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DEPARTMENT OF CHEMICAL ENGINEERING

Dr. Alexander Archibald
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May 18, 2015

Dear Dr. Archibald,

With this letter I submit a revised version of our manuscript for your consideration. We appreciate this opportunity to refine and improve the content of the manuscript based on suggestions of the three reviewers and the Executive Editor, and we hope you find it acceptable for publication in *GMD.*

I attach to this letter a response to the reviewers' and editor's comments and a revised version of the manuscript with changes tracked.

Sincerely,

V.F.McNeill

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Responses to Reviewer 1

We thank the reviewer for his or her comments, and we respond to them in bold, inline below.

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.

> **GAMMA and simpleGAMMA are both models that predict SOA formation, given input parameters including aerosol parameters. The aqueous phase chemical mechanism (i.e. component terms in r_{ij} in Equation 1) was reduced for simpleGAMMA.**

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.

> **simpleGAMMA and GAMMA have both been tested for ambient RH values from 40-80% (e.g. deliquesced conditions for sulfate aerosol), initial aerosol pH values ranging from 1-4. We have taken as a test case ammonium sulfate aerosols with the size distribution of Whitby (1978), but simpleGAMMA has been applied for a variety of particle compositions in Budisulistiorini et al. (2015). Aerosol water content and inorganic activity coefficients were established based on these parameters using E-AIM. The calculated aerosol liquid content varies on the order of ~10^{-12} to 10^{-11} $cm^3\ cm^{-3}_{air}$, depending on RH and pH. The range of SOA mass predicted by simpleGAMMA and GAMMA for these test conditions can be seen in Figures 2 and 4.**

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 experimental 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 strength 9 M) to be 3×10ˆ7 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).

> **The uptake parameters used represent our best understanding of the valid parameters for deliquesced aerosols. They are not valid for non-aqueous aerosols. The values of these parameters, including the Henry’s Law constant for IEPOX as the reviewer mentions, have significant uncertainty associated with them, largely because relatively few experimental studies have been conducted to reduce this uncertainty. We have added some discussion of these points to the text.**

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.

As stated in the text, reversible glyoxal oligomerization has been factored into GAMMA in its usage of an effective Henry's Law coefficient that captures gas-aerosol partitioning with these reactions in place. The concept of the effective Henry's Law constant in systems like this is discussed in detail by Schwartz (1986), and this is the reason for that reference in the passage the reviewer refers to. We have added more references regarding reversible glyoxal oligomerization to the earlier part of that sentence for clarity. In the case of glyoxal, the effective Henry's Law constant, which is based on a detailed analysis of laboratory measurements for uptake to deliquesced aerosols (Sumner et al. 2014) also takes into account phenomena such as "salting in."

SOA mass is reported as the total organic mass in the particle at the end of the simulation. If aerosol liquid water content changes during the simulation, the aqueous and gas phase will equilibrate according to eqs. (1)-(3). The mass of semivolatile organic material remaining after complete particle dehydration is an interesting question which is outside the scope of this study. We will note that complete aerosol dehydration is probably less environmentally significant than cloudwater evaporation to yield SOA. Laboratory studies have shown that the drying phase of the cloud-aerosol cycle leads to accelerated SOA formation, via mechanisms which are not well-understood and therefore not ready for inclusion in models (DeHaan et al. 2011, Nguyen et al. 2012)

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.

First, we note that the McNeill et al. (2012) study and the test simulations presented in this work were for ammonium sulfate aerosols with no significant transition metal ion content, and therefore Fenton chemistry would not be active. However, following up on the reviewer's suggestion, we have implemented transition metal ion chemistry for iron, copper and manganese, including Fenton reactions, into GAMMA following CAPRAM 3.0 in order to test the effect of these mechanisms on OH concentrations and therefore SOA chemistry. Using the test conditions of CAPRAM 3.0 (initial concentrations of $[Fe^{+3}]_0$ = 5e-6 M, $[Cu^{+}]_0$ = $[Mn^{3+}]_0$=2.5e-7 M for urban conditions, $[Fe^{+3}]_0$ = 5e-7 M, $[Cu^{+}]_0$ = $[Mn^{3+}]_0$=2.5e-8 M for remote conditions) and other conditions as described in McNeill et al. (2012), we find that the aqueous aerosol SOA chemistry is still OH-limited and the predicted product distributions do not change. Despite the lack of observed effect, we expect this may actually be an overestimate of the impact of TMI chemistry because ambient

studies have indicated that iron-containing minerals are not homogenously distributed across the aerosol population (Moffet et al., 2012). This will be the subject of a future study.

The issue of additional unknown sources of OH was mentioned in the discussion session of the original manuscript, but we have expanded this.

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 abstract) 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.

The reviewer is correct that there is an error in that sentence – as noted, the work of Ervens and coworkers has pointed to cloudwater chemistry being OH limited, due to mass-transfer limitations (Ervens et al. 2014). However, despite this OH limitation, as the reviewer also noted, studies from multiple groups including our own GAMMA simulations (McNeill 2015 Figure 2) show that SOA production in cloudwater is, indeed, dominated by aqueous phase photochemistry, unlike our findings for aqueous aerosol SOA. The reviewer is also correct that Henry's Law constants for dilute solutions (or pure water), rather than aerosol conditions, should be used for cloudwater simulations, and we do that when simulating cloudwater conditions in GAMMA. However, the real point that we wish to make in this passage is that any condition which is dominated by aqueous-phase photochemistry should not be simulated using simpleGAMMA. The sentence has been modified to read: "*simpleGAMMA is not recommended for the treatment of aqueous SOA formation in cloud water, which is dominated by aqueous phase photochemistry*."

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).

The model has not been 'tweaked'. Under high-NOx conditions, GAMMA's aqueous-phase acid formation chemistry is dominated by the formation of succinic acid via two photo-radicalized CVOC species, the dominant source for which is glyoxal. As succinic acid has comparable molecular mass (118 g/mol) to the molecular weight of the two glyoxal molecules that comprise it (116 g/mol), the predicted overall aaSOA mass is therefore very similar for the two models.

Minor comments

Abstract: 'aaSOA' has not been defined.

> **The definition of aaSOA as aqueous-aerosol SOA has been added.**

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 CO_2). If the bulk OA is characterized, 'oxygenation state' might be more appropriate.

> **The reference to Hodzic et al has been added. We will change to the term "degree of oxidation" to be consistent with common usage in the field (Kroll et al., 2011).**

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.

> **Here, "bulk aqueous uptake" is used in contrast to "surface reactive uptake" (i.e. the "bulk" is the bulk volume of the aerosol). We have deleted the word "bulk" for clarity.**

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 1 – 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.

> **We agree that this was confusing. For purposes of clarity, the figures for both GAMMA and simpleGAMMA have been recalculated with the updated values, listed in Table 1, instead of the original values from McNeill 2012. The language in the text has been changed to reflect this change.**

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

> **The loss terms for tetrols and IEPOXOS are not known at this time, so this is not treated in GAMMA or simpleGAMMA. This will be implemented as more information becomes available with respect to the photochemical aging and aqueous chemistry of these species. The lack of loss features will result in an overprediction of these two species with respect to total SOA mass. This effect will be added to the Discussion section.**

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

> **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 NOx are sufficient to perturb gas-phase OH chemistry.**

References

De Haan, D. O.; Hawkins, L. N.; Kononenko, J. a; Turley, J. J.; Corrigan, A. L.; Tolbert, M. a; Jimenez, J. L. Formation of nitrogen-containing oligomers by methylglyoxal and amines in simulated evaporating cloud droplets. *Environ. Sci. Technol.* **2011**, *45*, 984–991.

Galloway, M. M., Chhabra, P. S., Chan, a. W. H., Surratt, J. D., Flagan, R. C., Seinfeld, J. H. and Keutsch, F. N.: Glyoxal uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions, Atmos. Chem. Phys., 9(10), 3331–3345, doi:10.5194/acp-9-3331-2009, 2009.

Kroll, J. H., Ng, N. L., Murphy, S. M., Varutbangkul, V., Flagan, R. C. and Seinfeld, J. H.: Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds, J. Geophys. Res., 110(D23), 1–10, doi:10.1029/2005JD006004, 2005.

Kroll, J. H., Donahue, N. M., Jimenez, J. L., Kessler, S. H., Canagaratna, M. R., Wilson, K. R., Altieri, K. E., Mazzoleni, L. R., Wozniak, A. S., Bluhm, H., Mysak, E. R., Smith, J. D., Kolb, C. E. and Worsnop, D. R.: Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol., Nat. Chem., 3(2), 133–9, doi:10.1038/nchem.948, 2011.

Lin, G., Sillman, S., Penner, J. E. and Ito, A.: Global modeling of SOA: the use of different mechanisms for aqueous phase formation, Atmos. Chem. Phys., 14, 5451–5475, doi:10.5194/acpd-13-29629-2013, 2014.

Moffet, R. C., Furutani, H., Rödel, T. C., Henn, T. R., Sprau, P. O., Laskin, A., Uematsu, M. and Gilles, M. K.: Iron speciation and mixing in single aerosol particles from the Asian continental outflow, J. Geophys. Res. Atmos., 117(D7), n/a–n/a, doi:10.1029/2011JD016746, 2012.

Volkamer, R., Ziemann, P. J. and Molina, M. J.: Secondary Organic Aerosol Formation from Acetylene (C_2H_2): seed effect on SOA yields due to organic photochemistry in the aerosol aqueous phase, Atmos. Chem. Phys., 9(6), 1907–1928, doi:10.5194/acp-9-1907-2009, 2009.

