

We thank the reviewer for his/her comments on our paper. To guide the review process we have copied the reviewer comments *in black italics*. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper (**in bold text**).

Anonymous Referee #3

Knote et al. implemented a number of SOA formation pathways from glyoxal into a regional model, used the model to simulate SOA formation over California, and compared model results to measurements during CARES/CalNex. They showed that the glyoxal SOA simulated by the various proposed production pathways can differ by a factor of 10. Key uncertainties include whether glyoxal SOA formation is surface-based or volume-based, whether it is reversible, and whether it is dependent on aerosol state

My initial response to the title of this paper was enthusiasm, as a thorough comparison between the different proposed pathways of glyoxal SOA formation and a comparison with high-temporal resolution measurements would be an important contribution to the current glyoxal-SOA debate. Unfortunately, the paper turn out to be much less informative. The most that can be drawn from the paper is that the glyoxal SOA simulated using the current proposed pathways differ by as much as a factor of ten. Well, if indeed the differences are that large between the pathways, surely the AMS measurements can tell us something about which one(s) are way out of the ball park? But this kind of information was not given in the paper. I recommend major revision to the paper before publication.

We thank the reviewer for his comments and hope we addressed them in a satisfactory manner.

Major comments:

R2.1 The implementation of different glyoxal-SOA formation pathways into the model is a major undertaking. However, the ways these pathways were implemented was confusing. I realize that some of these pathways have only been demonstrated qualitatively, such that key parameters are not available or highly uncertain. However, even the parameterization of the SIMPLE pathway contradicts lab results. For example (Page 26712, lines 7-8) the authors stated: "There is no experimental evidence so far to determine whether this surface uptake can also take place on aerosols of any phase state, or whether a liquid phase is necessary". This is not true, c.f. Liggio et al. (2005) (JGR, 110D11,). (I think the glyoxal-SOA formation in Stavrakou et al. (2009) and Fu et

al. (2008) both take place only on wet aerosols and on cloud droplets.) Here the authors applied SIMPLE glyoxal surface uptake to the dry aerosol surface, and not at all to cloud droplet surface.

Our statement that there is no experimental evidence for the surface uptake has been removed from the manuscript. The sentence mentioned by the reviewer (p 14, l 5-7) has been rewritten and now states:

There is evidence that the chemical composition of the seed aerosol could have considerable effect on the uptake coefficient (Liggio et al., 2005; Trainic et al., 2011), a fact that we did not include in our simulations due to the lack of an experimentally supported parameterization.

Also, the sentence on p 29, l 5-9 (Unless it can be shown in laboratory studies [...]) has been removed from the manuscript.

Unfortunately the reviewer does not provide any examples of what has been confusing to him/her in particular, so we were unable to further improve the manuscript in response to this comment. It is further unclear to us why our implementation of SIMPLE should “contradict lab results” - we implement a surface uptake on aerosol particles based on an uptake coefficient similar to Liggio et al., 2005; Volkamer et al., 2007; Fu et al., 2008; Trainic et al., 2011; Washenfelder et al., 2011 in a formulation commonly used in atmospheric modeling (e.g. Ervens and Volkamer, 2010). There is no mentioning in the manuscript that we use the dry aerosol diameter for available surface area. In fact, the wet diameter resulting from water uptake calculations in the aerosol module MOSAIC is used. We agree with the reviewer that this is not what is done in Fu et al., 2008, or Stavrakou et al., 2009, (where they apply it only to aqueous aerosols), but it is comparable to the imbalance calculations of Volkamer et al., 2007 or Washenfelder et al., 2011.

The manuscript has been updated to respond to reviewers suggestions:

In the abstract, the sentence on p 3, l 15-18 now reads:

Our results indicate that a mechanism based only on a reactive (surface-limited) uptake coefficient leads to higher SOA yields from glyoxal compared to a more detailed description that considers aerosol phase state and chemical composition.

On p 14, l 1-5 now reads:

This latter pathway was used in previous global (Fu et al., 2008; Stavrakou et al., 2009), regional (Li et al., 2013), and other model studies (Volkamer et al., 2007; Washenfelder et al., 2011; Waxman et al., 2013) for scenarios without explicit glyoxal gas-to-particle partitioning and particle-phase chemistry.

On p 14, l 20 ff:

[...] is parameterized as surface uptake, only depends on available aerosol surface area, and does not consider aerosol chemical composition. Here, we implemented it without consideration of the phase state of the aerosol to estimate an upper limit of SOA production from glyoxal. Notably, Trainic et al. 2011 observed that surface limited uptake was highest under conditions when only interfacial water was present, and reproduced surface uptake limited SOA formation rates reported in Liggio et al., 2005. The VOLUME case assumes that SOA is formed through [...]

On p 23, l 4 we corrected a mistake in the text (it did read “consider aerosol chemical composition” before)

In SIMPLE we do not consider aerosol phase state, which allows for constant SOA production as long as there is aerosol surface area available.

