Reply to comments of Hartmut Herrmann (Referee #2)

This submission reminds me of discussions which happened in the very early 1990s on the role of liquid water clouds on tropospheric ozone. Somehow, I thought, atmospheric multiphase chemistry moved on in the 30 years since then but this can hardly be seen fm the perspective of this submission. It would be great to widen the scope here at least to a certain extent.

Thank you very much for the helpful comments. Please find in black the original comments and in red our replies.

Wouldn't it be useful to compare the cloud effects on ozone for a simpler and a more advanced chemical aqueous phase scheme eveen beyond the 150 rxn schemes for which Tost et al. (2007) and Jöckel et al. (2016) are cited ? Jöckel et al cites SCAV Tost et al. (2006, 2007, 2010) - here we turn in a circle, however incomplete as Tost et al. (2010) is not mentioned by Rosanka et al. Why not?

We agree with the reviewer that a comparison between a simple and advanced chemical aqueous-phase mechanisms is needed and therefore forms the basis of this manuscript. A detailed in-cloud oxidation scheme, which is suitable for global model applications, was not available for our study. Therefore, we developed the detailed in-cloud oxidation scheme JAMOC in our companion paper within the box model CAABA and apply it on a global scale using EMAC in this paper. When JAMOC is applied within EMAC, it represents the phase transfer of more than 350 species, includes 43 equilibria, and 289 photo-oxidation reactions. In the revised manuscript, we adjusted the description of the different aqueous-phase mechanisms used (Sect. 2.1.1.), in order to further illustrate their differences. In addition, a new table has been added (now Table 1), which summarises the characteristics of the different gas- and aqueous-phase mechanisms used. The table also includes the number of species that are partitioned into cloud droplets, the number of equilibria, and photo-oxidation reactions.

Tost et al. (2010) investigate the influence of convection parameterisations on the chemical composition. Here, the different schemes result in varying precipitation patterns and varying vertical distributions of cloud and precipitable water. This ultimately influences the scavenging efficiency. Since the same convection parameterisation is used across all EMAC simulations, the relative change is not directly influenced by this. Still, the magnitude of the changes might differ with another convection parameterisation used. However, investigating the influence of varying convection parameterisation on the total magnitude is outside the scope of this study.

I would really appreciate a reactions table with all reactions and rate constants which are being used and their respective sources.

We fully agree that complete information about the reaction mechanism, rate constants, and references is necessary for a thorough review. We have already published this, as indicated at the bottom of page 2 in the originally submitted version: "For the detailed in-cloud OVOC oxidation scheme, the Jülich Aqueous-phase Mechanism of Organic Chemistry (JAMOC) suitable for global model applications is developed and implemented into the atmospheric chemistry mechanism Module Efficiently Calculating the Chemistry of the Atmosphere (MECCA) in our companion paper by Rosanka et al. (2020a)." In the revised version of the manuscript, we now include an additional table (now Table 1) that summarises the characteristics of the gas- and aqueous-phase chemical mechanism used in each simulation. For the table of the reactions used in the simple (Scm) and EMAC's standard mechanism (ScSTA), the reader may find the mechanism tables in the listed references.

What developments have been seen in the field which are not implemented in the applied aqueous chemistry schemes and, if so, why not ?

We agree with the referee that understanding the recent developments and missing representations in the newly developed mechanism (JAMOC) is very important in order to understand the limitations of the simulations performed. Therefore, we included a detailed description on the mechanism development and limitations in our companion model description paper by Rosanka et al. (2020). This also includes a short review of the recent advancements. Repeating this information in this manuscript does not fit the idea of companion papers. Therefore, please refer to our companion paper for the mechanism limitations.

What if the limitation in the aqueous mechanism on small compounds artificially changes the effects expected to be observed with a broader arsenal of cloudwater organics? Would the findings of the paper still hold ?

We expect that even if a broader set of organics was transferred into cloud droplets, they would still react with OH, leading to the formation of HO_2. If the number of organics treated in JAMOC was increased and if we assume that each of the organics reacts with OH with a rate coefficient of $k_{C,OH} = (3.8 \pm 1.9) \times 10^{8}\ M^{-1}\ s^{-1}$ (Arakaki et al., 2013), the predicted in-cloud OH concentration would be different. Therefore, we expect that the magnitude of the predicted change for each individual organic could vary but the overall tendency would stay the same. At the same time, the increased formation of HO_2 would increase the in-cloud destruction of O_3. In the future, we plan to expand JAMOC to include the oxidation of additional organic compounds.

I rate the switching of of the Fenton reaction as fatal. I cannot understand why this is done. Fenton is one of the most important OH sources. As a judgement of the aqueous scheme: How do your OH/HO2 concentrations compare to state-of-the-art models and measurements ? The paper tells how Fe valuse could be assessed and there are other ways on top of this - this has been done already.

We understand the concerns of the referee that the missing Fenton's chemistry will influence the resulting impact of JAMOC. In our box model calculations presented in Sect. 3, we predict average in-cloud concentrations of 1.3×10^{-13} M and 2.5×10^{-8} M for OH and HO_2, respectively. These values are very similar to the predictions of the box-model mechanism CLEPS (see Fig. 4 in Mouchel-Vallon et al., 2017) and observations and predictions by Tilgner et al. (2013) and Arakaki et al. (2013). We expect that the missing Fenton's chemistry will therefore mainly influence the resulting impact in magnitude but the tendency will stay the same. Although we think that the effect of iron emissions in EMAC is not within the scope of this study, this is already work in progress, and we plan to present Fenton's chemistry in EMAC in a future publication. Overall, we intend this paper and our companion paper in GMD (Rosanka et al., 2020) to be a starting point for further aqueous-phase mechanism developments in EMAC. In the revised version of the manuscript, we now include a short analysis of the in-cloud OH and HO_2 concentrations in CAABA.

I appreciate the comments of Jos Lelieveld on the earlier days of aqueous phase modelling. It would be desirable to include all available information to give an accurate lookback.

We greatly appreciate the comments of Jos Lelieveld and have implemented them accordingly. We have expanded the introduction of the revised manuscript. It now includes a discussion on the impact of aqueous-phase chemistry on the formation of secondary organic aerosol (SOA). In addition, we now include a review on aqueous-phase mechanisms currently applied in regional and global models.

Overall, I feel the paper needs more work.

Following your comments and the comments of the first referee, we revised the manuscript by adding the following aspects:

- The discussion on the aqueous-phase O_3 chemistry was updated following the recommendations of Jos Lelieveld.
- The introduction was expanded to include a review on the importance of aqueous-phase processes on the formation of SOA.
- The aqueous-phase mechanisms available in other global and regional models are reviewed in the introduction.
- We expanded the description of the organics explicitly reacting in JAMOC in Sect. 2.1.1.
- An additional table has been added, which summarises the characteristics of the gas- and aqueous-phase mechanisms used in each simulation.
- Sect. 3 now includes a discussion of the OH and HO_2 concentrations predicted within the cloud droplets modelled by CAABA.
- An appendix was added, which includes the definition of $\sum$OVOCs used in Figs. 2 and 3.

- Table 3 (previously Table 2) now includes a comparison to the gas-phase OH budget presented by Lelieveld et al. (2016).
- The O_x budget presented in Table 5 (previously Table 4) now includes a multi-model comparison and a comparison to the budgets presented in TOAR.
- The IASI O_3 retrieval has been improved over deserts (e.g. Sahara) in Figure 11.

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