

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

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We thank the reviewer for his or her helpful comments and respond to them inline below.

General Comments:

In the manuscript by Woo et al., a simplified aqueous aerosol phase model (simpleGAMMA) is presented. The model is contrasted with the larger GAMMA model that includes more species and reactions. Close agreement was observed between the models due to the prevalence of two dominant reactive aqueous pathways involving IEPOX and glyoxal. As mentioned by the authors, simpleGAMMA may be coupled

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with larger-scale atmospheric chemistry models. This appears to be the main motivation for the development of simpleGAMMA and is of interest to the modeling community. However, the paper requires more detailed discussions in three major areas before I recommend publication: (1) comparison of the chemistry and computational performance of simpleGAMMA relative to updated large-scale models such as CMAQ or CAMx, (2) the range of applicability of simpleGAMMA to aerosols that aren't predominantly aqueous (i.e. < 50% by weight of water) and (3) the role of aerosol pH in aerosol phase chemistry is more controversial than depicted in the Results section when describing high and low NO_x regimes.

RESPONSE: We thank the reviewer for the insight and comments. These points are discussed further below.

Detailed Comments: 1. As mentioned in the second paragraph of the introduction, current atmospheric models such as CMAQ have been updated to include cloud organic chemistry and aqueous aerosol processes (i.e. Carlton et al. 2008; Pye et al. 2013 in reference list). While this paper compares the results of simpleGAMMA with its predecessor (GAMMA) in addition to showing agreement with CMAQ (Pye et al., 2013), it should more explicitly distinguish the capabilities of simpleGAMMA relative to recently updated models. Exactly how does simpleGAMMA potentially improve upon existing models with regards to chemical mechanisms and computational performance? A more detailed discussion in the introduction/discussion sections would be extremely useful in demonstrating the value of simpleGAMMA to the wider community.

RESPONSE: simpleGAMMA provides a method to represent aaSOA formation in 3D models. As stated in the paragraph referred to by the reviewer, “aqueous aerosol... SOA formation is yet not widely represented in 3D atmospheric chemistry and air quality models... aqueous aerosol processes are just beginning to be represented.” Other approaches exist including reactive uptake formulations such as those used by Pye et al. (2013) for IEPOX and Fu et al. (2008) and others for glyoxal. Potential issues with reactive uptake formulations stem from the fact that they represent two or more

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physical processes (reversible uptake of VOCs followed by aqueous phase reaction) as one irreversible reactive uptake step. Lin et al. (2014) and Knote et al. (2014) found that a surface reactive uptake formulation for glyoxal led to significantly higher predicted SOA mass than a reversible multiphase representation of the chemistry. The authors are currently collaborating with Dr. Havala Pye on a detailed intercomparison of the simpleGAMMA aqueous aerosol SOA formation scheme and the Pye et al. (2013) IEPOX SOA formation scheme from CMAQ. The CMAQ scheme has been implemented into the simpleGAMMA box model framework for purposes of direct comparison of the IEPOX SOA formation mechanisms from simpleGAMMA and CMAQ. Discussion contrasting the reactive uptake approach to the simpleGAMMA approach has been added to the Discussion section.

2. The model is advertised to describe the chemistry of SOA formation in the aqueous aerosol phase. Under ambient conditions, cloud chemistry will necessarily involve an aqueous phase containing a lot of water. However, aerosol particles are expected to have a wider range of water content. What is the range of applicability of simpleGAMMA at lower particle hydrations and particle sizes? For example, it is known that the rate of some aerosol phase reactions such as the hydrolysis of epoxides to form alcohols depend on the concentration of water (Piletic et al. 2013, Phys. Chem. Chem. Phys., 15, 18065-18076). This is not explicitly taken into account by equation 5 in the paper (derived from the work Eddingsaas et al. 2010) because those reactions were conducted in bulk water solutions where the concentration of water is essentially constant (55.5M) and lumped into k_{H^+} : $k_{H^+} = k_{hydrolysis}[H_2O]$. Piletic et al. 2013 and Pye et al. 2013 have taken the water concentration into account by readjusting the Eddingsaas k_{H^+} to be $9e-4 \text{ M}^{-2}\text{s}^{-1}$ by dividing the measured k_{H^+} by 55.5M. This k_{H^+} is effectively a third order rate constant where the rate depends on the concentrations/activities of IEPOX, H^+ and H_2O . These considerations are important for describing the kinetics of hydrolysis or hydration reactions in somewhat dry aerosol particles.