Nguyen, T. B.; Lee, P. B.; Updyke, K. M.; Bones, D. L.; Laskin, J.; Laskin, A.; Nizkorodov, S. A. Formation of nitrogen- and sulfur-containing light-absorbing compounds accelerated by evaporation of water from secondary organic aerosols. *J. Geophys. Res.* **2012**, *117*, D01207, doi:10.1029/2011JD016944.

Reviewer 2

We thank the reviewer for his or her comments, and we 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 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 NOx regimes.

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.

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 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 kH+: kH+ = khydrolysis[H2O]. Piletic et al. 2013 and Pye et al. 2013 have taken the water concentration into account by readjusting the Eddingsaas kH+

to be 9e-4 M-2s-1 by dividing the measured kH+ by 55.5M. This kH+ is effectively a third order rate constant where the rate depends on the concen trations/activities of IEPOX, H+ and H2O. These considerations are important for describing the kinetics of hydrolysis or hydration reactions in somewhat dry aerosol particles.

> **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 NOx conditions). Figures have been updated to reflect this change.**

3. In the results section, both high NOx and low NOx conditions are discussed. In section 3.1 under low NOx 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 NOx 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.

> **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 NH4+ does not imply insensitivity to pH, since H+ ions protonate the epoxide ring more efficiently than NH4+. 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^+ dependence 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?

> **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 NOx 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.

Reviewer 3

We thank the reviewer for his or her comments, and we respond to them in bold, inline below.

Woo et al. presents a simple version of the GAMMA model, with a main focus on aerosol uptake of IEPOX and glyoxal. This is a short paper, and the work does not present enough new knowledge, at its present form. In the GAMMA paper (McNeill et al., 2012), the authors have already identified the major contribution pathways to aaSOA formation in their model (the uptake of glyoxal and IEPOX). This work simply extracts the relevant reactions of these two pathways and produces a simplified version of GAMMA. The authors then find that this simpleGAMMA behaves very much similar to GAMMA, but with a lower computation cost. While I agree with most comments from the other two reviewers, I have a few more comments:

1. Sensitivity to aqueous OH. As one of the two reviewers pointed out, aqueous OH can be largely enhanced by Fenton reaction. What is the sensitivity of modeled SOA to aqueous OH?

As stated in response to Reviewer 1, first, we note that the McNeill et al. (2012) study and the test simulations presented in this work were for ammonium sulfate aerosols with no significant transition metal ion content, and therefore Fenton chemistry would not be active. However, following up on the Reviewers' suggestions, we have implemented transition metal ion chemistry for iron, copper and manganese, including Fenton reactions, into GAMMA following CAPRAM 3.0 in order to test the effect of these mechanisms on OH concentrations and therefore SOA chemistry. Using the test conditions of CAPRAM 3.0 (initial concentrations of $[Fe^{+3}]_0$ = 5e-6 M, $[Cu^{+}]_0$ = $[Mn^{3+}]_0$=2.5e-7 M for urban conditions, $[Fe^{+3}]_0$ = 5e-7 M, $[Cu^{+}]_0$ = $[Mn^{3+}]_0$=2.5e-8 M for remote conditions) and other conditions as described in McNeill et al. (2012), we find that the aqueous aerosol SOA chemistry is still OH-limited and the predicted product distributions do not change. Despite the lack of observed effect, we expect this may actually be an overestimate of the impact of TMI chemistry because ambient studies have indicated that iron-containing minerals are not homogenously distributed across the aerosol population (Moffet et al., 2012). This will be the subject of a future study.

The issue of additional unknown sources of OH was mentioned in the discussion session of the original manuscript, but we have expanded this.

2. Aqueous diffusion. According to Schwartz (1986), aqueous diffusion may play an important role in the aqueous system. Have this been considered in the GAMMA model?

Aqueous diffusion is not accounted for in GAMMA or simpleGAMMA, that is, Henry's Law equilibration is assumed to occur instantaneously and no spatial concentration gradients within the particle are considered. This likely leads to an overestimate of OH chemistry when this very fast-reacting species is taken up from the gas phase. However, since we have found aqueous aerosol chemistry to be OH-limited and aqueous phase photochemistry does not dominate aaSOA formation, inclusion of aqueous phase diffusion limitations in this calculation would not change our results or the

formulation of simpleGAMMA. Aqueous phase diffusion may also be important for relatively large droplets. We have made note of this in the text.

3. Correction for ionic strength. If this is a highly concentrated aqueous solution, the aqueous kinetics should be corrected for the ionic strength. Have this been considered in this model?

As stated in the GAMMA paper (McNeill et al. (2012)), "…*with the exception of the rate constant in the Eddingsaas (2010) mechanism for SOA formation from IEPOX, the influence of ionic strength on the reaction rates is not considered in the current version of GAMMA due to a lack of necessary thermodynamic data.*" As stated by Herrmann et al. (*Chemosphere* 2003, *52*, 485-502) in reference to their model, CAPRAM, "*At the current state the influence of ionic strength effects on the kinetic behaviour, i.e. the consideration of activity coefficients, or, alternatively, kinetic salt effects are not included in these model studies due to very sparse thermodynamic data especially for the ions and radical ions*." The IEPOX reaction mentioned in the aforementioned passage from McNeill et al. (2012) is the only aqueous reaction explicitly considered in simpleGAMMA. The effect of ionic strength on the Henry's Law constants of glyoxal and IEPOX is accounted for through the use of experimentally determined H* values for uptake to deliquesced aerosols.

It seems to make more sense if authors can include an implementation of simpleGAMMA into a 3-D model, and show some results from that. That will justify its publication in GMD. The current content seems a little bit thin, in my opinion. But I will leave this to the editor to decide.

The implementation of simpleGAMMA into several different 3D models is currently underway (see, for one example, Jathar et al. 2014). This manuscript provides the necessary description of simpleGAMMA to form the foundation for those studies. The demonstration of simpleGAMMA's application to modeling ambient measurement data can be found in Budisulistiorini et al. (2015).

Response to Executive Editor

Dear authors, In my role as Executive editor of GMD, I would like to bring to your attention our Editorial: http://www.geoscientific-model-development.net/gmd_journal_white_paper.pdf http://www.geosci-model-dev.net/6/1233/2013/gmd-6-1233-2013.html This highlights some requirements of papers published in GMD, which is also available on the GMD website in the 'Manuscript Types' section: C181 GMDD 8, C181–C182, 2015 Interactive Comment Full Screen / Esc Printer-friendly Version Interactive Discussion Discussion Paper http://www.geoscientific-model-development.net/submission/manuscript_types.html In particular, please note that for your paper, the following requirements have not been met in the Discussions paper – please correct this in your revised submission to GMD.

"– The paper must be accompanied by the code, or means of accessing the code, for the purpose of peer-review. If the code is normally distributed in a way which could compromise the anonymity of the referees, then the code must be made available to the editor. The referee/editor is not required to review the code in any way, but they may do so if they so wish. "

"– All papers must include a section at the end of the paper entitled "Code availability". In this section, instructions for obtaining the code (e.g. from a supplement, or from a website) should be included; alternatively, contact information should be given where the code can be obtained on request, or the reasons why the code is not available should be clearly stated. "

"– All papers must include a model name and version number (or other unique identi- fier) in the title. " In the case of your manuscript, please include a version number.

Also, following instructions in the "Code Availability" section, it is not clear how the code is available from mcneill-lab.org/gamma - please clarify how to thus access your code. Yours, Bob Marsh

We thank the editor for his comments. In response, we have:

1) added a version number for simpleGAMMA to the title of the revised manuscript

2) clarified the language in the "Code Availability" section of the manuscript to make it clear that more information is available at mcneill-lab.org/gamma and the code can be obtained by contacting vfm2103@columbia.edu, and

We will also provide a version of the code for the reviewers and editor.

simpleGAMMA v1.0 – A reduced model of secondary organic aerosol formation in the aqueous aerosol phase (aaSOA)

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Abstract

There is increasing evidence that the uptake and aqueous processing of water-soluble volatile organic compounds (VOCs) by wet aerosols or cloud droplets is an important source of secondary organic aerosol (SOA). We recently developed GAMMA (Gas-Aerosol Model for Mechanism Analysis), a zero-dimensional kinetic model that couples gas-phase and detailed aqueous-phase atmospheric chemistry for speciated prediction of SOA and organosulfate formation in cloudwater or aqueous aerosols. Results from GAMMA simulations of SOA formation in aerosol water (aaSOA) (McNeill et al. (2012), *Environ. Sci. Technol.* 46(15) 8075-8081) indicate that it is dominated by two pathways: isoprene epoxydiol (IEPOX) uptake followed by ring-opening chemistry (under low-NO_x conditions) and glyoxal uptake. This suggested that it is possible to model the majority of ~~aqueous aerosol phase SOA~~aaSOA mass using a highly simplified reaction scheme. We have therefore developed a reduced version of GAMMA, simpleGAMMA. Close agreement in predicted aaSOA mass is observed between simpleGAMMA and GAMMA under all conditions tested (between pH 1-4 and RH 40-80%) after 12 hours of simulation. simpleGAMMA is computationally efficient and suitable for coupling with larger-scale atmospheric chemistry models or analyzing ambient measurement data.

1 Introduction

Quantifying the sources of tropospheric aerosol material is important for accurate modeling of air quality and climate. In-situ processes leading to the formation of new organic aerosol material, collectively known as secondary organic aerosol (SOA) formation, are poorly constrained in atmospheric chemistry models (Kanakidou et al., 2005; Hallquist et al., 2009; Hodzic et al., 2010). Disagreement between model results and observations of the quantity, degree of oxidation, and location of organic aerosols in the atmosphere has suggested an incomplete representation of SOA formation pathways in models (Heald et al., 2005; Jimenez et al., 2009). In the past decade, the uptake of water-soluble volatile organic compounds (VOCs) into cloud droplets or aerosol water, followed by aqueous-phase chemical processing, has received increased attention as a possibly important source of SOA (Blando and Turpin, 2000; Ervens et al., 2011). It is thought to be especially significant in the case of isoprene-derived SOA formation. This is because most of the gas-phase oxidation products of isoprene, are, like isoprene itself, highly volatile, however some, like glyoxal (GLYX), isoprene-derived epoxydiols (IEPOX) (Paulot et al., 2009; Surratt et al., 2010), and methacrylic acid epoxide (MAE) (Lin et al., 2013), are water-soluble. These species also undergo reactive processing in the aqueous phase of cloud droplets or aerosols, increasing their uptake from the gas-phase.

