

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 #2

The authors have performed a detailed study of glyoxal contributions to SOA formation in California during CARES/CalNex using a version of WRF-Chem which they have updated for this purpose. The work should be suitable for publication in ACP after the following issues are addressed.

We thank the reviewer for his/her comments and hope we could address them in a satisfactory manner.

R1.1 - It is my understanding that cloudwater processing of glyoxal to form SOA was not considered in this study (this was confirmed on line 396 but should be made clear earlier in the manuscript). The authors should discuss the potential errors (or lack thereof) introduced by this choice. Could this contribute to the overestimation of glyoxal concentrations above 2000 m (line 381)?

We did not consider cloudwater processing (see also reply C1.1 to S. Y. Wang). To make it clear that we did not include it we have altered the introduction which now reads:

(p 4, l 13)

Recent studies further indicate that SOA formation in the aqueous phase may be important (Lim et al., 2010; Ervens et al., 2011). Here we investigate SOA formation from glyoxal in or on deliquesced aerosols. Glyoxal is the smallest dicarbonyl [...]

and (p 6, l 13)

Several pathways to form SOA from glyoxal within deliquesced aerosols were added, including reversible partitioning.

We agree with the reviewer that not considering this sink might contribute to the overestimation above 2000m and have correspondingly added a sentence at the end of the penultimate paragraph in section 3 (p 19, l 3):

[...] which would lead to a suppression of OH, and consequently to an underestimation of glyoxal concentrations. At least part of the overestimation above 2000 m may also be due to glyoxal consumption by SOA formation within cloud water (refer e.g. to Carlton et al., 2008), which we did not consider in this study.

The main sinks for glyoxal in the model are reaction with OH [...]

R1.2 - Line 16 – this statement is a bit misleading: “surface uptake is found to be the main contributor. . .” This sounds as if a glyoxal SOA formation mechanism that scales with aerosol surface area was shown to provide the best agreement with the field data, which I don’t believe was the case. Yes, the surface uptake mechanism was shown to result in higher yields of glyoxal SOA than the other pathways, and this may be what the authors meant to say. However, perhaps the emphasis on this mechanism should be reduced a bit, considering that in the conclusions of the manuscript (line 631-634) the authors state that, until additional experimental evidence exists to support this modeling approach, it may not be justified and models which rely on this mechanism may overestimate glyoxal SOA formation.

Indeed we intended to state that the surface uptake gives the highest SOA yields compared to the volume processes, for the range of parameterizations used in this study. We changed this paragraph of the abstract (p 3, l 15ff) so it 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. In the more detailed simulations, surface uptake is found to give the highest SOA mass yields compared to a volume process and reversible formation. We find that the yields of the latter are limited by the availability of glyoxal in aerosol water, which is in turn controlled by [...]

R1.3 - Line 19-20, abstract: This point is stated in such a way that it may be interpreted incorrectly. Glyoxal uptake at high salt concentrations is still high enough to be considered “substantial,” even if it no longer increases linearly with salt concentration due to kinetic limitations. No one would argue that an H^* of 10^{-7} M/atm is insubstantial.

The formulation in the manuscript has been imprecise. What hinders the substantial partitioning to the particle phase is the time dependence (“tau1” in the manuscript) of the increase in Henry’s law constants. We have rephrased this sentence (p 3, l 22-24) and it now reads:

A time dependence in this increase prevents substantial partitioning of glyoxal into aerosol water at high salt concentrations.

It is this time dependence that we remove in the FAST and FAST_PH sensitivity studies to investigate its effects.

R1.4 - Line 37-38 – *Quite a few seminal laboratory studies are missing from this list: Kroll et al. (2005), Liggio et al. (2005), Galloway et al. (2009), Volkamer et al. (2009). McNeill et al. (2012) doesn't belong in this list - it was a modeling study (see below).*

The list (p 4, l 15-18) has been adapted and now reads:

Laboratory measurements for glyoxal (Kroll et al., 2005; Liggio et al., 2005; Carlton et al., 2007; Noziere et al., 2009; Galloway et al., 2009; Volkamer et al., 2009) confirmed that it partitions into the particle phase [...]

