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

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