Despite mounting evidence that aqueous atmospheric chemistry is a significant source of SOA, aqueous aerosol and cloudwater SOA formation is not yet widely represented in 3D atmospheric chemistry and air quality models. This is due, in part, to the challenges of bridging scales between the detailed information generated by laboratory experiments, and simplified representations suitable for implementation in 3D models, which can afford to carry relatively few chemical tracers. Including cloudwater organic chemistry in large scale atmospheric chemistry models has improved agreement with observations (Carlton et al., 2008; Myriokefalitakis et al., 2011; Liu et al., 2012), but aqueous aerosol processes are just beginning to be represented (Pye et al., 2013; Knote et al., 2014; Lin et al., 2014).

Previously, we developed GAMMA (Gas-Aerosol Model for Mechanism Analysis), a zero-dimensional kinetic model that couples gas- and detailed aqueous aerosol-phase chemistry for speciated prediction of SOA and organosulfate formation in the aqueous aerosol phase under ambient or laboratory conditions (McNeill et al., 2012; Woo et al., 2013). GAMMA represents aaSOA formation in terms of ~~bulk~~ aqueous uptake followed by aqueous-phase reaction (Schwartz, 1986). GAMMA includes IEPOX chemistry following Eddingsaas et al. (2010), and uses the effective Henry's Law constant, H*, constrained by aerosol chamber studies (Sumner et al., 2014) to describe glyoxal uptake and dark reactions, as well as detailed photochemical organosulfate formation and brown carbon formation from glyoxal, methylglyoxal, and acetaldehyde (Woo et al., 2013). For more information regarding other specific mechanisms included in GAMMA, as well as rate constants for these reactions and other physical parameters, the reader is referred to McNeill et al. (2012) (including the Supporting Information) and Woo et al. (2013).

Simulations using GAMMA indicate that the IEPOX pathway dominates aaSOA formation, leading to up to ~0.9 μg m^{-3} of SOA mass under conditions typical of the rural SE USA (McNeill et al., 2012). Pye and coworkers predicted similar mean concentrations (0.6-1.0 μg m^{-3}) of IEPOX-derived SOA mass for the SE USA in Summer 2006, using CMAQ with a surface reactive uptake formulation of IEPOX aaSOA formation (Pye et al., 2013). In urban (high-NOx) environments, aaSOA is primarily formed via glyoxal uptake (McNeill et al., 2012).

This predominance of two aaSOA formation pathways involving relatively few species, compared to the total number of aqueous compounds tracked by GAMMA, suggests that it is possible to model the majority of aqueous aerosol phase SOA mass using a highly simplified reaction scheme, which is computationally efficient and suitable for coupling with larger-scale atmospheric chemistry models. GAMMA has therefore been used as a guide to develop a reduced mechanism for aaSOA formation, simpleGAMMA. simpleGAMMA reduces the total number of tracked aqueous species from 140 to 4 (glyoxal, IEPOX, 2-methyltetrol, and IEPOX organosulfate), with 2 species partitioning between the gas and aqueous aerosol phases (glyoxal and IEPOX), and a single aqueous-phase chemical process (reactive uptake of IEPOX), compared to 118 in GAMMA.

2 simpleGAMMA: Model Description

As in GAMMA, the time evolution of the aqueous aerosol phase concentration (C_i, in mol/L) of a given chemical species *i* is described in simpleGAMMA by the following differential equation (Schwartz, 1986):

$$\frac{dC_i}{dt} = \frac{k_{mt,i}}{\boldsymbol{R}T} P_i - \frac{k_{mt,i}}{H_i^* \boldsymbol{R}T} C_i + \sum_k r_{ik,aq} \qquad (1)$$

Here, P_i is the gas-phase partial pressure of species i, H^*_i is the effective Henry's Law constant, $\boldsymbol{R}$ is the universal gas constant, and T is temperature. The rates $r_{ik,aq}$ represent chemical reactions in the aerosol phase that can act as sources or sinks for a given species. $k_{mt,i}$ is the gas-aerosol mass transfer coefficient for species i, given by:

$$k_{mt,i} = \frac{1}{\frac{R^2}{3D_{g,i}} + \frac{4R}{3\omega_i \alpha_i}} \qquad (2)$$

where R is the aerosol particle radius, $D_{g,i}$ is the gas-phase diffusion coefficient, ω_i is the thermal velocity, and α_i is the accommodation coefficient. A suitable gas-phase chemical mechanism should be employed, and the loss or gain of species to/from the aerosol phase should be accounted for, following, for example:

$$\frac{dP_i}{dt} = -k_{mt,i} a_L P_i + \frac{k_{mt,i} a_L}{H_i^*} C_i + \sum_j r_{ij,gas} + E_i - D_i \qquad (3)$$

where a_L is the aerosol aqueous liquid volume fraction (cm^3 cm^{-3} of air), $r_{ij,\mathrm{gas}}$ is the rate of gas phase reaction j that species i participates in, and E_i and D_i are the emission and deposition rates of species i, respectively.

Note that simpleGAMMA is a reduced version of the *aqueous-phase mechanism* of GAMMA (McNeill et al., 2012). The gas-phase mechanism of GAMMA was not changed because it is intended that simpleGAMMA take gas phase concentration fields as inputs from an external source, i.e. from field measurements or from existing models of atmospheric chemistry, which have gas-phase chemical mechanisms but lack representations of aqueous aerosol phase SOA formation. For tests reported here, we ran simpleGAMMA with the full gas phase mechanism of GAMMA, following Eqs. (1)–(3). A full description of the gas and aqueous phase mechanisms of GAMMA, the simulation conditions, and results can be found in McNeill et al. (2012). ~~We note that, subsequent to the publication of McNeill et al. (2012), the gas and aqueous phase chemistry of methacrylic acid epoxide (MAE) was introduced to the full version of GAMMA following Lin et~~

~~al. (2013). The predicted contribution of this pathway to aaSOA was minor compared to IEPOX and glyoxal, consistent with the findings of Pye et al. (2013). Therefore, it is not included in simpleGAMMA.~~

The processes leading to aaSOA formation in simpleGAMMA are a subset of those represented in GAMMA, and they with the goal of minimizing the number of aqueous-phase tracers and species being exchanged between the gas and aerosol phases, while maximizing the aaSOA mass captured compared to that as predicted by GAMMA after 12 hours of simulated chemistry, assuming no initial aerosol-phase organic mass. The detailed comparison of GAMMA and simpleGAMMA output under a range of typical environmentally relevant conditions can be found in the following section. The aqueous phase species tracked in simpleGAMMA are: IEPOX, glyoxal, 2-methyltetrol, and IEPOX organosulfate. Mass transfer between the gas and aerosol phases only occurs for IEPOX and glyoxal. 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 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.~~ and they represent our best understanding of the valid parameters for deliquesced aerosols. They are not valid for non-aqueous aerosols. The values, especially H* for IEPOX (Budisulistiorini et al., 2015), have significant uncertainty associated with them, largely because relatively few experimental studies of H* for uptake of these species to deliquesced aerosols are available in the literature (Kampf et al., 2013; Gaston et al., 2014; Nguyen et al., 2014).

We note that, subsequent to the publication of McNeill et al. (2012), the gas and aqueous phase chemistry of methacrylic acid epoxide (MAE) was introduced to the full version of GAMMA following Lin et al. (2013). The predicted contribution of this pathway to aaSOA was minor compared to IEPOX and glyoxal, consistent with the findings of Pye et al. (2013). Therefore, it is not included in simpleGAMMA.

Reversible hydration and oligomerization chemistry of glyoxal in the aqueous phase (Whipple, 1970) is captured using the effective Henry's Law constant, H* (Schwartz, 1986). Therefore, those processes are not represented explicitly in either GAMMA or simpleGAMMA, in order to avoid double counting. The aqueous processing of IEPOX to form 2-methyltetrols (tetrol) and and

IEPOX organosulfate (IEPOXOS) is represented as one reactive process following a simplified version of the mechanism of Eddingsaas et al. (2010):

IEPOX (aq) → (1-β) tetrol + β IEPOXOS (4)

Here, we apply a value for the branching ratio, β, of 0.4, which is an estimate based on the measurements of Eddingsaas and coworkers for the most concentrated bulk solution they studied. The rate constant for the reaction, k_1, is a function of proton activity and nucleophile concentrations, again following Eddingsaas et al. (2010). We have modified the formula to include the possible protonation of IEPOX (aq) by ammonium as observed by Nguyen et al. (2014).

$$k_1 = \cancel{k_{H^+}} \left(\frac{[H_2O]}{55.1}\right) k_{H^+} a_{H^+} + k_{SO_4^{2-}}[SO_4^{2-}]a_{H^+} + k_{HSO_4^-}[HSO_4^-] + k_{NH_4^+}[NH_4^+]$$

~~(4~~(5)

Here, a_{H^+} is the H$^+$ activity, $k_{H^+} = 5 \times 10^{-2} s^{-1}$, $k_{SO_4^{2-}} = 2 \times 10^{-4} M^{-1} s^{-1}$, and $k_{HSO_4^-} = 7.3 \times 10^{-4} M^{-1} s^{-1}$. The ammonium rate constant, $k_{NH_4^+}$, was calculated using GAMMA and the results of the chamber study of Nguyen et al. (2014) to be $1.7 \times 10^{-5} M^{-1} s^{-1}$.

