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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Global modeling of SOA: the use of different mechanisms for aqueous phase formation" *by* G. Lin et al.

Anonymous Referee #1

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This manuscript presents results from global modeling studies in order to explore the role of secondary organic aerosol formed in the aqueous phase of clouds and aerosol particles (aqSOA). Several approaches for the description of aqSOA formation are applied based on past laboratory and/or model studies. The results are compared to each other and to observations. SOA comprises a large fraction of total particulate matter in the atmosphere; however, current models cannot fully reproduce its total burden properties and spatial and temporal evolution. Several contemporary models include descriptions of varying complexities to predict formation of SOA by condensation of semivolatile gas phase species. However, the role of the formation of aqSOA has not been comprehensively evaluated yet on a global scale, even though many recent laboratory, field and model studies suggest its potential importance. The current study

tries to fill this gap by using a global model. While I appreciate the effort in extending a global model by explicit and detailed chemistry, I think that many conclusions drawn from these calculations represent overstatements. Given the numerous uncertainties in our current understanding of aqSOA formation in both cloud and aerosol water, I do not think that a detailed comparison to observations is particularly meaningful and any agreement between observations and model could be easily a 'right answer for the wrong reasons'. In addition, there seem to be numerous misunderstandings in interpreting reaction parameters as used in the applied aqSOA mechanisms; these affect the predicted aqSOA net formation rates and thus the interpretation of the results. The value of a model study as performed here is to reveal the great inconsistencies that exist based on different aqSOA schemes. The results should not be used to claim 'realistic aqSOA predictions' but rather to discuss parameters that most sensitively affect predicted aqSOA rates and thus should be focus of future lab and field studies. If the tone of the paper can be changed in this regard and if my comments below are addressed, this manuscript might have the potential to become a useful benchmark in the current SOA model literature.

Major comments

1) One of the main conclusions of the study should be that an uptake coefficient ('gamma' for surface-limited process) leads to vastly different results than explicit chemistry. While this is hinted at, reasons for these discrepancies are not fully discussed. Does this mean that deriving gamma in lab studies is not useful? Is there any way to use a single parameter instead of an explicit chemistry scheme? Does the derived uptake parameter of ∼1e-5 (Section 3.3) indeed lead to the total and spatial aqSOA burden as predicted by the explicit scheme or merely to the same total SOA mass? If not, what does it tell us about the applicability of any gamma?

2) The comparison of Case 1 and Case 4 (different cloud liquid water fields) reveals great differences in predicted aqSOA. Some more quantitative remarks on the uncertainties in predicting cloud properties vs predicting aqSOA should be given.

3) Any observation-model comparison should be discussed more cautiously. As pointed out above, I do not think that comparing absolute numbers is useful, but rather relative trends should be discussed. Given the great uncertainties in terms of aqSOA mechanisms and cloud properties, I think that currently a 'good agreement' between observations and model prediction should be considered as being fortuitous instead of claiming a robust understanding of the underlying processes.

4) Most of the aqSOA formation and loss rates, as used in the explicit scheme, depend directly on the concentration of the OH radical in the aqueous phase (OHaq). The difference between Case 1 and Case 5 is the inclusion of Fe chemistry that significantly increases the OHaq concentration. Even though a number of OHaq reactions is included in the model, they likely only comprise a very small number of OHaq sinks in 'real' atmospheric water since the total water-soluble organic carbon mass includes hundreds of different compounds (a small fraction of which can usually only be identified). In order to discuss these effects, predicted OHaq levels should be presented (e.g. as an additional panel in Figure 5) and compared to data derived based on measurements, e.g. by Arakaki et al.(2013)

5) The approach in Case 1 double-counts several processes. (i) The gamma values were derived from laboratory studies based on the loss rate of glyoxal (or related compounds). This loss rate is equal to the (absolute) net production rate of oligomers, and organic acids (and other products). Thus, including OH chemistry AND gamma values is not consistent since all uptake processes and chemical reactions (including organic acid formation and loss) are captured by the measured gamma values. (ii) In Table S3, the reaction of GLYX+OH (R1) is included, in addition to the lumped reaction (R25). This approach double-counts the loss of glyoxal in the aqueous phase. If both reactions are to be kept in the mechanism, a branching ratio should be estimated and the sum of both rate constants should amount to the measured, recommended value as cited for R1.

