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Interactive comment on “In-cloud oxalate formation in the global troposphere: a 3-D modeling study” by S. Myriokefalitakis et al.

Anonymous Referee #2

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The authors present a global model study to predict oxalic acid (oxalate) mass that is formed in the aqueous phase of cloud droplets and aerosol particles. The role of formation of aqueous phase processes for secondary organic aerosol (SOA) formation has gained increasing attention over the past years; however thorough comparisons to other SOA sources on large scales are scarce. The current model study tries to close this gap and provides a first estimate of the global oxalate budget. The authors perform comparisons with observations and show that the predicted oxalate masses are quite reasonable. As an explorative model study, it definitely falls into the scope of ACP. However, I have several comments that need to be addressed in order to justify assumptions made in the chemistry module that directly impact the predicted oxalate masses.

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General comments:

1) The average predicted oxalate fraction of 13-19% of the total organic carbon seems huge. In order to justify this number - comparisons of oxalate/sulfate, oxalate/SOA (or WSOC) and oxalate/OC should be presented in addition to the results in Figure 5.

- it should be clarified what the predicted OC includes, what uncertainties it bears and how it compares to measurements.

2) Several of the reaction parameters seem to be based on misinterpretations of literature data. These values have a direct impact on the predicted oxalate formation rates. While I understand that using more appropriate parameters would require a whole set of new simulations, I suggest to either point out the inappropriate assumptions and their consequences or to present at least a few updated simulations.

- The base case simulation S1 assumes Henry's Law constants for SOA precursors (glyoxal, methylglyoxal, etc) to be higher by two orders of magnitude than Henry's Law constants K_H in pure water because of the 'ionic strength effect in cloud water'. However the ionic strengths in the laboratory experiments that are referred to (Ip et al., 2009) was much higher than encountered in cloud water (micromolar). In addition, the generalization of the increase in K_H for all compounds seems an exaggeration as (i) for methylglyoxal no such effect is known, (ii) for glyoxylic and glycolic acid this enhancement factor seems to be too high.

- I am afraid that the K_H values for acids in table S3 'double count' the acid dissociation and thus imply a too strong partitioning of glyoxylic acid into the aqueous phase which would directly affect the oxalic acid formation, in particular above the ocean where aerosol is likely to be basic and thus an overly high effective Henry's Law constant $K_H(\text{eff})$ would be calculated by the applied approach. The intrinsic K_H for glyoxylic acid is 28.67 (Ip et al., 2009) and only the effective $K_H(\text{eff})$, i.e. including dissociation K_{diss} is on the order of 10^4 $K_H(\text{eff}) = K_H (1 + K_{\text{diss}}/[\text{H}^+])$ The same is true for K_H of oxalate. Correcting $K_H(\text{eff})$ for oxalate might not impact the model results significantly

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as it is assumed in the model that all oxalate remains in the particle phase. However, even this latter assumption might be an overestimate for realistic conditions as it has been shown that oxalate does exist in the gas phase and thus is not fully contained in the particles.

- The value of the Henry's Law constant of OH (9000 M atm⁻¹) is the highest reported in the literature. Values that are based on thermodynamic calculations (cf Sander et al.) are at least two orders of magnitude smaller and should be preferred over estimated ones. The applied value crucially biases the oxalate formation rate in the aqueous phase as it increases the OH aqueous concentration.

- The authors make the assumption that in aerosol water 20% of the predicted SOA yield is oxalate. The assumption behind this value should be further explained (e.g. by means of Figure 9, Lim et al., ACP 2010).

3) The introduction is very long and could be shortened. In addition, several references seem inappropriate and should be carefully checked (see my specific comments below).

Specific comments

p. 488, l. 20: The statement that SOA model generally underestimate SOA mass is somewhat outdated. More recent simulations that include semivolatile species predict a much better model/observation comparison than the cited factor of 5-100.

p. 489, l. 1: The study by Weber et al. does not suggest a specific mechanism (gas or aqueous phase) for the formation of water-soluble organic carbon.

p. 489, l. 18: the formation of low-volatility compounds has not been observed but rather 'suggested' based on observations.

p. 489, l. 20: The study by Ervens and Volkamer is not a laboratory study. Better to cite 'Volkamer et al., ACP, 2009' here.

