Geoscientific
Model Development
Discussions

Interactive comment on "simpleGAMMA – a reduced model of secondary organic aerosol formation in the aqueous aerosol phase (aaSOA)" by J. L. Woo and V. F. McNeill

Anonymous Referee #1

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The authors present a reduced version of their previously published GAMMA model (Gas-Aerosol-Model for Mechanism Analysis) that targets secondary organic aerosol (SOA) formation in aerosol water. The current study presents a reduced version of the model to be implemented in regional and global models that cannot include as much detail as the full GAMMA. SOA formation in the aqueous phase is not included in many models yet due to the lack of understanding of the underlying processes and the complexity of the few available mechanisms. Therefore, simpleGAMMA is a timely study that might provide some progress in model development. However, in my opinion it is premature and misleading and needs more work until it can be implemented in large-scale models to reliably predict SOA formation. At the very least uncertainties

should be discussed more carefully. Currently, I do not think that (simple)GAMMA can be used for any general aqueous aerosol SOA prediction under ambient conditions. I am aware that some of my comments below address not only simpleGAMMA but also GAMMA in general. However, the fact that GAMMA has been published and used already does not justify its major shortcomings. Since the current manuscript should be a stand-alone paper, uncertainties of GAMMA in general should be also discussed here. Therefore, I cannot recommend publication of this manuscript in its present form.

Major comments

1) I got confused while reading the manuscript what GAMMA or simpleGAMMA indeed is. Is it a 'model', i.e. a code that predicts SOA formation on aerosol particles whereas also the aerosol specifications etc. are an input or a 'mechanism', i.e. a module that lists chemical reactions? Has the mechanism been reduced or have input parameters been tested and can therefore be generalized? Wording and definitions along these lines should be carefully revised.

2) For what ranges of aerosol parameters (number concentration, sizes, water content etc) has GAMMA been tested? What is the variability of the resulting SOA mass and how well does it compare to simpleGAMMA? Such comparison should be shown in the manuscript.

3) Are the uptake parameters (mass accommodation, Henry's law constants etc) valid for any aerosol? E,.g. in the study by Nguyen et al. (2014) it is mentioned that "Henry's Law may not be an appropriate description of the IEPOX reactive uptake experiments performed on the liquid water of suspended aerosols, as the aerosol water layers represent highly non-ideal solutions and the OA formation is kinetically limited." So, their KH value was derived based on experiments specific to the experiential conditions, i.e. aerosol surfaces and volumes. This uncertainty should at the very least be discussed and consequences should be pointed out. In addition it is stated by Nguyen et al that "The Henry's Law partitioning of IEPOX was measured on NaCl particles (ionic

strengthâĹij9 M) to be 3×10^7 M atm-1" This composition dependency should be discussed and cautioned. If simpleGAMMA were to be used for any ambient aerosol, different values for both KH can be expected as it has been also suggested for glyoxal by Ervens and Volkamer (2011).

4) The sentence "Reversible hydration and oligomerization chemistry of glyoxal in the aqueous phase is captured using H*(Schwartz, 1986). . ." is misleading. - Why is Schwartz cited here? This paper refers to the kinetic uptake of trace gases. - Several studies have shown that oligomerization is not responsible for the apparent enhanced uptake of glyoxal, but salting-in effects due to the dissolved solutes (e.g., Galloway et al., Geophys. Res. Lett, 2011; Kampf et al., Envrion. Sci. Technol. 2013) - How was the SOA mass determined in the model? If this mass is formed due to oligomerization which is a reversible process, how was the amount determined that remains in the particle phase when the water amount (RH) decreases? Such effects will be crucial when parameterizations of oligomerization will be implemented in models that simulate ambient conditions.

5) The discussion of a possible role of OH chemistry contains several errors/misconceptions: a) Tilgner et al. (J. Atmos. Chem., 2013) have shown that the Fenton reaction (Fe2+ + H2O2) might be way more important as an OH source in aerosol water than the direct uptake and H2O2 photolysis. There, I assume that OH chemistry might have been greatly underestimated in GAMMA and might not be as negligible as suggested. b) I do not understand the sentence: "simpleGAMMA is not recommended for the treatment of aqueous SOA formation in cloud water, which is not OH limited and is dominated by aqueous phase photochemistry." I think there are several misconceptions here: - I agree that (simple)GAMMA should not be applied for cloud water. However, the reason for this is rather that the Henry's law constants were derived for conditions more similar to aerosol water. The one for glyoxal is orders of magnitude smaller on pure water; I am not sure that the one for IEPOX is available under such conditions. - In the study by Ervens et al. (2014) it is stated (in the ab-

stract) that "This [OH] limitation manifests itself as an apparent surface dependence of aqSOA formation. We estimate chemical OH(aq) production fluxes, necessary to establish thermodynamic equilibrium between the phases (based on Henry's law constants) for both cloud and aqueous particles. Estimates show that no (currently known) OH(aq) source in cloud water can remove this limitation, whereas in aerosol water, it might be feasible." Therefore, the OH limitation in aerosol water is greater than in cloud water. The reason for a possibly smaller role of photochemistry in aerosol water is not the OH limitation but the fact that all other solute concentrations are higher and thus oligomerization reactions are more likely and partitioning (Henry's law constants) is enhanced due to ion effects. This should be more correctly and carefully discussed.

6) In Figure 3, the comparison between GAMMA and simpleGAMMA results are shown. The differences are greatest at 9h with ~20% organic acids. Does this slice represent products from OH reactions? If so, given that these processes are not included in simpleGAMMA, how is it possible that simpleGAMMA results in the same total mass? Has the model been 'tweaked'? If so, how valid is this 'tweaking' for other model conditions (cf. Comment 2).

Minor comments

Abstract: 'aaSOA' has not been defined.

Introduction: 2nd sentence: (i) The study by Hodzic et al., ACP (2010) should be cited here that shows that total SOA mass can be predicted. I do agree with the fact that this might be for wrong reasons as individual properties (e.g. oxygenation state) are still biased. (ii) 'oxidation state' usually refers to a single atom within a molecule (e.g. +4 for C in CO2). If the bulk OA is characterized, 'oxygenation state' might be more appropriate.

p. 465, l. 23: It is not clear what is meant by 'bulk aqueous uptake'. The study by Schwartz describes the kinetic uptake of trace gases and can be applied to bulk phases or individual droplets.

p. 468: I got confused by this text: "The effective Henry's Law constants (H*) and accommodation coefficients used to describe uptake for these species are given in Table 1. Note that these H* values have been updated based on advances in the literature since McNeill et al. (2012), but the model intercomparisons performed in this study were performed using the McNeill et al. (2012) H* values, for consistency". Which are the data in Table 11 – the updated ones or the original ones? It might be clearer if both sets are added to Table 1 with a brief explanation in the Table or footnote which data have been or should be used.

p. 468, Eq-4: Are any loss terms of tetrols or IEPOXOS are known? How is this dealt with in the mechanism?

p. 470, l. 12/13: How is the OH chemistry in the gas phase perturbed? Can you elaborate?