

Replies to anonymous referee #1

The authors have satisfactorily addressed most of my comments. I only have a few minor additional remarks that could be addressed in a revised manuscript. Line numbers refer to the new manuscript without annotations.

Thank you very much for your additional review. It is good to hear that our adjustments to the manuscript are satisfactory. Please find in black your original comment and in red our reply.

l. 30: “Such a SOA formation could have a significant influence on tropospheric HOx chemistry and NO₂ photolysis, which in turn affect O₃.”

Comment: The meaning of this sentence is not clear. Are you suggesting that due to the increased SOA burden, photolysis rates in the atmosphere are influenced? As mentioned in my previous report, the total OH (and HO₂) budgets are likely not largely influenced by the reactions in the aqueous phase. Just the presence of clouds suppresses the formation of OH in the gas phase.

SOA is known to influence the aerosol optical depth and thus NO₂ photolysis (Tie et al., 2005). Additionally, SOA may act as cloud condensation nuclei (Andreae and Rosenfeld, 2008). An increase in the SOA burden would thus lead to changes in cloud cover, which in return would further influence the photolysis of NO₂. In our companion paper (Rosanka et al., 2020), we find that when using JAMOC, the global tropospheric HOx budget is reduced by about 7 %. Following your comment, we changed this sentence to: “By scattering, SOA is known to influence the aerosol optical depth (AOD), leading to a reduction in NO₂ photolysis (Tie et al., 2005). In addition, SOA may act as a cloud condensation nuclei (CCN) (Andreae and Rosenfeld, 2008) affecting cloud properties. An increased formation of SOA would thus influence tropospheric HOx and O₃ chemistry.”

l. 116: “The dehydration of many gem-diols is slower than the typical lifetime of cloud droplets “

Comment: The typical lifetime of cloud droplets is on the order of several minutes. However, in the cited literature Doussin and Monod (2013), dehydration constants on the order of $k(\text{dehydr}) = 0.0015 - 0.025 \text{ s}^{-1}$ are listed which yields a half life of gem diols of 30 - 460 s ($= \ln 2 / k(\text{dehydr})$). Thus, I do not think that it can be generalized that gem diols do not dehydrate in cloud droplets.

We agree that the typical lifetime of a cloud droplet is in the order of several minutes. However, their typical evaporation timescale is less than 100 s (Jarecka et al., 2013). Thus, the dehydration of some gem-diols is shorter than the typical evaporation timescale of warm cloud droplets. We understand that our original formulation might be misleading and further elaboration is needed. In addition, the use of “many” might be not appropriate. Thus, we changed this formulation to: “The typical lifetime of a warm cloud droplet can be several minutes but their typical evaporation timescale is less than 100 s (Jarecka et al., 2013). Following the dehydration constants presented by Doussin and Monod (2013), the dehydration of some gem-diols can be slower than the typical cloud droplet evaporation timescale. Additionally, their rapid transfer across the phases is expected to affect the gas-phase concentration of gem-diols, for which no other significant source is known. This process could be an important removal of gem-diols from the aqueous-phase, without yielding the original aldehyde. Therefore, their outgassing is considered for use with the models representing evaporating clouds like the EMAC model (following Sect. 2.2).”

l. 160: “The formation of oligomers within cloud droplets is known to be a source of in-cloud SOA formation”

Comment: I think that the authors misunderstand the difference between oligomers and cloud SOA. I agree that SOA formation in clouds may be an efficient SOA source. However, this SOA is mostly not composed of oligomers. Tan et al. (2009) and others discussed that SOA formation in clouds does not lead to oligomers but can be largely explained by the oxidation of small organics (e.g. glyoxal) by OH leading to oxalic acid and other carboxylic acids. While in the study by Lin et al. (2012) the same reactive uptake coefficients for aerosol and clouds were used (in accordance with an earlier global model study), these authors also state “Furthermore, the same uptake coefficient for both cloud droplets and aqueous aerosols cannot account for the differences in the chemistry of carbonyl compounds between cloud water and aerosol water (Lim et al., 2010; Ervens and Volkamer, 2010).” Thus, they are aware that different chemical pathways exist in cloud and aerosol but could

not account for it back then due to the lack of appropriate reaction parameters.

Therefore, I suggest to either remove the introductory sentence of this section or to reword it to “The formation of oligomers within the atmospheric aqueous phase is known to be a source of SOA.”

Thank you very much for the clarification. We agree that your formulation is more suited. Therefore, we changed it in the revised manuscript.

l. 202: “In general, the photolysis of organic compounds competes with the other oxidation pathways (see Sect. 2.5) and is a major source of OH. In Rosanka et al. (2020a), the photolysis of OVOCs is estimated to be more than four time higher than the photolysis of H₂O₂.”

Comment: 1) This reads as if all organics can act as OH source. Please specify that only organic peroxides are photolysed.

We agree with the referee that our formulation could imply that all organics photolyse. However, only specifying “organic peroxides” here could be misleading because also non organic peroxides undergo photolysis (e.g. pyruvic acid) in JAMOC. Therefore, we changed it to: “In general, the photolysis of some organic compounds (e.g. organic peroxides, pyruvic acid) competes with other oxidation pathways (see Sect. 2.5) and can be a source of OH.”

Comment: 2) Please add a reference to an experimental study that demonstrates the much higher photolysis rate of organics as compared to H₂O₂.

Experimental studies reporting aqueous-phase photolysis rates are rare, and we are not aware of any experimental study performing a direct comparison of organic photolysis rates to H₂O₂. In addition, it is important to notice that some of the photolysis rates used in JAMOC are taken from the gas-phase and scaled using an enhancement factor to account for scattering effects. Thus, in the model the relative magnitude between J(H₂O₂) and J(organics) is mainly the one based on the experimental data for the gas phase. The values reported in Rosanka et al. (2020) are modelling results that provide a global tropospheric in-cloud OH budget and a comparison to experimental data is thus limited and hardly possible. Following your comment, we propose to rewrite the sentence to the following: “In Rosanka et al. (2020a), a global tropospheric in-cloud OH budget is presented. When using JAMOC, EMAC predicts that about 40 % of all in-cloud OH is produced from the photolysis of a selection of organic compounds. However, Fenton chemistry is not considered by Rosanka et al. (2020) and the relative contribution is therefore expected to be overestimated.”

Comment: 3) Typo: it should be ‘times’ not ‘time’ in the last sentence.

Following our suggestions to your “Comment: 2)”, this typo no longer exists.

References

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