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Comment

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 #2

Received and published: 5 March 2015

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 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

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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 NOx regimes.

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.

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

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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.

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.

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?

Interactive comment on Geosci. Model Dev. Discuss., 8, 463, 2015.

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