The rate constant term k_{H^+} from Eddingsaas et al (2010) has been scaled to account for variable water concentrations within the seed aerosol at different pH and RH conditions, consistent with recent literature (Piletic et al., 2013; Pye et al., 2013). The architecture of the simpleGAMMA program is similar to that of GAMMA (McNeill et al., 2012). simpleGAMMA and GAMMA were originally written in MATLAB (MathWorks, Inc.), utilizing the stiff initial value ~~ODE~~ordinary differential equation solver `ode15s.m`, but simpleGAMMA is also available in Fortran. Required input parameters for simpleGAMMA are: gas phase concentration fields for IEPOX and glyoxal, aerosol pH, aerosol size distribution or volume-weighted average aerosol diameter, aerosol liquid water content, and aerosol sulfate and bisulfate concentrations. The test simulations in this study were for the same conditions as the high-NOx and low-NOx scenarios in McNeill et al. ~~(2012). As~~

~~in that study, the seed aerosols were assumed here to be composed of~~(2012), with one exception: for the low-NOx simulation, the initial gas-phase mixing ratio of IEPOX is assumed to be 780 ppt, instead of zero. This was the steady state value after three simulated day-night cycles in GAMMA, in the absence of aerosol uptake. In all other simulations, the seed aerosols were assumed to be initially composed solely of deliquesced ammonium sulfate, following the size distribution of Whitby (1978), with aerosol loadings of 4.0 μg/m^3 (rural conditions, following Tanner et al. (2009)) or 20 μg/m^3 (urban conditions, following Jimenez et al. (2003)). Initial inorganic aerosol composition was determined by E-AIM outputs for the defined initial pH and RH values.

3 Results

Low-NOx (Rural) Conditions

Similar to what was observed in McNeill et al. (2012), under simulated rural (low-NOx) environments, both GAMMA and simpleGAMMA predict that aaSOA is dominated by IEPOX and its aerosol-phase reaction products. The evolution of aaSOA mass as predicted over 12 hours of dawn-to-dusk simulation under low-NOx conditions using GAMMA and simpleGAMMA is shown in Figure 1 (for aerosol pH = 1 and 45% RH~~ 65%).~~). The pie charts compare the aaSOA composition predicted by both models at 3, 6, 9, and 12 hours of simulation. ~~The accumulation of aaSOA under low NO_x conditions is highly dependent on the formation of gas-phase IEPOX. Although~~Close agreement in predicted aaSOA mass and its composition can be seen between the two models. Small differences arise due to the fact that, although identical gas-phase mechanisms and initial conditions were used in this model intercomparison, the gas-phase chemistry, especially gas-phase OH, is perturbed by the differences in ~~the aqueous-phase mechanisms and~~ gas-aerosol mass transfer between the two models. ~~IEPOX formation is relatively slow, resulting~~ Specifically, VOCs which may partition into the particle phase in ~~differences in predicted aaSOA composition between the two models in early simulation hours as IEPOX levels build~~GAMMA but not simpleGAMMA are present in the gas phase~~. After six hours of simulation time the high molecular masses of IEPOX and its substitution products overtake and dominate the aaSOA composition.~~ in higher concentrations in simpleGAMMA, creating an increased sink for OH.

Figure 2 shows the total aaSOA mass predicted by GAMMA and simpleGAMMA for 12 hours of simulation under low-NOx conditions, with varying aerosol pH and RH. Like GAMMA, simpleGAMMA predicts maximum aaSOA formation under low-NOx conditions when aerosol pH is low and RH is low (but not so low as to cause aerosol efflorescence). This is because in-particle processing of IEPOX is initiated by protonation, so conditions which maximize the in-particle proton concentration yield the highest IEPOX processing. Close agreement (to within ~~15~~30%) exists between aaSOA mass predicted by GAMMA and by simpleGAMMA for ~~RH > 50%,~~pH 1, and ~~for all RH values~~within 0.02 μg m^{-3} for aerosol pH ~~>~~≥ 2.0. ~~For RH ≤ 45%, the~~The highly efficient in-particle IEPOX chemistry at low pH ~~(pH < 2.0)~~ leads to larger discrepancies ~~(up to 40%)~~ between the two models.

High-NOx (Urban) Conditions

aaSOA mass as predicted by GAMMA is dominated by "dark" uptake of glyoxal under high-NOx conditions (McNeill et al., 2012). Gas-phase IEPOX formation is expected to be minor in this regime (Paulot et al., 2009). A comparison of evolved aaSOA mass and composition under high-NOx conditions as predicted by GAMMA and simpleGAMMA can be seen in Figure 3. Figure 4 shows total aaSOA mass predicted by the two models after 12 hours of simulation under high-NOx conditions, with varying aerosol pH and RH. Close agreement (within 0.01 μg m^{-3}) in predicted total aaSOA mass exists between simpleGAMMA and GAMMA for all relative humidity and pH values tested. Like GAMMA, under high NO_x conditions simpleGAMMA predicts increasing aaSOA formation with increasing RH (and therefore increasing aerosol liquid water content), and no pH dependence, consistent with glyoxal dark uptake being the dominant aaSOA formation mechanism~~.~~ (Kroll et al., 2005; Galloway et al., 2009; Volkamer et al., 2009). The increased uptake at higher RH amplifies small differences in gas phase chemistry between simpleGAMMA and GAMMA, due to differing gas-phase OH sinks in the two models, as described above. GAMMA predicts some contribution to aaSOA mass by photochemical production of succinic acid (vis. Figure 3~~);~~), which is not included in simpleGAMMA. However, since glyoxal is the dominant precursor for succinic acid formation~~, this leads~~ and the molecular weight of succinic acid (118 g/mol) is comparable to ~~only a small difference in overall~~ the molecular weight of the two glyoxal molecules that comprise it (116 g/mol), the predicted overall aaSOA mass ~~between GAMMA and~~

~~simpleGAMMA, which does not include in-particle photochemistry.~~is therefore very similar for the two models.

Computational performance

The goal of simpleGAMMA is to faithfully represent aaSOA formation with a low number of tracers, in order to simplify the implementation of aqueous aerosol SOA formation in ~~3D~~3-D models (by coupling the gas-phase schemes of those models with simpleGAMMA). However, simpleGAMMA is also computationally faster than GAMMA when run as a box model, as described in this study, due to the reduced number of tracers and reactions in the aqueous phase (recall that the gas phase mechanisms of GAMMA and simpleGAMMA were identical for purposes of this study). In ten simulations with starting aerosol pH 1 and 65 % ambient RH, computational run-time for simpleGAMMA under low-NOx conditions spanned between 10~~–~~–12 ~~seconds~~s for 12 ~~hours~~h of simulation, compared to 33~~–~~–42 ~~seconds~~s for GAMMA. These runs were performed on an Intel Core i7-3520M CPU @2.90 GHz PC, using MATLAB R2014b with the solver `ode15s.m` Time steps to completion between simpleGAMMA and GAMMA were comparable ~~(∼~~(∼11,000 and ~~∼~~∼14,000 respectively) (indicating similar stiffness in the two models) but simpleGAMMA necessarily utilized less memory cache due to the smaller number of aqueous-phase species and reactions.

4 Discussion and Outlook

The agreement between GAMMA and simpleGAMMA indicate that this reduced framework can be useful to represent aaSOA mass formation over a variety of relevant ambient conditions. Coupling of simpleGAMMA with regional and global scale 3D atmospheric chemistry models (Jathar et al., 2014) and its application to analysis of ambient measurement data (Budisulistiorini et al., 2015) is currently underway.

While we have demonstrated good agreement between simpleGAMMA and GAMMA, the limitations of GAMMA also apply to simpleGAMMA; for example, neither model includes a treatment of oxidative aging of aaSOA at this time due to a lack of kinetic and mechanistic data. As a result, overprediction of total aaSOA mass is likely (Budisulistiorini et al., 2015). The only sources of aqueous-phase OH in GAMMA are HOOH photolysis or Henry's Law transfer of OH from the gas phase. Therefore we, like others (Waxman et al., 2013; Ervens et al., 2014), have observed OH-limited chemistry in the aqueous aerosol phase using GAMMA, and this informed the simpleGAMMA formulation. ~~For this reason, simpleGAMMA is not recommended for the treatment of aqueous SOA formation in cloudwater, which is not OH limited and is dominated by aqueous phase photochemistry.~~While transition metal ion chemistry, a possible source of OH (Herrmann et al., 2015), was not included in the first version of GAMMA (McNeill et al., 2012) due to the focus on ammonium sulfate aerosols in that study, these mechanisms may be active in ambient aerosols. Preliminary calculations in GAMMA show that including transition metal ion (Fe^{+3}, Cu^{+2}, Mn^{+3}) chemistry following CAPRAM 3.0 (Herrmann et al., 2005) does not perturb the predicted aaSOA yield or product distribution. Aqueous-phase diffusion is not accounted for in GAMMA or simpleGAMMA, that is, Henry's Law equilibration is assumed to occur instantaneously and no spatial concentration gradients within the particle are considered. This likely leads to an overestimate of OH chemistry when this very fast-reacting species is taken up from the gas phase. However, since we have found that aqueous phase photochemistry does not dominate aaSOA formation, inclusion of aqueous phase diffusion limitations in this calculation would not change our results or the formulation of simpleGAMMA. Aqueous phase diffusion may also be important for relatively large droplets such as those encountered in marine aerosols.

simpleGAMMA is not recommended for the treatment of aqueous SOA formation in cloudwater, which is dominated by aqueous phase photochemistry. The role of UV light in aaSOA formation by glyoxal is unresolved (Galloway et al., 2009, 2011; Volkamer et al., 2009; Kampf et al., 2013). A recent data analysis study using GAMMA (Sumner et al., 2014) suggested a possible role for photo-enhanced chemistry in aaSOA formation by glyoxal involving organic photosensitizers such as fulvic acid (Monge et al., 2012). This chemistry can be represented in simpleGAMMA by including irreversible glyoxal uptake with $\gamma \sim 10^{-3}$ during sunlit hours, consistent with Fu et al. (2008), who based their representation on the experiments of Liggio et al. (2005), and with Waxman et al. (2013). A reactive uptake formulation was also used to represent aaSOA formation by IEPOX by Pye et al. (2013). While reactive uptake may be the best alternative for representing unknown processes such as glyoxal surface photochemistry, potential issues with reactive uptake formulations stem from the fact that they generally represent two or more physical processes (e.g., 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.