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p. 490, l. 25 ff: This text seems redundant as the formation of organosulfates etc is mentioned before.

p. 491, l. 2: Hennigan et al., 2008b reports on the WSOC/NO₃ ratios, not on aqueous phase processes.

p. 491, l. 7-10. This sentence seems a bit out of place here.

p. 493, Section 2: - Some brief information on the organic aerosol module might be useful. What precursors are included? How do model predictions compare to observations?

- does ISORROPIA include water uptake by organics? If so, what assumptions are made on OA hygroscopicity? If not, how would affect the results (e.g. SOA formation in aerosol water)?

p. 494, l. 9: How is GLX (glyoxylic acid) partitioning treated outside of clouds? Is vapor-pressure related partitioning assumed?

p. 494, l. 18: Strictly, SO₂, CO₂ are not acids.

p. 494, l. 20: Are organic salts captured by ISORROPIA (e.g., ammonium oxalate) ?

p. 495, l. 25: Reword as the ionic strength and composition of cloud water can certainly be better constrained than the effect of these parameters on the solubility of organics.

p. 495, l. 28: I do not understand this sentence. What is meant by 'interstitial cloud'?

p. 496, l. 21: why do you assume here a fraction of 1% oxalate? In the introduction, references were cited that suggested 0.1%.

p. 497, l. 2: the rate constant depends both on ammonium activity and pH which not necessarily implies ionic strength (ionic strength could be also introduced by ions other than ammonium)

p. 497, l. 14: In the study by Ervens and Volkamer, it was discussed that SOA formation

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is either initiated by photochemical processes or it occurs in the dark (on much longer time scales) which can be described by a reversible uptake and higher Henry's Law constants. Mixing both approaches, i.e. applying reaction 14 (Table S1) AND higher KH does not seem reasonable to describe a photochemical scenario.

p. 498, l. 21f: It is interesting that you predict almost the same amounts of oxalate from glyoxal and methylglyoxal even though the latter only forms oxalate by a process of more steps (i.e. methylglyoxal \rightarrow pyruvic acid \rightarrow acetic acid \rightarrow oxalate vs glyoxal \rightarrow glyoxylic \rightarrow oxalate). Can you comment on that? Are the methylglyoxal concentrations higher?

p. 499, l. 16: Where does the value of $4.7e7$ come from? In the table the highest value is $1.9e8$.

p. 500, l. 2: Clarify. The Figure caption says 'annual mean', not monthly mean.

p. 500, l. 12: Is the statement on higher aqueous phase OH concentrations in summertime a model result? Higher biogenic concentrations in summer might suppress OH concentrations.

p. 500, l. 16: Can you give a number on the contribution of aqueous phase H_2O_2 photolysis to the total OH(aq) concentration? In general, this contribution is thought to be less than direct uptake (cf Herrmann et al., Atmos. Environ. 2005).

p. 501, l. 1-5: The other SOA contributions should be discussed here. What are the main precursors? What assumptions are made in the partitioning, e.g. which fraction of (organic?) aerosol mass is assumed to absorb newly formed SOA?

Table 1: - do you mean 'GLY concentrations above the ocean'? 'Oceanic' implies glyoxal concentration in ocean water.

Table 2: Can you comment on the fact that in some lines 'net chemical production' – 'deposition' does not add up to zero?

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Figure 6: Add the information that the model results shown are from simulation S3. Why has this case been chosen for comparison?

Supplemental information:

It should be clarified whether the following mistakes are only typos in the tables or in the model code.

Table S1: - R19 and 20: The products should be 0.85 GLX- + 0.15 HCHO (not HCOO-)

- R25: Why '+ 2 OH'?

- footnote h: What is the maximum value of $j(\text{H}_2\text{O}_2)$ that has been assumed? I.e. under what conditions is $k = 4 \text{ s}^{-1}$?

Table S2: It should be $\text{HO}_2 = \text{O}_2^- + \text{H}^+$, not $\text{OH}^- + \text{H}^+$

p. 5, l. 81-86: How sensitive are the results towards the assumed droplet diameter for the calculated uptake rate? If there is a huge sensitivity, wouldn't it be more appropriate to assume different droplet diameters above land and ocean?

Technical comments

p. 489, l. 5: replace 'higher O:C content' by 'higher O:C ratio' or 'higher oxygen content'.

p. 495, l. 1: Add 'water' after 'cloud'.

p. 496, l. 14: Reorder: (potential) primary combustion sources

p. 498, l. 10: Remove 'here'

p. 502, l. 16: Add 'for' after 'accounted'

Figures 1-4: Use a larger font size for legends and headers.

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