R1.5 - Line 45 – *The box model simulations of McNeill et al. (2012) should be included in this list.*

The list of box modeling studies (p 4, l 24-25) has also been adapted and now reads:

Formation of SOA from glyoxal has been studied with steady-state box models (Volkamer et al., 2007; Lim et al., 2010; McNeill et al., 2012; Waxman et al., 2013) and [...]

R1.6 - Line 65-66 – *It's not correct to say there is no previous study of glyoxal-SOA formation in a 3D regional model. Formation of SOA by glyoxal via cloudwater processing has been modeled in CMAQ by Carlton and coworkers (studies which should be cited here). Perhaps what the authors mean to say is that SOA formation by glyoxal via aerosol phase processes has not been studied in a 3D regional model.*

Indeed this has been our intention. However, reviewer 2 also pointed out that the study of Li et al., 2013, already investigated formation within deliquesced aerosols on the regional scale, albeit only using a simple surface uptake (see response to R2.5). The sentence (p 5, l 20-21) has been rephrased and now reads

[...] and pointed out the importance of particle pH, and phase state for the rate of SOA formation from glyoxal. There is no previous study of glyoxal-SOA formation

within deliquesced particles incorporating these findings in a 3-D regional model.

The work of Carlton et al. is now cited as well (see response to R1.1).

R1.7 - Line 142 - *the authors should clarify what is meant by “inversion-based emissions”*

We refer here to the VOC/CO emission ratios derived in Borbon et al., 2013. The sentences (p 8, l 26-28) have been rephrased and now read:

Note that for acetone, benzene, and xylenes the emission amounts based on VOC/CO ratios from Borbon et al., 2013, are much higher than reported in CARB. Simulations made with these inversion-based amounts showed [...]

R1.8 - Line 163- *The way that this is worded, it sounds like uptake of glyoxal into particles in the model does not impact the gas-phase glyoxal concentration. I don't believe that this is the case after reading section 4.3.3., so some clarification may be in order. If this is the case, please justify*

Gas-phase glyoxal concentrations are indeed affected by the aerosol sink. We have rephrased the sentence (p 9, l 19-20) and added another one, so that the paragraph now reads:

Glyoxal is removed from the atmosphere by photolysis, OH oxidation, dry deposition and through partitioning into aerosols. A detailed description of the aerosol sink for glyoxal follows in section 2.3.2, and the reader is invited to consult Figure 14 showing the effect of this sink on gas-phase glyoxal concentrations. A constant dry [...]

R1.9 - Line 189 – *“There is no clear scientific consensus on how glyoxal might form SOA.” This is an overstatement. SOA formation by glyoxal has been one of the most intensely studied topics in atmospheric chemistry over the past 8 years or so. The scientific community knows quite a lot about its mechanisms, and there are only a few points of controversy.*

We would agree with the reviewer's suggestion if the topic of this work was cloud water. But we disagree with the reviewer on this point since our paper deals with aerosol water. It is true that SOA formation from glyoxal has been a topic of increasing interest over the past 8 years, with extensive work on bulk laboratory and smog chamber studies as well as (indirect) observational evidence in the field. However, there is still very limited work done

in actual aerosols. In fact, it is one of the main points we try to make in our work, that there are fundamental assumptions that still need to be made to implement this knowledge into models. When we compare the different proposed mechanisms we find SOA production differs by a factor of 15. If there would be consensus, there would not be controversy whether a surface or a volume process (or both) is actually dominating. Furthermore, the efficiency of the surface uptake, the increase in Henry's law constants, the effects of mass transfer limitations/viscosity are all based on very recent experimental data that has only been evaluated using model aerosols / bulk solutions and understanding of their dependence on environmental parameters (like aerosol components like organics, nitrate, sodium chloride; acidity; dependence on photochemical processes) is still topic of current research.

R1.10 - *Line 193 - What does "interactions between irreversible and irreversible formation pathways are still unknown" mean? These pathways simply interact via their competition for glyoxal monomer in the aqueous phase.*

It was our intention to point out that we don't know whether dimers and oligomers are accessible to the irreversible reactions (instead of only non-hydrated monomers). The sentence has been removed, as the topic is mentioned later on (p 13, l 8ff) in a more concise manner.

