

Reply on Referee #2

The manuscript by Wieser et al. presents an updated multiphase chemical mechanism in the CAABA/MECCA model, designed to improve predictions of secondary organic aerosol (SOA), particularly via aqueous oxidation pathways. The manuscript was submitted as a development and technical paper, which describe technical updates leading to model improvements, including new parameterizations. Such papers are expected to include a significant amount of evaluation. The manuscript largely fits this description and is appropriate for GMD. However, the manuscript is lacking clarity and specificity in several key areas, which are noted below. It is recommended that these areas be addressed before the manuscript is further considered for publication in GMD.

Thank you for your helpful comments and editorial corrections!

Major scientific comments:

1. Processes and phases included in the base version of CAABA/MECCA. The language regarding SOA formation is sometimes unclear in the context of whether this model only includes SOA formation via aqueous uptake (aqSOA) or whether gas-particle partitioning to a mostly organic phase is also included. This needs to be better clarified and considered in the discussion of the model updates and results. It is particularly confusing in 3.2, where it is unclear what is being evaluated. The authors state that analysis of the LVOCs is useful as an assessment on potential SOA formation, but then also go on to say they analyzed the total gas, aqueous, and aerosol mixing ratios. The results in 3.2 and 3.3 seem to focus only on LVOC production, to understand how much aqSOA forms, the authors also need to couple that with aqueous solubility and reactive uptake. Additionally, if the compounds are of sufficiently low volatility, there will be competition for partitioning to a mostly organic phase if present. On pp. 15-16, it is not clear what O/C ratios are being compared. Literature reported O/C ratios for SOA are typically based on bulk composition of the condensed phase (organic and/or aqueous depending on analytical technique). It seems that those values are being compared with the O/C ratio for all LVOCs, independent of phase. These are not the same thing.

The model does not account for SOA formation from either aqueous uptake or volatility-based partitioning, as submodules for these processes are not available in the box model we have used here. How competitive these processes are will be tested at a second stage by means of global model simulations. This box model study is meant to give a first assessment of the impact of the improved and extended oxidation mechanism.

The O/C ratio is calculated from all compounds categorized as LVOC in the gas and the aqueous phase. We agree that it is more appropriate to calculate the O/C ratio for the aqueous phase only. In warm and humid environments, like the one during the SOAS campaign, we expect aerosol water to be important for the phase partitioning of LVOC. Therefore, we think that a comparison with model results is meaningful. We adapted the O/C calculation accordingly.

2. Activity coefficients. The manuscript has no discussion of activity coefficients, or effective Henry's law constants (i.e., salting in or salting out). This is a major omission. The effective Henry's law constants of organic compounds in the aqueous particles will be composition dependent and may deviate significantly from the Henry's law constant for a pure water. It is particularly important for the compounds with moderate solubility. This has been widely discussed in the literature from both experimental and theoretical perspectives.

We agree with Referee #2, that "salting in" and "salting out" can influence Henry's law solubility constants. These non-linear effects could be easily accounted for in the model. However, they are not yet considered because of the lack of Sechenov constants (Sander, 2015). On the other hand, the enhancement of effective Henry's law coefficients relative to the intrinsic ones is strongly affected by aqueous-phase chemical reactions as well. For instance, it is known that the hydration of carbonyl compounds like formaldehyde and glyoxal increases the Henry's law coefficients by 2-3 orders of magnitude. This major effect is explicitly accounted for by our kinetic model. We extended Sect. 2.1 by the mentioned model limitations "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 insufficient data availability (Sander, 2015)."

3. Mechanism details. While the mechanism details can be obtained from the code and other external documents, it is suggested that the SI be expanded to more clearly define the differences between the original and updated mechanism and any changes that were made to published data (e.g., reaction rate constants, branching ratios, etc.) as implemented in the new mechanism. The text is very minimal and non-specific on these aspects, which reduces the clarity and reproducibility of this work. To provide some examples: 1) On p. 3 line 76, the authors discuss redistributing the product yields for isoprene + NO₃. How are these redistributed? Does this affect any prior performance evaluations? 2) The authors describe that the new chemical mechanism for limonene was based on MCM, and on p. 4 line 83 state “low-yield reaction pathways are excluded”. What was the cutoff yield value? How was this determined? 3) Similarly, the authors describe implementation of the new n-alkane mechanism based on Atkinson et al. (2008), and on line 96 state that the “mechanism is simplified” to only cover oxidation at specific sites and only one H-abstraction process. Which sites? How was this determined? Does this affect prior performance evaluation? What is the implication of these choices in the context of this model application? Line 115-What is considered fast? What is the rate (s⁻¹) cutoff value? These are only some examples, but such detail is important for all new mechanisms and updates presented in this manuscript, especially if modified from published literature.

We agree with Referee #2, that the manuscript lacks some information regarding the choices made in the mechanism creation. We excluded too in-depth explanations from the text to ensure readability and convenience of the text. To give an improved overview of the mechanism and important assumptions/simplifications, we have extended the "Reaction kinetics and mechanisms" chapter in the SI by dividing it into additional sub-chapters containing further information.

