possible for the aerosol to be phase separable into organic phase and inorganic phase or form homogeneous phase. Without the assumption and the suitable criteria of the model to a specific aerosol conditions, it is difficult to understand the usage of model.

CAABA/MECCA does not contain a specific submodule which describes SOA. In the manuscript, SOA is accounted as low volatile organic compounds (LVOC) that exhibit an Henry's law solubility constant larger than 10^8 M/atm (see Sect. 3.2) and are present in gas or aqueous phase. These LVOC can only dissolve and react in deliquescent aerosols but not in a organic apolar medium. The partitioning of LVOC to the latter will be considered in the global model, where MECCA is coupled to a SOA submodule based on the VBS (Pozzer et al., 2022). This box model study is intended to demonstrate the possible influence of the update of the chemical mechanism. Our results are relevant for conditions with relatively high humidity and temperature where glass-transition and phase-separation are not expected. Nevertheless, a global model study assessing the impacts of the mechanism update on the predictions of SOA distribution is planned. To clarify this more generally we extended the abstract with the following addition "The extensions in CAABA/MECCA will be ported to the 3D-atmospheric model MESSy for a comprehensive evaluation of the impact of aqueous-phase chemistry on SOA at a global scale in a follow up study."

2. There is no demonstration of model against laboratory data or simulation in regional scale. It is hard to know whether the simulation of the SOA model is suitable to apply to ambient air.

We see the point of Referee #1. However, our manuscript is meant as a *model description* paper as defined by the GMD journal. We plan an evaluation of the updated model against laboratory/observational data, but this will be submitted as a separate paper (see above).

3. In addition to IEPOX, there are other chemical species that can form oligomers via acid-catalyzed reactions. The authors needs to clarify limitation in the model.

We agree with Referee #1 that there are additional species able to form oligomers via acid-catalyzed reactions. Examples are the oligomerization of glyoxal, which has been shown to yield more particulate matter under acid catalysis or further epoxides other than IEPOX (Jang and Kamens, 2001; Lim et al., 2010). Oligomers from glyoxal and methyl glyoxal are already implemented in our mechanism (Rosanka et al., 2021). To the previous version of the scheme we add the acid catalyzed reactive uptake and oligomerization of IEPOX as this is known to be among the most sources of SOA.

4. Line 9 (Abstract): Only up to C8 but it is characterized as "long-chain alkanes". Probably not appropriate to say C8 and below are long-chain alkanes considering they do not form any SOA.

We agree, this is stated incorrectly in the manuscript. We changed the line to "n-alkanes (5 - 8 C atoms)" and deleted "long-chained" in following lines. We also agree that C5-C8 n-alkanes have a comparably low SOA yield, but there are several impact factors and limitations to consider. Alkanes with a high SOA yield are predominantly high molecular weight alkanes, as the yield increases with chain length. On the other hand, the implementation of these compounds would require a much more sophisticated mechanism with many more reactions to account for the SOA formation. Including all of them would highly complicate and slow down global multiphase chemistry simulations, due to a strong increase in memory and computational demand for the integration of the very stiff chemical ODE. Compared to cyclic alkanes, β -scission of the alkoxy radicals from linear alkanes is more likely to yield smaller and more volatile compounds. However, this is generally the case for highly elevated NO_x concentrations under which experiments have been conducted, e.g. Lim and Ziemann (2009). The corresponding SOA yields for alkanes are then often used in air quality models, e.g. Pye and Pouliot (2012). However, under low-NO_x conditions it

