

Interactive comment on “Glyoxal processing outside clouds: towards a kinetic modeling framework of secondary organic aerosol formation in aqueous particles” by B. Ervens and R. Volkamer

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We thank the reviewer for his/her considerate and careful comments that helped to clarify and improve several sections of the manuscript. We respond in detail to all comments below.

General Comments: The authors have done an extensive literature search. They have characterized and synthesized theory, laboratory results and modeling approaches well and bring them together in important and meaningful ways. Their assertion that ob-

C5108

served O:C ratios in ambient SOA can be explained by models considering these processes is a crucial point. This is an important paper and I recommend it for publication in Atmospheric Chemistry and Physics. The authors should consider the following comments.

Specific Comments: Reviewer comment 1.) Abstract: line 10 Processing in aerosol particles yields 2-3 orders of magnitude more SOA than dilute cloud droplets. Do the authors mean more SOA mass for a particular time period, or for the lifetime of an atmospheric particle versus the lifetime (or contact time) of a cloud droplet? Is this true in urban and remote environments? This should be clear in the abstract.

Response: We agree that this statement in the abstract was misleading. The fact, we tried to express referred to Figure 4 in the manuscript. We reworded the text in the abstract ‘These additional aqueous phase processes enhance the SOA formation rate in particles and yield two to three orders of magnitude more SOA than predicted based on reaction schemes for dilute aqueous phase chemistry for the same conditions (liquid water content, particle size)’.

Reviewer comment 2.) Units and explanations for the various terms in all of the equations would be helpful, in particular because of the combination of gas- and aqueous-phase terms which makes balancing units complicated (e.g., Eqn 10 in section 3.1).

Response: We have added units to the variables in all equations or in the explanations right below the respective equations. In addition, we added a list of all reaction parameters, together with their units, at the end of the manuscript (‘Appendix’).

Reviewer comment 3.) As the authors mention, SOA in atmospheric models typically consider only absorptive partitioning. In general, these models neglect adsorption of semi-volatile material. Adsorption is proportional to available particle surface area. Can the authors describe their results that demonstrate a dependence on particle surface area in the context of adsorption? Would adsorption be insufficient to explain all results?

C5109

Response: We did a rough 'order-of-magnitude' estimate in order to check if adsorption, i.e. the formation of a monolayer of glyoxal on the particle surface, could explain the main fraction of observed glyoxal uptake and particle growth. Assuming a size of a glyoxal molecule of 7 \AA^2 and an average surface area of the aerosol distribution of $\sim 500 \text{ microm}^2 \text{ cm}^{-3}$ in the experiments by Volkamer et al., (2009) (cf Figure 5c), it can be calculated that $500 \text{ microm}^2 \text{ cm}^{-3} / 7 \times 10^{-8} \text{ microm}^2 \text{ cm}^{-3} = 7.1 \times 10^9 \text{ cm}^{-3}$ (or $0.7 \text{ microg m}^{-3}$ SOA) correspond to a monolayer of glyoxal on the particle surface. The observed increase in SOA mass was on the order of $\sim 3\text{-}20 \text{ microg m}^{-3}$ (assuming a SOA density of 2 g cm^{-3}) and thus about 4-30 times higher than a monolayer would suggest. Beyond a monolayer, it can be assumed that glyoxal partitions into the new layer which can be characterized as absorption instead of adsorption. In addition, it is likely that glyoxal – which is highly water-soluble – indeed partitions into the aqueous phase of particles which is corroborated by the correlations in Figure 5a. For most seeds, we do not see any evidence of a surface-controlled uptake for any seed other than ammonium-sulfate (cf Figure 5c) and thus we conclude that such pathways do not dominate SOA formation.

Reviewer comment 4.) An important and useful aspect of equation 10 is that it removes the need to define certain particle parameters (e.g., radius of the H₂O part only, surface area) which are difficult to accurately calculate and typically not characterized well in atmospheric models. This makes Equation 10 appealing to atmospheric modelers and the authors may want to highlight this point.

Response: We highlighted this advantage in Section 3.1 and pointed it also out in the abstract that this equation might be a considerable simplification. However, it should be cautioned that it might oversimplify the presentation of glyoxal particle phase reactions and its application needs to be evaluated for a wider parameter range such as systematic investigation of composition effects.

Reviewer comment 5.) Equation 10: The authors' work demonstrates an increase in predicted SOA mass when there is increased liquid water available (high LWC).

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Equation 10 as written shows $d[\text{SOA}]/dt$ inversely proportional to LWC. This is not intuitive.

Response: The reviewer is right. The equation had been wrongly written (though correctly applied). We have corrected the equation in the manuscript that reflects now based on the laboratory studies that no dependence on the LWC can be seen and we suggest in the text the possible catalytic role of ammonium sulfate in the observed glyoxal uptake experiments. – We caution its general application to other seeds as we cannot evaluate these catalytic processes any further based on the sparse data sets.

Reviewer comment 6.) In Section 4.1, the authors apply the same uptake parameters to dilute and highly concentrated solutions. Can the authors provide an estimate of whether in highly concentrated "solutions" the uptake would be higher or lower, that is, does this approximation provide a higher or lower bound?

Response: Unfortunately there is no literature that gives values for mass accommodation coefficients γ as a function of solute concentration (ionic strength). However, there are studies that show that the reactive uptake coefficient γ of various gases increases with increasing solute concentrations of different salts (Davidovits et al., Chem. Rev. 2006 and references therein). γ combines both physical processes (mass accommodation) and chemical loss processes in the aqueous phase. An increase in γ is usually explained by additional aqueous phase processes of the trace gas but contributions of an enhanced α on concentrated solute surfaces cannot be excluded. Based on literature data it cannot be decided if also this physical process of mass accommodation (α) is additionally affected by ionic strength. We added a sentence at the end of Section 4.1. to point out this uncertainty.

Reviewer comment: Minor Technical Comments: Figure 6: the maximum value in the y-axis for panels "c" and "e" is half that of the other panels and for "f" and "g", each y-axis is orders of magnitude different. Can authors make the y-axes the same, or put a note in the figure caption?

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Response: We have changed the axes in figures 6c and e to be the same as 6 a, b, d. In addition we added a note in the figure caption to point out the log scale in Figures 6 f and g. We have changed the layout of Figure 6 by presenting Figures 6f and g in a separate panel to make clear their differences (only dark reactions; results presented on log scale) to the rest of the figure.

Reviewer comment: Figures 3 and 7 would be easier to read and interpret in color.

Response: The new Figures 3 and 7 are in color. In addition, we added explanatory panels to Figure 3, and added the absolute masses to the legend of Figure 7.

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