R1.11 - *Fig 3 – please change the quotation marks on "salting-in" to the English style.*

The quotation marks have been changed as requested.

R1.12 - *Line 234 – The ammonium-catalyzed pathway presented by Noziere et al. and related studies such as Galloway et al. (2009) has been observed to be reversible. The authors should provide a rationale for treating it as irreversible here and mention it in the text.*

The ammonium-catalyzed formation rate of oligomers is implemented according to Noziere et al., J. Phys. Chem., 2009, where they show an irreversible reaction (quotations from this work in green italics): "[...] *the kinetic studies in this work were based on absorption of a product at 209 nm (Figure 2).*" (Noziere et al., J. Phys. Chem., 2009, p. 232, left column, "Experimental section" 2.), and "*Rapid formation of the band at 209 nm evidenced an irreversible step, [...]*" (Noziere et al., J. Phys. Chem., 2009, p. 233, right column, "Results and Discussion" 1.b). It is unclear whether the products observed in Noziere et al., 2009 are indeed the same as those observed in Galloway et al., 2009.

p 26711 | 8ff has been extended, and now reads:

The relationship between reversible and irreversible pathways is not well understood. On one hand, assuming that the ammonium-catalysis channel forms only irreversible products probably represents an upper limit estimate of the SOA formed from this volume process. On the other hand, reversibly formed oligomers do not evaporate easily; in fact the oligomer formation may even be accelerated as the concentration of monomer building blocks increases during the water evaporation process (De Haan et al., 2009). Furthermore we assume that the total concentration in the monomer pool, which includes hydrated forms, is the only particulate glyoxal concentration available to the ammonium-catalyzed reaction. In practice also other forms of reversibly formed oligomers may be available for the ammonium-catalyzed reaction.

The OH pathway is [...]

R1.13 - Line 256 – *The authors need to offer more insight into the physical underpinning of the photochemical surface uptake mechanism for glyoxal. Without any insight into the nature of this uptake, it's impossible to evaluate the modeling approach or know whether or not it is appropriate to extrapolate parameters derived from chamber studies to the environment. A speculative list of plausible physical mechanisms that could motivate this modeling approach, but which need further study, would be sufficient.*

The reference to Ervens and Volkamer, 2010, on p 13, l. 20, was erroneously kept in the text from an older version of the manuscript. It is important to note that the way the surface uptake has been parameterized in Ervens and Volkamer, 2010, is different from our approach. We do not consider it to be dependent on photochemistry / OH concentration, as was clarified by Kampf et al., 2013. We have hence modified this sentence which now reads:

The third irreversible pathway describes a surface uptake as [...]

Furthermore, the symbol used to denote the uptake coefficient (γ_{phot}) has been changed to only γ to reflect this.

The physical underpinning of the surface uptake in our manuscript is hence based on textbook knowledge about collisions between molecules and particles ($0.25 \cdot A \cdot \omega \cdot \text{Gly}_g$) and a “catch-all” probability (γ) that the glyoxal molecule is lost to the particle. We assume here that γ is the probability of an irreversible uptake of glyoxal on particle surfaces of any kind, and not e.g. as part of a quasi-equilibration between gas and particle phase (e.g. Langmuir-type adsorption).

We added a sentence to section 2.3.2 (p 14, l 5ff) to clarify this point:

This latter pathway was used in previous global (Fu et al., 2008; Stavrakou et al., 2009), regional (Li et al., 2012), 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. γ here represents the probability of an irreversible reactive uptake of glyoxal into the particle. 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 backed parameterization.

We also more clearly defined the nature of the uptake coefficient in p 26701 l 15-16:
Our results indicate that a mechanism based only on a reactive (surface limited) uptake coefficient, [...]

R1.14 - Line 505 – “constant” should probably be “content”

Changed accordingly.

R1.15 - Line 526 – “. . .40% of glyoxal. . .” I think there is a word missing here. SOA?

Thank you for this catch. Yes, it was missing. Now reads (p 24, l 23-26):

If we assume that gas-particle partitioning of glyoxal has no time dependence (instantaneous equilibration, FAST simulation), then the contribution of volume pathways increases notably, now forming about 40 % of SOA from glyoxal in LA and 20 % in ESCV.