- is known that the RO₂ from oxidation of large alkanes react mostly with HO₂ yielding compounds with hydroxy, hydroperoxy and carbonyl moieties (Srivastava et al., 2022). The latter are of lower volatility compared to the carbonyl compounds under high-NO_x. Additionally, emission data of various alkanes are scarce. We decided to incorporate n-alkanes up to C₈, to include alkane SOA at least partly in simulations. Especially for octane, measurements show a moderate SOA yield (in comparison to other alkanes) and observations show high emission rates (see supplementary material of McDonald et al. (2018)).
5. Line 12 (Abstract): “aqueous phase” has no hyphen here but is hyphenated in the previous sentence (Line 11). We adjusted “aqueous phase” to “aqueous-phase” in the entire manuscript.
6. Line 14 (Abstract): “LVOC is...” should be replaced with “LVOC are...” We changed this in the revised manuscript.
7. Line 33. Please provide a more detailed explanation on the impact of aqueous-phase oxidation products on the vertical distribution of SOA in the atmosphere would enhance the understanding. Generally, aqueous- and gas-phase oxidation takes place at different timescales (Seinfeld and Pandis, 2016) and aqueous reactions depend on available cloud or aerosol water, aqueous phase properties (pH) and dissolved pollutants, while both reaction types depend on gas phase pollutants. This can impact model simulations in different ways, depending on the chosen scenario. Carlton et al. included in-cloud secondary organic aerosol formation (processing of glyoxal and methylglyoxal) in the CMAQ model and found a general increase of organic PM mass, but an especially strong increase at high altitudes (Carlton et al., 2008). Models have significant issues in reproducing the vertical profile of measured concentrations of organic aerosols, e.g. Pai et al. (2020). Also the global model of which MECCA is part of is no exception (Pozzer et al., 2022). Therefore, we expect lower model biases when our updated chemical mechanism is used in the global model EMAC. We adjusted the paragraph in the manuscript as follows "Additionally, products from aqueous-phase oxidation are formed at different time-scales than from gas-phase oxidation. Combined with aqueous- and gas-phase properties (pollutants, pH), this impacts the vertical distribution of SOA in the atmosphere depending on the simulation setup (Seinfeld and Pandis, 2016; Hodzic et al., 2016)".
8. Line 90: "... small oxidized compounds like " Should be "... small, oxidized compounds like glyoxal." We changed this in the revised manuscript.
9. Figure 1: Unclear what happens in the abstraction of the red H step. It seems like some compound must be being released from the mechanism other than the ones shown. I can see maybe H₂O from the OH and one O atom from the radical but how is the red H involved? Fig 1. displays the abstraction of the blue hydrogen and subsequent reactions. The red hydrogen can be abstracted similarly, and the color is meant to identify the hydrogen as alternative route (described in the caption). We agree that the missing depiction of the released molecule can lead to confusion, thus it was added to the figure together with an indicator that the red hydrogen poses an alternative route.
10. Henry's solubility. In aqueous aerosol, there will be electrolytic inorganic species which can influence the solubility of organic species. The salt composition and humidity can influence organics' Henry's constants. The authors need to clarify the impact of salts on gas-particle partitioning of organic species. We agree with Referee #1, that "salting in" and "salting out" can influence the Henry's law solubility constants. However, these effects usually do not change the solubility by more than an order of magnitude (Yu and Yu, 2013) and cannot explain the up to 10⁶ times larger Henry's law coefficients for small organics derived from field measurements (Nah et al., 2018; Shen et al., 2018). Nevertheless, even potential large salting-in effects have been shown to be insufficient for explaining high concentrations of organic aerosols in winter haze events in China (Gkatzelis et al., 2021). Additionally, reaction rate constants can depend on the ionic strength of the solvent (Mekic and Gligorovski, 2021). These non-linear effects are not accounted for in the model, due to their complexity and unknown influence parameters (Sander, 2015). The authors are not aware of any influence of humidity on Henry's law solubility constants. We extended Sect. 2.1 with "Non-linear effects like "salting in" and "salting out" influence Henry's law solubility constants. The model does not account for these effects, due to the implementation com-

plexity and insufficient data availability (Sander, 2015).".

100 **11.** Section 2.3.1: Phase partitioning is simulated through Henry's law constants. Can this model handle dry conditions without an aqueous phase? It seems like this would be necessary in a global SOA model.

In CAABA/MECCA the aqueous phase can be deactivated to simulate dry condition, but the model does not include an additional aerosol submodule. Thus, compounds would remain in the gas phase. In the global model MESSy, which shares the same chemical mechanism (MECCA), refined aerosol microphysics and various kinds of uptake processes are included and
105 can be used under different conditions (Pringle et al., 2010; Tsimpidi et al., 2014; Pozzer et al., 2022).

12. Please check the legend in Fig. 5. Legend for aldehydes is missing.

The aldehydes do have a separate legend in the right-hand plot of Fig. 5. They are divided in a similar color scheme as chosen for the alcohols.

110 **13.** Line 215. Please check figure number. It should be Fig. S17, not Fig. S11.
The Figure reference has been changed in the revised manuscript.

14. Line 216 - 218. Is this because the concentration of the BASE run is high regardless of temperature conditions (Fig. 6)?
115 While you have provided a reference, further explanation about why the increase in the SOA precursor from isoprene is expected in the global model would be needed.