4. The evaluation should focus on how the mechanism updates affect the performance of CAABA/MECCA as has been previously evaluated, and using experimental data where available. There is too much general comparison with one-off published literature results, which are inconclusive in the context of model performance, and too much speculation of how the mechanism will improve global model performance. Evaluation is also needed for the new Henry's law constants and their dependence on temperature, as compared with the base model.

A comparison to earlier evaluations of CAABA/MECCA concerning the content of the mechanism update is hardly possible. This is due to the fact that mostly radical and VOC mixing ratios were analyzed in previous assessments, rather than the stable products (Sander et al., 2011, 2019; Taraborrelli et al., 2012; Nölscher et al., 2014; Hens et al., 2014; Mallik et al., 2018). The comparison between the OLD and the BASE run is intended to display how and in which size range the model is impacted by the update. With secondary organic aerosols being the main interest of further investigations, we decided to restrict this to LVOC, as these are a proxy for SOA. Additionally, Figs. S10-S14 display the change in key radical mixing ratios (NO, NO₂, NO₃, OH, and O₃) (previously Figs. S10-S16). We improved the diagrams to give a more comprehensive overview of the differences between the runs. Ultimately, this work is a new approach to comparing changes to the mechanism by looking into specific properties of products. This can be used as the basis for future evaluations.

Henry's law coefficients are only newly included for species introduced with the mechanism update. For species in the base model, the temperature dependency was added, if missing. Therefore, a direct comparison to the base model would not lead to conclusive results. We indicated this in Sec. 2.3 in the revised manuscript. Further replacements and additions together with a complete assessment of the newly added constants are planned for future work.

85 Minor scientific comments:

1. The authors note that limonene was added to simulate a wide range of monoterpenes. It would be useful to know what other monoterpenes are included. Limonene is known as having one of the highest SOA yields under most (if not all) reaction conditions. Thus including limonene to expand the range makes sense only if monoterpenes with low yields are well represented. Related to comment #2 above, what small adjustments based on Vereecken and Peeters were introduced for beta-pinene? The authors note lack of a compelling chemical mechanism for monoterpenes including camphene. Several camphene mechanism papers have been published recently including: Li et al., 2022 ACP; Subramani et al., 2021 Chemosphere; Afreh et al., 2021 ACP, and Mehra et al., 2020 ACP.

α - and β -pinene are implemented in the model with a refined mechanism. The carene, camphene, and sabinene schemes were implemented based on α - and β -pinene (similar products and kinetics were assumed). We agree with Referee # 2, that there are sufficient papers on the camphene oxidation mechanism, to create a refined scheme. Nevertheless, we decided to update the mechanisms of the listed monoterpenes, if compelling information for all of them is available. To clarify this in the text, we

added/modified "The oxidation of these monoterpenes will be re-introduced as soon as new experimental/theoretical results are accessible, including a compelling mechanism for all individual compounds. Several mechanistic studies involving camphene have been published recently (Li et al., 2022; Subramani et al., 2021; Afreh et al., 2021)." to Sec.3.2.

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2. Line 100: The statement about significant amounts of SOA precursors is unexpected in the methods and also unsupported. We agree with Referee #2 and excluded the statement.

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3. Line 163: What is the rationale for choosing GROHME over HenryWIN? This is not made clear in the discussion. GROHME has a larger training set and shows better performance towards multi-functional molecules (Raventos-Duran et al., 2010). We added the statement "We chose GROHME over HenryWIN because it contains a larger default training set and a better performance towards multi-functional molecules."

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4. Line 200: Does this mean that the model does not include new particle formation? Or does it mean that gas-particle partitioning to an organic phase is not considered (see also major scientific comments #1)? The model does not include particle formation. The effects on both processes will be tested in the global model. Aerosol nucleation is treated in the MESSy submodels NAN and IONs (Ehrhart et al., 2018). SOA formation is specifically treated by ORACLE (Tsimpidi et al., 2014).

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5. Line 217-218: The suggestion of increased isoprene SOA precursors is unclear and unsupported. Increase because of what? In a global model you also have the temperature dependence of emissions and possibly deposition, so I'm not sure how the box model sensitivities are being translated to expectations for a global model. Similar comment on lines 226-227: There is not strong support for the logic connecting the box model observations (particularly when many monoterpene mechanisms are not included) to expected global model results.

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We agree with Referee #2, that box model results do not intrinsically implicate similar changes in the global model. However, it was already demonstrated in experiments and models that the consideration of IEPOX and consequent products enhances SOA precursors and yield from isoprene oxidation (Carlton et al., 2009; Budisulistiorini et al., 2017). Thus, the increased LVOC yield in the box model together with literature results raises the expectation of an increase of SOA precursors, at least under low-NO_x conditions.

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We agree with Referee #2's comment on lines 226-227. The exclusion of the monoterpenes complicates the assessment of whether the total SOA yield is increased with the updated scheme. We excluded the statement.

Editorial comments:

We have reordered the figures in the supplementary information and corrected the typo.

130 References

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