We previously predicted using GAMMA that glyoxal is the main contributor to aqueous aerosol-phase "brown carbon" formation by carbonyl-containing VOC precursors (Woo et al., 2013). Following that work, it is straightforward to track the formation of light-absorbing glyoxal derivatives in simpleGAMMA, with concentration-dependent aerosol light absorption calculated in post-processing. However, we note that fast photobleaching of aerosol brown carbon formed via this pathway has been demonstrated, limiting its potential impact on atmospheric chemistry and climate (Sareen et al., 2013; Woo et al., 2013; Lee et al., 2014).

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Code Availability

For more information and to access the simpleGAMMA program, please visit mcneill-lab.org/gamma or contact V. Faye McNeill, vfm2103@columbia.edu. simpleGAMMA was originally written in MATLAB (MathWorks, Inc.) and is also available in Fortran.

References

Blando, J. D. and Turpin, B. J.: Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of plausibility, Atmos. Environ., 34(10), 1623–1632, doi:10.1016/S1352-2310(99)00392-1, 2000.

Budisulistiorini, S. H., Li, X., Bairai, S. T., Renfro, J., Liu, Y., Liu, Y. J., McKinney, K. A., Martin, S. T., McNeill, V. F., Pye, H. O. T., Nenes, A., Neff, M. E., Stone, E. A., Mueller, S., Knote, C., Shaw, S. L., Zhang, Z., Gold, A. and Surratt, J. D.: Examining the effects of anthropogenic emissions on isoprene-derived secondary organic aerosol formation during the 2013 Southern Oxidant and Aerosol Study (SOAS) at the Look Rock, Tennessee, ground site, Atmos. Chem. Phys. Discuss., 15(5), 7365–7417, doi:10.5194/acpd-15-7365-2015, 2015.

Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S. P., Mathur, R., Roselle, S. J. and Weber, R. J.: CMAQ Model Performance Enhanced When In-Cloud Secondary Organic Aerosol is Included: Comparisons of Organic Carbon Predictions with Measurements, Environ. Sci. Technol., 42(23), 8798–8802, doi:10.1021/es801192n, 2008.

Eddingsaas, N. C., VanderVelde, D. G. and Wennberg, P. O.: Kinetics and products of the acid-catalyzed ring-opening of atmospherically relevant butyl epoxy alcohols., J. Phys. Chem. A, 114(31), 8106–13, doi:10.1021/jp103907c, 2010.

Ervens, B., ~~Sorooshian, A., Lim, Y. B. and Turpin, B. J.: Key parameters controlling OH-initiated formation of secondary organic aerosol in the aqueous phase (aqSOA), J. Geophys. Res. Atmos., 119(7), 3997–4016, doi:10.1002/2013JD021021, 2014.~~

~~Ervens, B.,~~ Turpin, B. J. and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, Atmos. Chem. Phys., 11(21), 11069–11102, doi:10.5194/acp-11-11069-2011, 2011.

Ervens, B., Sorooshian, A., Lim, Y. B. and Turpin, B. J.: Key parameters controlling OH-initiated formation of secondary organic aerosol in the aqueous phase (aqSOA), J. Geophys. Res. Atmos., 119(7), 3997–4016, doi:10.1002/2013JD021021, 2014.

Fu, T., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M. and Henze, D. K.: Global budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, J. Geophys. Res., 113(D15), 1–17, doi:10.1029/2007JD009505, 2008.

Galloway, M. M., Chhabra, P. S., Chan, a. W. H., Surratt, J. D., Flagan, R. C., Seinfeld, J. H. and Keutsch, F. N.: Glyoxal uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions, Atmos. Chem. Phys., 9(10), 3331–3345, doi:10.5194/acp-9-3331-2009, 2009.

Galloway, M. M., Loza, C. L., Chhabra, P. S., Chan, a. W. H., Yee, L. D., Seinfeld, J. H. and Keutsch, F. N.: Analysis of photochemical and dark glyoxal uptake: Implications for SOA formation, Geophys. Res. Lett., 38(17), 1–5, doi:10.1029/2011GL048514, 2011.

Gaston, C. J., Riedel, T. P., Zhang, Z., Gold, A., Surratt, J. D. and Thornton, J. A.: Reactive Uptake of an Isoprene-derived Epoxydiol to Submicron Aerosol Particles., Environ. Sci. Technol., 48(19), 11178–11186, doi:10.1021/es5034266, 2014.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R. and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9(14), 5155–5236, doi:10.5194/acp-9-5155-2009, 2009.

Heald, C. L., Jacob, D. J., Park, R. J., Russell, L. M., Huebert, B. J., Seinfeld, J. H., Liao, H. and Weber, R. J.: A large organic aerosol source in the free troposphere missing from current models, Geophys. Res. Lett., 32(18), 2–5, doi:10.1029/2005GL023831, 2005.

Herrmann, H., Tilgner, A., Barzaghi, P., Majdik, Z., Gligorovski, S., Poulain, L. and Monod, A.: Towards a more detailed description of tropospheric aqueous phase organic chemistry: CAPRAM 3.0, Atmos. Environ., 39(23-24), 4351–4363, doi:10.1016/j.atmosenv.2005.02.016, 2005.

Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M. and Otto, T.: Tropospheric Aqueous-Phase Chemistry: Kinetics, Mechanisms, and Its Coupling to a Changing Gas Phase., Chem. Rev., doi:10.1021/cr500447k, 2015.

Hodzic, A., Jimenez, J. L., Madronich, S., Canagaratna, M. R., DeCarlo, P. F., Kleinman, L. and Fast, J.: Modeling organic aerosols in a megacity: potential contribution of semi-volatile and intermediate volatility primary organic compounds to secondary organic aerosol formation, Atmos. Chem. Phys., 10(12), 5491–5514, doi:10.5194/acp-10-5491-2010, 2010.

Jathar, S. H., Cappa, C. D., McNeill, V. F. and Kleeman, M. J.: Examining New Pathways of Secondary Organic Aerosol Formation in a 3D Model: Role of Absorbed Water, Multi-generational Aging, Intermediate-Volatility Organics and Aqueous Chemistry, in AAAR Annual Meeting, p. 379., 2014.

Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R. C., Zhang, X., Smith, K. A., Morris, J. W. and Davidovits, P.: Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer, J. Geophys. Res., 108(D7), 8425, doi:10.1029/2001JD001213, 2003.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U. and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere., Science ~~,~~(80-.)., 326(5959), 1525–1529, doi:10.1126/science.1180353, 2009.

~~Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R. C., Zhang, X., Smith, K. A., Morris, J. W. and Davidovits, P.: Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer, J. Geophys. Res., 108(D7), 8425, doi:10.1029/2001JD001213, 2003.~~

Kampf, C. J., Waxman, E. M., Slowik, J. G., Dommen, J., Pfaffenberger, L., Praplan, A. P., Prévôt, A. S. H., Baltensperger, U., Hoffmann, T. and Volkamer, R.: Effective Henry's Law Partitioning and the Salting Constant of Glyoxal in Aerosols Containing Sulfate., Environ. Sci. Technol., 47(9), 4236–44, doi:10.1021/es400083d, 2013.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, a., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G. and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5(4), 1053–1123, doi:10.5194/acp-5-1053-2005, 2005.

Knote, C., Hodzic, A., Jimenez, J. L., Volkamer, R., Orlando, J. J., Baidar, S., Brioude, J., Fast, J., Gentner, D. R., Goldstein, A. H., Hayes, P. L., Knighton, W. B., Oetjen, H., Setyan, A., Stark, H., Thalman, R., Tyndall, G., Washenfelder, R., Waxman, E. and Zhang, Q.: Simulation of semi-explicit mechanisms of SOA formation from glyoxal in aerosol in a 3-D model, Atmos. Chem. Phys., 14(12), 6213–6239, doi:10.5194/acp-14-6213-2014, 2014.

Kroll, J. H., Ng, N. L., Murphy, S. M., Varutbangkul, V., Flagan, R. C. and Seinfeld, J. H.: Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds, J. Geophys. Res., 110(D23), 1–10, doi:10.1029/2005JD006004, 2005.

Lee, H. J. J., Aiona, P., Laskin, A., Laskin, J. and Nizkorodov, S. A.: Effect of Solar Radiation on the Optical Properties and Molecular Composition of Laboratory Proxies of Atmospheric Brown Carbon., Environ. Sci. Technol., 48(17), 10217–10226, doi:10.1021/es502515r, 2014.

Liggio, J., Li, S.-M. and McLaren, R.: Heterogeneous reactions of glyoxal on particulate matter: identification of acetals and sulfate esters., Environ. Sci. Technol., 39(6), 1532–41, 2005.

Lin, G., Sillman, S., Penner, J. E. and Ito, A.: Global modeling of SOA: the use of different mechanisms for aqueous phase formation, Atmos. Chem. Phys., 14, 5451–5475, doi:10.5194/acpd-13-29629-2013, 2014.