This is correct. As an increase in LVOC is found at varying conditions compared to the previous chemical mechanism and this change can be attributed to the IEPOX mechanism, a total increase of isoprene derived SOA precursors is expected in the global model. In the current mechanism, aqueous processing of isoprene products is not considered, even though IEPOX
120 reactive uptake was found to be the most dominant SOA contributor (from isoprene). Thus, an increase of the total isoprene SOA is expected in global model runs, especially in low NOx regions (see Marais et al. (2016) for IEPOX contribution).

15. Line 224. The previous sentence stated that the oxidation by ozone and NO3 is dominant before sunrise. What is the effect of the limonene NO3 mechanism? Table 1 mentioned that the main reactant of d-limonene is ozone. Please briefly describe the
125 effect of NO3 on d-limonene.

We have to admit that the presented update does not contain limonene NO3 reactions. To display the influence of limonene NO3 anyhow, we have extended the mechanism with missing reactions for test purposes. The resulting large-LVOC do not change significantly at nighttime, but the large-LVOC at the end of the full modeled day increases by 4.8%. Medium-LVOC and total LVOC are barely influenced. We will include these reactions in the next mechanism update! The discussion of the
130 present manuscript is scarcely impacted by the missing reactions.

16. Line 254. What are the factors that the box model neglects and what are the potential effects?

With respect to aerosols the box model neglects dry and wet deposition, a complex scheme describing aerosol micro-physics, condensation of gases regarding their volatility (solely Henry's law is taken into account) and a general scavenging scheme.
135 This limits the possible scenarios that can be simulated by the box model. Potential effects on the presented results are the over prediction of liquid phase species due to missing deposition. For dry scenarios, the partitioning scheme additionally over predicts liquid phase species with high Henry's law coefficients. In sect. 3.4 we added "Wet and dry deposition and volatility based condensation are neglected in the model runs, which is expected to result in an over prediction of LVOC".

140 **17.** Line 256. Please provide the detail conditions of SOAS campaign applied in this study (e.g., temperature, humidity, and pollutant concentrations).

The SOAS conditions are applied for the aerosol salt concentrations (average salt concentration from SOAS) and the isoprene mixing ratio, to achieve a general estimation regarding the IEPOX SOA products. We extended table 3 and added a link to the detailed description in Sect. 3.1 to the text.

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18. Line 265 – 266. Please check figure number.

The Figure reference has been changed in the revised manuscript.

150 19. Line 271 – 272. I wonder if the model setup was based on the average value of the entire SOAS campaign or a specific case of SOAS campaign. If there are special cases showing high/low NO_x or high/low isoprene conditions during the campaign, box model can be performed for those cases. If the results show a good agreement with measurements in those cases, it will show the good quality of the box model under various conditions. If the final goal of this box model is to improve prediction of SOA concentration by applying it to the global model, it is necessary to show that the box model can produce reasonable results under more various conditions than the paper presents.

155 The model setup is based on average values from the SOAS campaign. Here it has to be noted that the box model approach was chosen, because of the much simpler test environment in comparison to the global model. We agree with Referee #1 that a more detailed review of the impact of the new chemistry under various conditions is necessary. But these simulations are planned to be executed in the global model, where more aerosol submodules are accessible (less limitations in the model) and a more in detail analysis is possible. In this manuscript, our main aim is to present the new chemistry update and display that the use of the new scheme likely will result in a more realistic formation of LVOC, with the major compounds being IEPOX products.

160 20. Line 297 - 298. The model was performed under various conditions and the results were presented. It would be beneficial to emphasize the significance of the results for each specific condition. If this box model is applied to the global model to predict the SOA concentration in global scale, please suggest expected outcomes and their potential role considering the variations in NO_x and temperature conditions.

165 The SOA yield is expected to be inversely proportional to the NO_x concentration. This is due to the higher volatility of reaction products from NO_x chemistry compared to products from competing reactions (e.g., hydroperoxide formation) for most dominant VOCs. The temperature influences multiple factors at the same time. Reactions are generally slower at lower temperatures and saturation concentrations in the liquid phase are increased. On the other hand, condensation of low volatile compounds on available aerosols is favored and more condensed aqueous phase is available at low temperatures. Generally, it is expected that SOA formation is anti-proportional to the temperature. We specified the simulated scenario by adding "This scenario is representative of a mildly polluted deciduous forest during summertime." to sect. 3.1 of the revised manuscript.

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