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RESPONSE: We thank the reviewer for this suggestion. We have implemented this scaling with respect to water concentration in eq. 5 (the aqueous phase reaction rate constant for IEPOX). Within the range of ambient RH and aerosol pH values tested in this work (as well as McNeill 2012 and Woo 2013) the molar water concentrations range from 18.3 to 39.1M. Using the revised rate constant, we calculate lower masses of generated IEPOX SOA than previously, but the trends do not change significantly (that is, IEPOX SOA formation still dominates aaSOA formation under low NO_x conditions). Figures have been updated to reflect this change.

3. In the results section, both high NO_x and low NO_x conditions are discussed. In section 3.1 under low NO_x conditions (pg. 470 line 20) it is stated that simpleGAMMA predicts maximum aaSOA formation when aerosol pH is low and RH is low. The strong pH dependence is ascribed to the acid-catalyzed hydrolysis of IEPOX. A recent paper has described the reactive partitioning of IEPOX onto non-acidified seeds (Nguyen et al. 2014, ACP, 14, 3497-3510) suggesting an insensitivity to pH. Additionally for high NO_x conditions (section 3.2 line 11), it is stated that the uptake of glyoxal exhibits no pH dependence. Studies by Liggio et al. 2005 (in reference list pg. 1536) do show some pH dependence which is why they included it in their reaction mechanism (scheme 1). The acid is once again acting as a catalyst present in the rate law for hydrolysis reactions of glyoxal much like IEPOX. The roles of acid and water in particles remain to be clearly elucidated in many aqueous phase processes. The paper should indicate this and include more citations to enrich the discussion of their results.

RESPONSE: The effect of ammonium ions on the aqueous phase processing of IEPOX, based on Nguyen et al. (2014), has already been implemented into this work (see eq. 5). It should be stated that the partitioning of IEPOX to non-acidified aerosols due to the participation of NH_4^+ does not imply insensitivity to pH, since H^+ ions protonate the epoxide ring more efficiently than NH_4^+ . Rather, it shows that the IEPOX reaction may also be active at higher pH compared to what was believed previous to Nguyen et al. (2014). We acknowledge the reviewer's point regarding the H^+ depen-

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dence observed by Liggio et al. (2005), but we will point out that pH-dependent reactive uptake of glyoxal to aerosols has not been observed in subsequent studies (Kroll et al., 2005; Galloway et al., 2009; Volkamer et al., 2009). The effective Henry's Law constant we use for glyoxal is derived from a detailed analysis of the laboratory data from those studies using GAMMA (Sumner et al. 2014), and therefore does not include pH dependence.

4. In Figure 1, why does simpleGAMMA begin to overestimate particle mass concentrations relative to GAMMA at long simulation times? I would have expected an underestimation at all times given that less species and reactions are present in simpleGAMMA. What is driving this effect?

RESPONSE: Although the gas phase mechanisms of GAMMA and simpleGAMMA are identical in this study, in simpleGAMMA, the tracked gas-phase species that do not have explicitly defined mass transfer coefficients defined in Table 1 do not partition into the aerosol phase. While not strong contributors to overall aaSOA mass, the increased gas-phase concentrations of some CVOC species (MGLY, MACR, etc.) and NO_x are sufficient to perturb gas-phase OH chemistry in simpleGAMMA as compared to GAMMA. Therefore, gas-phase IEPOX values are higher in simpleGAMMA. This, coupled with the lack of aerosol-phase loss terms for the IEPOXOS and tetrol species in the aqueous phase, leads to the overestimate you describe. The text has been updated to include more discussion of this point.

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