Lin, Y.-H., Zhang, H., Pye, H. O. T., Zhang, Z., Marth, W. J., Park, S., Arashiro, M., Cui, T., Budisulistiorini, S. H., Sexton, K. G., Vizuete, W., Xie, Y., Luecken, D. J., Piletic, I. R., Edney, E. O., Bartolotti, L. J., Gold, A., Surratt, J. D. and Ivan, R.: Epoxide as a precursor to secondary organic aerosol formation from isoprene photooxidation in the presence of nitrogen oxides., Proc. Natl. Acad. Sci. U. S. A., 110(17), 6718–23, doi:10.1073/pnas.1221150110, 2013.

Liu, J., Horowitz, L. W., Fan, S., Carlton, A. G. and Levy, H.: Global in-cloud production of secondary organic aerosols: Implementation of a detailed chemical mechanism in the GFDL atmospheric model AM3, J. Geophys. Res., 117(D15), D15303, doi:10.1029/2012JD017838, 2012.

McNeill, V. F., Woo, J. L., Kim, D. D., Schwier, A. N., Wannell, N. J., Sumner, A. J. and Barakat, J. M.: Aqueous-phase secondary organic aerosol and organosulfate formation in atmospheric aerosols: a modeling study., Environ. Sci. Technol., 46(15), 8075–81, doi:10.1021/es3002986, 2012.

Monge, M. E., Rosenørn, T., Favez, O., Müller, M., Adler, G., Abo Riziq, A., Rudich, Y., Herrmann, H., George, C. and D'Anna, B.: Alternative pathway for atmospheric particles growth., Proc. Natl. Acad. Sci. U. S. A., 109(18), 6840–4, doi:10.1073/pnas.1120593109, 2012.

Myriokefalitakis, S., Tsigaridis, K., Mihalopoulos, N., Sciare, J., Nenes, a., Kawamura, K., Segers, ~~a~~A. and Kanakidou, M.: In-cloud oxalate formation in the global troposphere: a 3-D modeling study, Atmos. Chem. Phys., 11(12), 5761–5782, doi:10.5194/acp-11-5761-2011, 2011.

Nguyen, T. B., Coggon, M. M., Bates, K. H., Zhang, X., Schwantes, R. H., Schilling, K. A., Loza, C. L., Flagan, R. C., Wennberg, P. O. and Seinfeld, J. H.: Organic aerosol formation from the reactive uptake of isoprene epoxydiols (IEPOX) onto non-acidified inorganic seeds, Atmos. Chem. Phys., 14(7), 3497–3510, doi:10.5194/acp-14-3497-2014, 2014.

Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kürten, A., St Clair, J. M., Seinfeld, J. H. and Wennberg, P. O.: Unexpected epoxide formation in the gas-phase photooxidation of isoprene., Science, 325(5941), 730–3, doi:10.1126/science.1172910, 2009.

Piletic, I. R., Edney, E. O. and Bartolotti, L. J.: A computational study of acid catalyzed aerosol reactions of atmospherically relevant epoxides., Phys. Chem. Chem. Phys., 15(41), 18065–76, doi:10.1039/c3cp52851k, 2013.

Pye, H. O. T., Pinder, R. W., Piletic, I. R., Xie, Y., Capps, S. L., Lin, Y.-H., Surratt, J. D., Zhang, Z., Gold, A., Luecken, D. J., Hutzell, W. T., Jaoui, M., Offenberg, J. H., Kleindienst, T. E., Lewandowski, M. and Edney, E. O.: Epoxide pathways improve model predictions of isoprene markers and reveal key role of acidity in aerosol formation., Environ. Sci. Technol., 47(19), 11056–64, doi:10.1021/es402106h, 2013.

Sareen, N., Moussa, S. G. and McNeill, V. F.: Photochemical Aging of Light-Absorbing Secondary Organic Aerosol Material, J. Phys. Chem. A, 117(14), 2987–2996, 2013.

Schwartz, S. E.: Mass-transport considerations pertinent to aqueous phase reactions of gases in liquid-water clouds, in NATO ASI Series, Vol. G6, edited by W. Jaeschke, pp. 425–471, Springer-Verlag, Berlin Heidelberg., 1986.

Sumner, A., Woo, J. L.-M. and McNeill, V. F.: Model Analysis of Secondary Organic Aerosol Formation by Glyoxal in Laboratory Studies: The Case for Photoenhanced Chemistry., Environ. Sci. Technol., 48(20), 11919–11925, doi:10.1021/es502020j, 2014.

Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R. C., Wennberg, P. O. and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene., Proc. Natl. Acad. Sci. U. S. A., 107(15), 6640–5, doi:10.1073/pnas.0911114107, 2010.

Tanner, R. L., Olszyna, K. J., Edgerton, E. S., Knipping, E. and Shaw, S. L.: Searching for evidence of acid-catalyzed enhancement of secondary organic aerosol formation using ambient aerosol data, Atmos. Environ., 43(21), 3440–3444, doi:10.1016/j.atmosenv.2009.03.045, 2009.

Volkamer, R., Ziemann, P. J. and Molina, M. J.: Secondary Organic Aerosol Formation from Acetylene (C_2H_2): seed effect on SOA yields due to organic photochemistry in the aerosol aqueous phase, Atmos. Chem. Phys., 9(6), 1907–1928, doi:10.5194/acp-9-1907-2009, 2009.

Waxman, E. M., Dzepina, K., Ervens, B., Lee-taylor, J., Aumont, B., Jimenez, J. L., Madronich, S. and Volkamer, R.: Secondary organic aerosol formation from semi- and intermediate- volatility organic compounds and glyoxal : Relevance of O / C as a tracer for aqueous multiphase chemistry, Geophys. Res. Lett., 40, 1–5, doi:10.1002/GRL.50203, 2013.

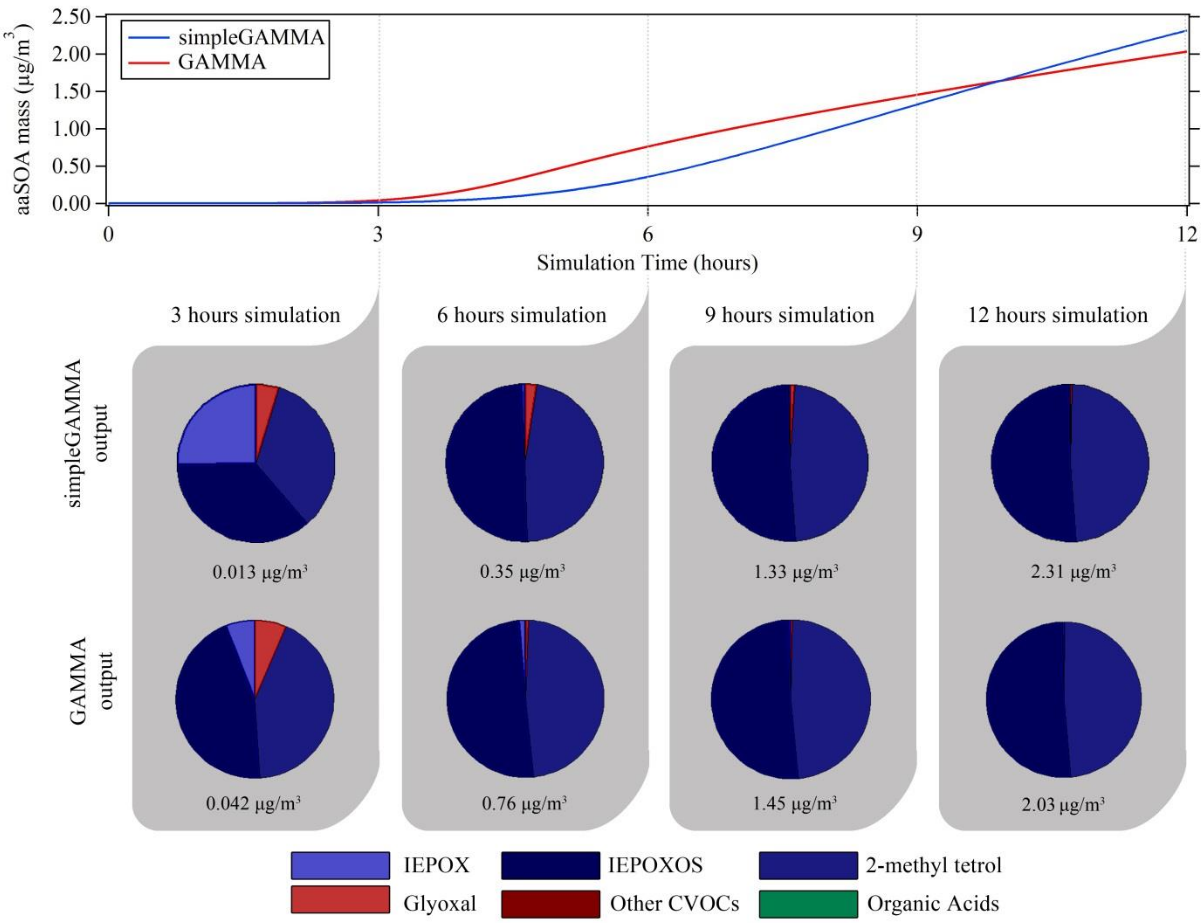
Whipple, E. B.: Structure of glyoxal in water, J. Am. Chem. Soc., 92(24), 7183–7186, doi:10.1021/ja00727a027, 1970.

Whitby, K.: The physical characteristics of sulfur aerosols, Atmos. Environ., 12, 135–159, doi:10.1016/j.atmosenv.2007.10.057, 1978.