6) Several studies suggest that oxalate and related carboxylates are present as (moderately or poorly) soluble salts or stable complexes in aerosol particles, e.g. Furukawa and Takahashi (2011). This means that oxalate in aerosol water might not be readily oxidized by OHaq but present as insoluble fraction. While I admit that not sufficient information might be available to fully include such effects in a model, uncertainties in terms of oxalate sinks and reservoir should be at least discussed.

7) Several model studies, e.g., Lim et al., (2010 and references therein) have shown that oligomers are not stable and decrease over time, likely due to further oxidation by OHaq. Neglecting their further oxidation, as done in the current study (cf p. 29644, l. 15), leads to an overestimate of their mass. Given that kinetic data are available, I suggest including their photochemical loss.

8) Using the explicit scheme, the loss of oxalate by OHaq will strongly depend on the pH value (R4-6 in Table S3). How is pH predicted in the current model and how does it compare to observations (or any measured proxy for pH, e.g. NH4/SO4)? Could differences in predicted pH also explain (part of) the differences between the current and previous model studies?

9) The uptake rates of both oxidants (OH, NO3) and organics from the gas into the aqueous phase will depend on the available surface area, both if the explicit chemistry scheme and the 'gamma approach' are used. For simplicity, an average cloud droplet size of 10 um is assumed (p. 29638, l. 3). For aerosol, it is not even clear whether a single size or a wet size spectrum is applied: It is stated that the 'effective radius' is calculated for sulfate aerosol. In radiation calculations, 'effective radius' usually refers to the ratio of the third to second moment of a size distribution, i.e. a single size characterizes the population. Is this really what you mean or is 'effective radius' here simply the 'wet radius' based on relative humidity and hygroscopicity? In any case, ideally the potential sensitivity or uncertainty in predicting realistic wet particle and cloud drop size distributions (also in the context with comment 2) and its impact on aqSOA prediction should be pointed out.

Specific comments

Abstract: It should be made clearer that all numbers refer to 'predicted' masses etc.

p. 29632, l. 5: Organic acids, such as oxalic, by itself have a fairly high vapor pressure. However, their salts have a sufficiently low vapor pressure to keep them in the condensed phase.

p. 29632, l. 20: Do you mean 'most abundant'? Or most important 'for what'?

p. 29632, l. 24f: This sentence seems somewhat out of place or redundant. The formation of aqSOA from MVK and MACR occurs via oligomerization or formation of other products that have been discussed in previous sentences.

p. 29633, l. 25: In the study by Ervens and Volkamer (2010), a surface-dependence for mixed sulfate/organic seed particles was found. Such particles are likely the best proxy for ambient particles, as opposed to particles composed of a single compound.

p. 29634, l. 5: Not really clear what 'in addition' refers to here. Maybe it can be just deleted.

p. 29635, l. 17: In many of these lab studies, the reaction mechanisms are derived based on detailed product studies and temporal concentration profiles. I suggest changing 'estimate' to 'derived' or 'developed'.

p. 29636, l. 8: Is the wet or dry surface of sulfate aerosol used to predict epoxide formation?

p. 29636, l. 10: Why is the used mechanism the 'most realistic one'?

p. 29639, l. 5: This is a quite bold statement. I suggest replacing 'generally' by 'relatively'.

p. 29639, l. 23: There is a huge body of literature that suggests that the Henry's law constant of glyoxal (and likely related compounds) is strongly enhanced in aerosol

water, e.g. (Kroll et al., 2005; Volkamer et al., 2009). Many laboratory studies, e.g. (Lim et al., 2010), for aqSOA formation in aerosol water are performed for high glyoxal concentrations ($\sim$ mM) that can be only achieved with such enhanced 'effective Henry's law constants'. Are any of such effects taken into account in the present study?

p. 29640, l. 13: Is there a threshold for LWC above which aqSOA in aerosol water is considered? I.e. do you mean 'deliquesced' by 'aqueous' here?