The purpose of our study was to investigate the importance of SOA formation from glyoxal in/on aerosols, and not cloud droplets. Several other studies (e.g. Carlton et al., 2008) already investigated this topic. We already addressed this topic in response to similar remarks by S. Y. Wang (C1.1) and Reviewer 1 (R1.1, R1.6).

R2.2 *There is no actual "validation" or "comparison" of model results against measurements. The comparisons between model and measurements were limited to meteorological fields, precursors concentrations, and a few aerosol parameters (e.g. other aerosol species). There is only one figure that compares the "BASE" OA simulation against measured OA. I am surprised that the authors did not show the OOA concentrations from the AMS and the glyoxal SOA simulated for comparison. How do the glyoxal SOA predicted by different pathways improve the simulated correlation with OOA and SO₄? These analyses might be more helpful in validating the different pathways.*

The entire section 3 of the manuscript is dedicated to evaluate the relevant modelled environmental parameters that can potentially affect the amount of glyoxal taken up into

aerosols and that have been measured during the simulation period and within the model domain. We give a quantitative description (Eqn. 7) of model performance and present a detailed comparison of the gas-phase precursors of glyoxal, its ambient concentrations, and its photochemical sinks. We do show comparisons against AMS measurements of both inorganic and total organic aerosol mass for surface measurements available (Figure 5). We consider this a sufficient evaluation of the modeling system, also considering that WRF-chem is not a new development but has been used in a vast number of studies, including the CARES/CalNex campaigns (see references in the manuscript, section 1, p 6).

We intentionally refrained from comparing against OOA from the AMS measurements for the following reasons: glyoxal makes a small contribution to total SOA over California. Direct measurements of glyoxal SOA products are necessary to provide an experimental constraint on the impact of glyoxal on SOA formation. Unfortunately direct measurements of particulate glyoxal reaction products are not available to our knowledge, and neither are dry deposition measurements. Thus those more direct comparisons are not possible at this point. Waxman et al., 2013 used the glyoxal-SOA impact on O/C as a tracer to compare with observations. This approach is unlikely to work in CA, where most SOA is formed via other mechanisms, and capturing SOA concentrations in models is notoriously difficult. The parameterization of non-glyoxal anthropogenic SOA used in our model is based upon a very simple parameterization of Hodzic and Jimenez, GMD, 2011, which is based on a fit to dilution-corrected ambient SOA observations vs photochemical age. Modeling the non-glyoxal SOA is expected to have differences with the measurements for a variety of reasons. If adding glyoxal SOA resulted in slightly better or worse comparisons at given times or locations, it would be difficult to extract any conclusions from such a comparison.

Thus, our results should be viewed as a sensitivity study of glyoxal. A new Figure 15 was added that describes that the potential for glyoxal-SOA formation is inhibited in CA due to the dry conditions, which lead to high particle viscosity (Kampf et al., 2013). The small SOA over CA is hence not because of a lack of potential to form SOA from glyoxal, but in large parts due to high viscosity/mass transfer limitations that do not apply in other parts of the country (e.g., Eastern US, see Figure 15). Several datasets are currently being generated over the Eastern US and will facilitate testing with our model. However, this is beyond the scope of this paper.

R2.3 The authors compared the measured and simulated glyoxal concentrations and stated that the SIMPLE parameterization overestimated the removal due to SOA formation. I would argue that, given the uncertainty in the photochemistry of glyoxal and its precursors, the differences between the glyoxal concentrations simulated by different

pathways shown here are trivial.

We reformulated why we think that SIMPLE potentially overestimates production of SOA from glyoxal (see response to comment R2.6). Our reasoning is not connected to a comparison between modelled and measured glyoxal concentrations, as we - just like the reviewer argues - fully acknowledge the difficulty to accurately represent glyoxal and precursor photochemistry. The discussion of Figure 14 (section 4.3.3, where we compare the effect of the aerosol sink on gas-phase glyoxal concentrations) is centered around the question whether different formation pathways (volume vs. surface) would lead to discernible changes in gas-phase glyoxal concentrations.

We do not consider the differences in gas-phase glyoxal shown here to be trivial at all, given that they

- * probe the relevance of electric effects that salts exhibit on SOA formation from multiphase chemistry, and the mass transfer limitations/viscosity effects on these rates of SOA formation in a 3D model
- * identify a strong West to East gradient in the relevance of glyoxal-SOA formation pathways.
- * provide guidance on where glyoxal-SOA impacts on aerosol bulk properties are expected, and could be tested by field campaigns in the future.
- * provide a link between the effect of the various parameterizations of the aerosol sink to a quantity that can be measured in field campaigns (i.e. gas-phase glyoxal).
- * give insight into the diurnal pattern of this effect. These diurnal patterns have been used in imbalance approaches to derive uptake coefficients (Volkamer et al., 2007) and to hypothesize about the nature of SOA formation from glyoxal (Waxman et al., 2013). Hence they allow other scientists to link their findings to our results.