Woo, J. L., Kim, D. D., Schwier, A. N., Li, R. and McNeill, V. F.: Aqueous aerosol SOA formation: Impact on aerosol physical properties, Faraday Discuss., 165, 357–367, doi:10.1039/c3fd00032j, 2013.

Table 1. Gas-aerosol mass transfer parameters in simpleGAMMA

Species	**Effective Henry's Law constant, H* (M/atm)**	**Accomodation Coefficient, α**	**References**
IEPOX	3×10^7	0.02	(McNeill et al., 2012; Nguyen et al., 2014)
GLYX	2.7×10^7	0.023	(Herrmann et al., 2005; Sumner et al., 2014)


aaSOA mass (µg/m^3)
2.50
2.00
1.50
1.00
0.50
0.00
simpleGAMMA
GAMMA
0
3
6
9
12
Simulation Time (hours)
3 hours simulation
6 hours simulation
9 hours simulation
12 hours simulation
simpleGAMMA output
GAMMA output
0.013 µg/m³
0.35 µg/m³
1.33 µg/m³
2.31 µg/m³
0.042 µg/m³
0.76 µg/m³
1.45 µg/m³
2.03 µg/m³
IEPOX
IEPOXOS
2-methyl tetrol
Glyoxal
Other CVOCs
Organic Acids

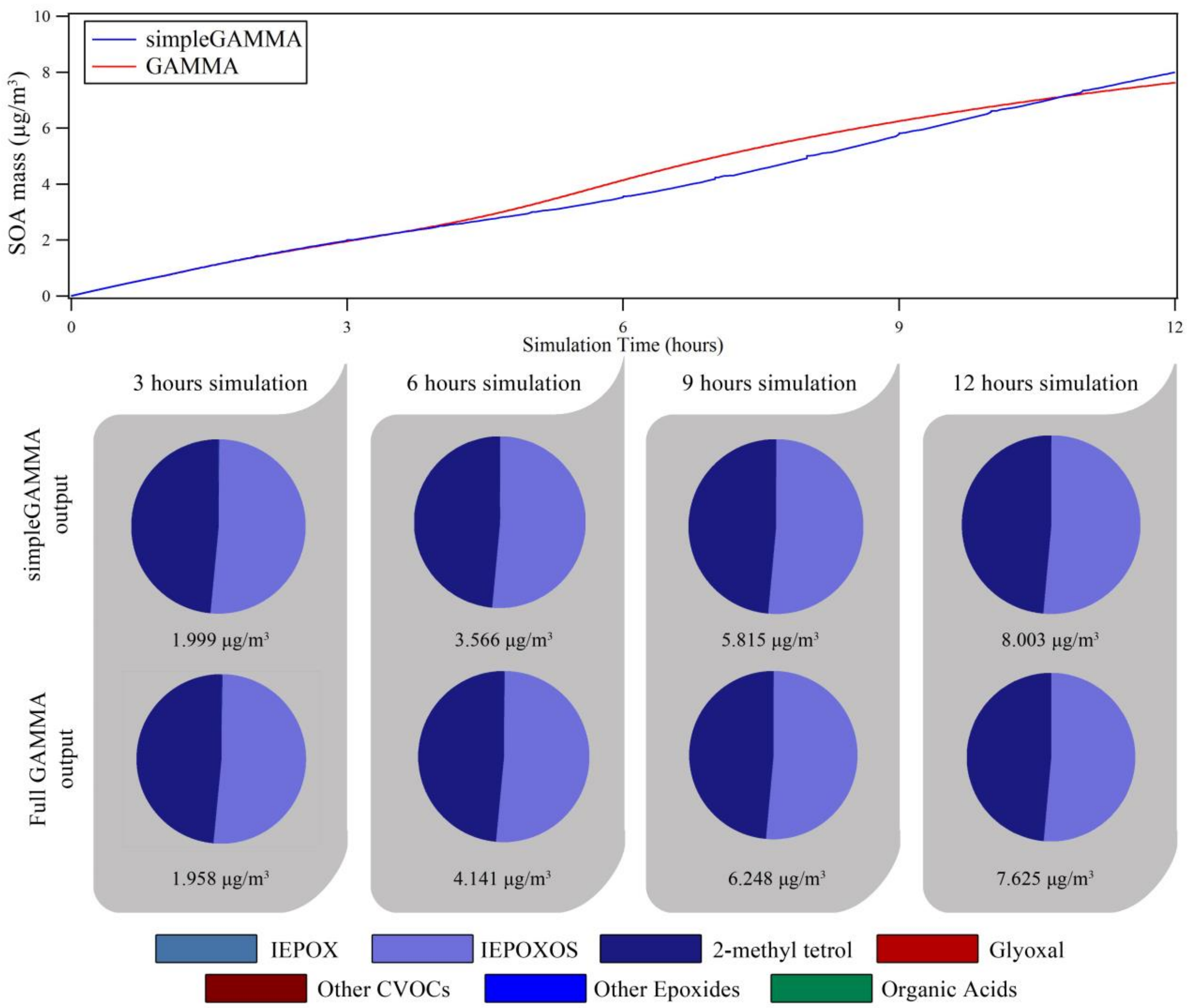


Figure 1. Comparison of simpleGAMMA and GAMMA under low-NOx conditions, ~~pH1~~pH 1, RH ~~65~~45%

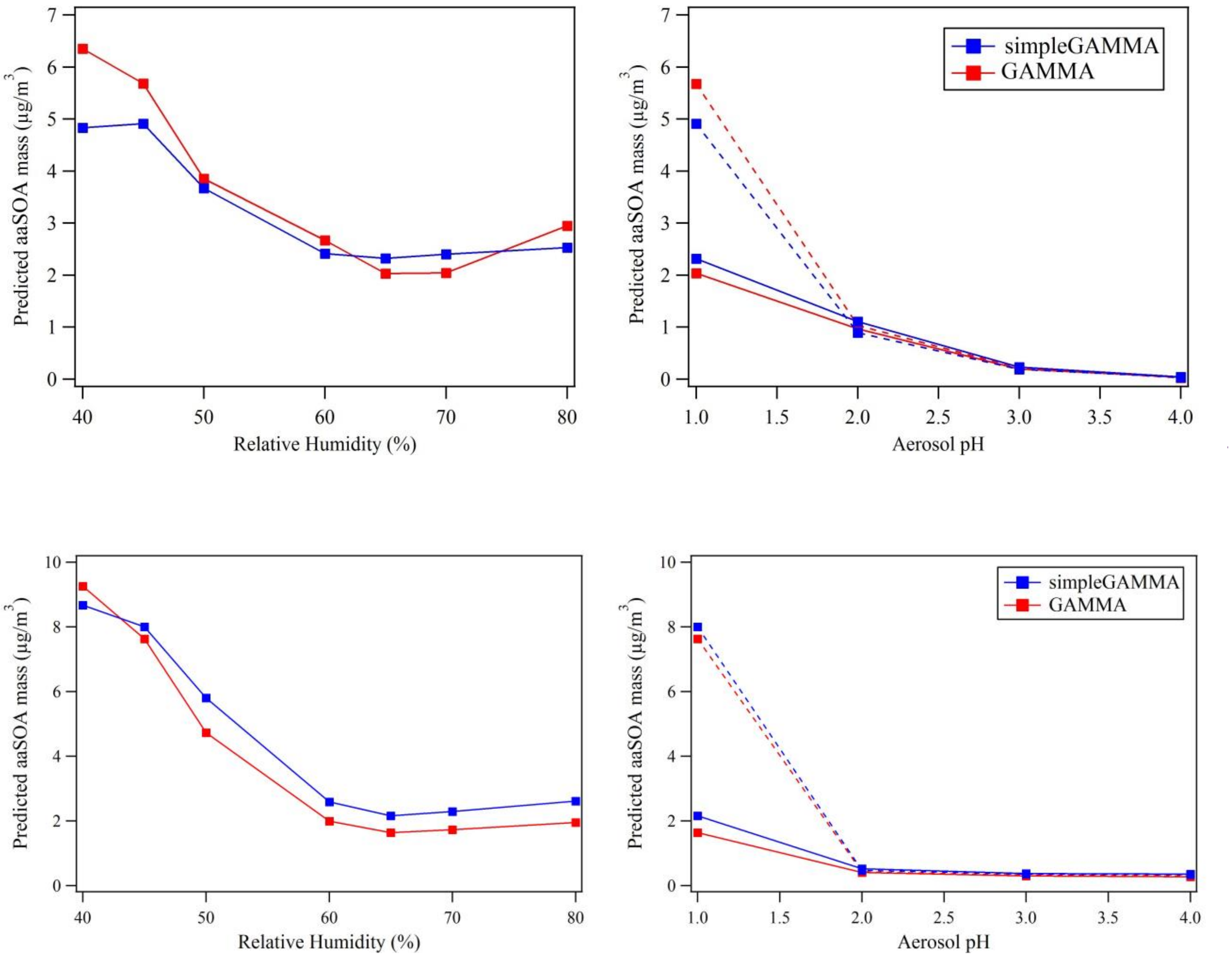
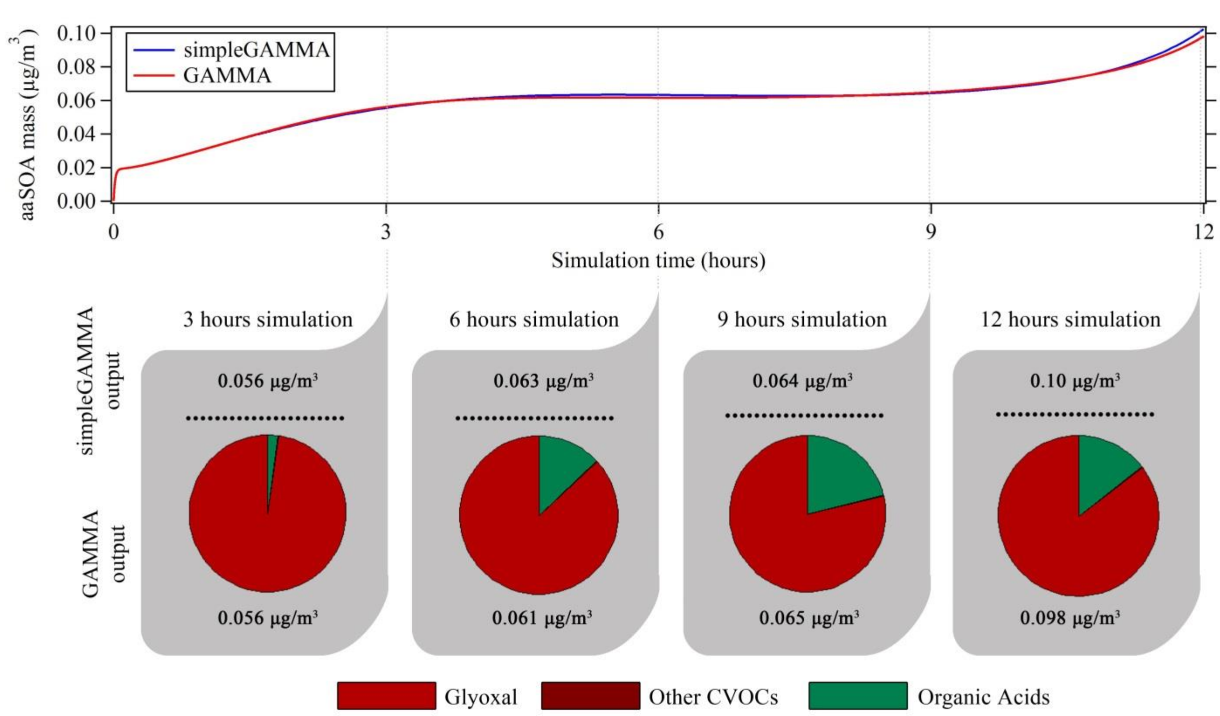