p. 29641, l. 8: This is ambiguous: Do you really predict (methyl)glyoxal concentrations based only on Henry's law or is the full kinetic uptake described (as stated earlier in the manuscript)?

p. 29642, l. 11f: Does this mean that only 0.00175% (3.5% * 5%) of dust aerosols contribute to dissolved iron? Are the resulting predicted iron concentrations comparable to measured ones in cloud water?

p. 29647, l. 12: This is not a comparison to the 'real atmosphere' but a model-model comparison.

p. 29648, l. 6: Does the lifetime of oxalate referred to here only describe its lifetime with regards to deposition? Depending on pH and OHaq (and Fe) levels, its chemical life time might be much shorter.

p. 29649, l. 1ff: Can you quantify the relative contributions of the OH reaction vs Fe-complex photolysis for oxalate destruction? How do these proportions compare to recent findings by Sorooshian et al. (2013)?

p. 29649, Section 3.6: This section is extremely vague and at most qualitative and does not add much to our understanding of uncertainties or underlying mechanisms of aqSOA formation. It should be updated and improved in light of my numerous comments in this review regarding uncertainties in the assumed aqSOA approaches.

p. 29652, l. 26: While on a different scale, there are numerous process model studies available that report detailed oxalate and LWC measurements, together with oxalate predictions, e.g., (Sorooshian et al., 2006; Wonaschuetz et al., 2012)

p. 29653, 1st paragraph: What is the predicted ratio of aqSOA/total SOA?

p. 29254, l. 8: Not clear. I assume you do not compare to measurements during pre-industrial times (?)

p. 29655, l. 26: What is the highest and lowest O/C ratio among the 26 SVOCs? How much variability would either limit introduce to the predicted overall O/C?

p. 29657, l. 25: Such a missing oxalate source was also suggested by Rinaldi et al. (2011)

p. 29657, l. 28: Add here that also the understanding of oxalate sinks and reservoirs (e.g. salts) needs to be improved.

Table 1: Case 1: This is not clear. Isn't the gas/particle transfer described by the kinetic approach? This, of course, does include Henry's law constants but would also account for possible 'non-equilibrium' situations.

Table 3: Caption should be improved: "Predicted global average production rates by individual reactions . . ." (or similar)

Table 5: Should that be 'aqSOA' in the caption?

Figure 2: Aren't these plots the same for all Cases except Case 4? Or is there any feedback between chemistry and LWC?

Figure 6: How do the results by Myriokefalitakis compare to your predictions? Can they be added to the figures in order to show if there is a systematic or random difference between model predictions?

Table S3 and S4: The products of GLY, MGLY, and PRV with NO3 are not discussed in the paper by Herrmann et al. (2005). While I assume that there is no study that reports them, a comment (footnote) should be added stating that they have been assumed to

be identical to those of the OH reaction.

Table S4, R1 and R3: As written, it suggests a second order rate constant. The original value by Creighton is expressed as first order rate constant. Is this accounted for in the reaction scheme used here? If so, '+ H2O' should be set in parentheses.

Technical comments

p. 29632, l. 20: to be part

p. 29632, l. 22: Add 'water' after 'cloud' (otherwise it might also include interstitial air)

p. 29633, l. 23: ..there IS still a range

p. 29635, l. 9: Should that be 'of SOA' or are you saying that in the new model, SOA can actually condense on both sulfate and SOA particles?

p. 29638, l. 26: remove 'from'

p. 29640, l. 19: Define MW

p. 29642, l. 2: in the Supplement

p. 29648, l. 25: 'Fe(III) complexes'. (Fe(III) salts are not photolysed)

p. 29650, Section 4: If the authors find a meaningful way to compare their model results to observations and decide to keep this section, I suggest dividing it into multiple subsections (e.g. 4.1. Oxalate; 4.2 AMS or PM measurements; 4.3 O/C ratio)

p. 29657, l. 8: dominates

p. 29657, l. 14: Overall

p. 29658, l. 7: two tropical

- Supplement: Check all super- and subscripts (e.g. Table S2, R10, R33; Table S4, R43-45) - Table S2: Column header: K298 (Mn S-1) should be replaced by k298 (Mn s-1) - Table S2, R51 seems wrong (charge balance)

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