Minor comments:

R2.4 1. Page 15, lines 20-22: "All cases except SIMPLE..., and in those no glyoxal SOA...": This sentence is confusing - please consider revising.

The sentence (p 15, l 20-22) has been rewritten, split into two, and now reads:

The aerosol phase state is calculated by the MOSAIC module at each time step. In all simulations, with the exception of SIMPLE, SOA formation from glyoxal is shut off if the aerosol is dry.

R2.5 2. Page 26703, line 20: "There is no previous study on glyoxal-SOA formation in a

3-D regional model.": a missing reference is Li et al. (2013), *Atmospheric Environment*, 76, 200-207, doi: 10.1016/j.atmosenv.2012.12.005

We thank the reviewer for pointing out this missing reference. Please refer to our response to reviewer 1 (R1.6) for an update to the sentence you refer to above.

We have also included the following sentence to the text on p 5, l 13-16:

Most previous studies did not consider aerosol properties other than surface area, or included reversible partitioning of glyoxal into deliquesced droplets. Li et al., 2013, investigated formation of SOA from deliquesced aerosols and cloud droplets on the regional scale in the Pearl River Delta with a simple surface uptake parameterization. Waxman et al., 2013, is the only study that [...]

Also we extended the listing of references on p 14, l 1-2, and p 14, l 20-22 to include Li et al., 2013:

This latter pathway was used in previous global (Fu et al., 2008; Stavrakou et al., 2009), regional (Li et al., 2012), and box model studies [...]

The SIMPLE case emulates previous modeling studies like Volkamer et al., 2007, Fu et al., 2008, Washenfelder et al., 2011 or Li et al., 2013, in which SOA formation from glyoxal is parameterized as surface uptake [...]

R2.6 3. Page 26725, lines 8-10: "The surface uptake coefficient finally was derived ...": The SIMPLE parameterization was not based only on mass-imbalance calculations, c.f. Liggio et al. (2005).

The manuscript has been revised at several points to reflect this (please also refer to responses R1.4 and R1.13). Additionally, paragraph 4.4 (p 27, l 8-26) has been removed as it did not provide new insights. The relevant information has been moved to the conclusions:

[...] exponential dependence of the rate constant. This is explained by the fact that, based on our current parameterization, the volume pathways are always limited by the availability of glyoxal in the liquid-phase, i.e. by the (time-dependent) increase in the Henry's law constant.

The SIMPLE simulation is based on chamber experiments and imbalance calculations, VOLUME only on laboratory results. HYBRID uses both, as do FAST

and FAST_PH. The latter two simulations are pure sensitivity studies, as there is no laboratory evidence so far to remove the kinetic limitation, and no basis to increase the pH value. Measurements of the effect of salts other than ammonium sulfate on the Henry's law constant of glyoxal are currently not available and would be desirable to further our understanding of glyoxal-SOA formation. Given that VOLUME is based on explicitly identified pathways we consider it a lower limit on SOA production from glyoxal. As the surface uptake in SIMPLE does not depend on particle properties and is active as soon as surface area is available, we can consider it an upper limit.

The effect of the aerosol sink on average gas-phase glyoxal concentrations in the LA basin ranges between 0 and 15%, with volume reactions [...]

R2.7 4. Some of the text in the figures are too small and illegible, e.g. Fig. 10, 12, and 13. Please consider revising.

We made sure that text in our figures is clearly legible at the size the figure will appear in the final manuscript. In case of the figures mentioned by the reviewer they are supposed to cover a full page width. In the online ACPD format, these figures are resized by Copernicus to fit the page height, which leads to a much less legible presentation than in the final manuscript.

Additional references used in the responses

Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S. P., Mathur, R., Roselle, S. J., & Weber, R. J. (2008). CMAQ model performance enhanced when in-cloud secondary organic aerosol is included: Comparisons of organic carbon predictions with measurements. *Environmental Science & Technology*, 42(23), 8798-8802.

Li, Nan, Tzung-May Fu, Junji Cao, Shuncheng Lee, Xiao-Feng Huang, Ling-Yan He, Kin-Fai Ho, Joshua S. Fu, Yun-Fat Lam, Sources of secondary organic aerosols in the Pearl River Delta region in fall: Contributions from the aqueous reactive uptake of dicarbonyls, *Atmospheric Environment*, Volume 76, September 2013, Pages 200-207, ISSN 1352-2310, <http://dx.doi.org/10.1016/j.atmosenv.2012.12.005>.

Trainic, M., Abo Riziq, A., Lavi, A., Flores, J. M., & Rudich, Y. (2011). The optical, physical and chemical properties of the products of glyoxal uptake on ammonium sulfate seed aerosols. *Atmospheric Chemistry and Physics*, 11(18), 9697-9707.