Figure 2. Comparison of predicted aaSOA after 12 hours of simulated time ~~as a function of~~ with respect to RH at pH 1 (left) and with respect to pH at 45% and 65% RH (right, dotted and solid lines respectively), low-~~NOx~~NOX conditions.


aaSOA mass (μg/m³)
0.10
0.08
0.06
0.04
0.02
0.00
simpleGAMMA
GAMMA
0
3
6
9
12
Simulation time (hours)
3 hours simulation
6 hours simulation
9 hours simulation
12 hours simulation
simpleGAMMA output
GAMMA output
0.056 μg/m³
0.063 μg/m³
0.064 μg/m³
0.10 μg/m³
0.056 μg/m³
0.061 μg/m³
0.065 μg/m³
0.098 μg/m³
Glyoxal
Other CVOCs
Organic Acids

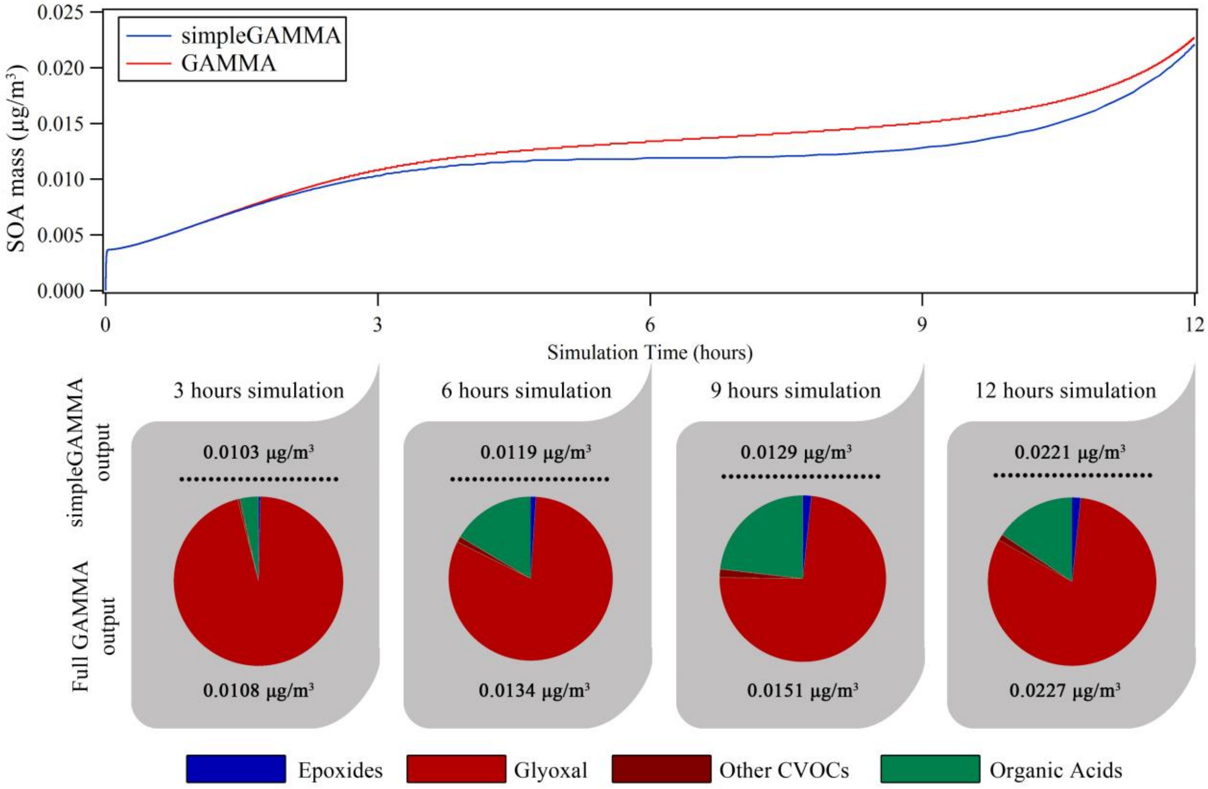
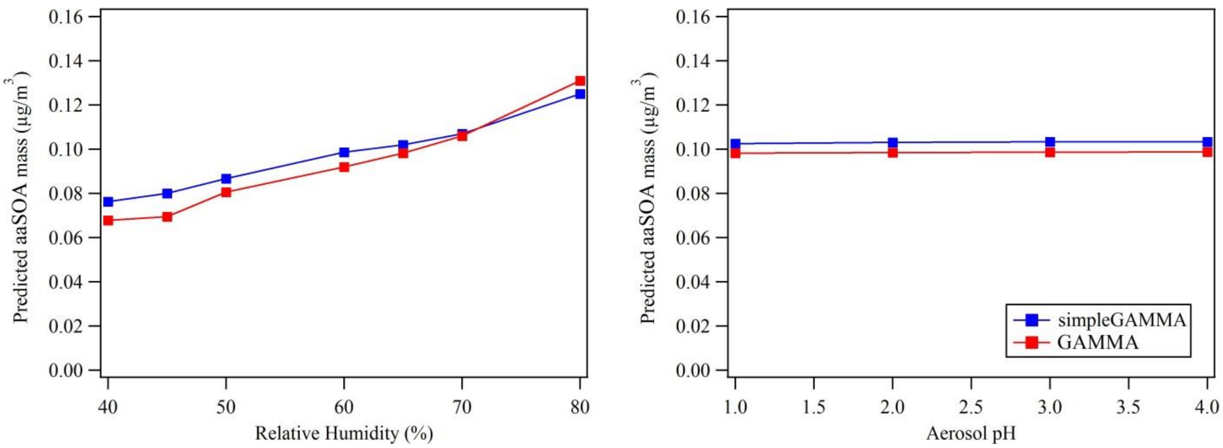


Figure 3. Comparison of high-NOx simpleGAMMA and the full high-NOx GAMMA, pH1, ~~RH65~~RH45.



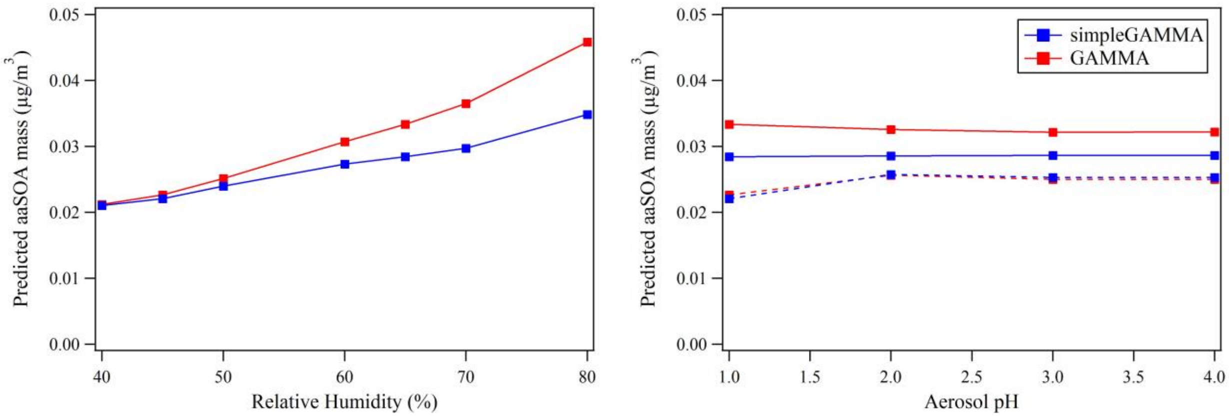


Figure 4. Comparison of predicted aaSOA after 12 hours of simulated time with respect to RH at pH 1 (left) and with respect to pH at 45% and 65% RH (right, dotted and solid lines respectively), high-NOx conditions.