

Interactive comment on “Oligomer formation in the troposphere: from experimental knowledge to 3-D modeling” by V. Lemaire et al.

Anonymous Referee #2

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The authors present a study using the regional model CHIMERE with a focus on secondary organic aerosol (SOA) formation due to oligomerization. They compare the results of two oligomerization representations, one by a kinetic approach and the other one by an equilibrium approach. For the latter one, either deliquesced aerosol or metastable aerosol is assumed which differ in the regard that in the former no aqueous phase oligomerization can occur if particles are present below their deliquescence relative humidity. Clearly, the role of particle phase reactions in SOA formation is a very timely topic. However, I am not sure what one can learn from the current study since merely results from the two parameterizations are compared to each other but not compared any measurements. Several parameters are identified to have an important impact on the results such as the solubility of oxidation products and oligomer

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precursors (Henry's law constants), the assumption of reversibility or irreversibility and the rate constant of oligomer formation in the particle phase. While I can see the value of such a study in order to identify the most important and uncertain parameters, I can recommend this study only for publication after consideration of the following major comments.

Major comments

1) Henry's law constant

a) In many recent studies, it has been discussed that for aerosol Henry's law constants are not directly applicable since the aqueous solutions are not ideal. Recently, correction factors, e.g. the Setschenov coefficient, have been applied. Therefore using a constant Henry's law constant for all conditions seems an oversimplification. This should be at least briefly discussed.

b) The sensitivity to the Henry's laws constant is not new and has been investigated previously in a regional model. The novelty of the current study as compared to a previous one (Knote et al., 2015) should be discussed.

2) Kinetic parameter

a) The oligomerization rate is represented by a first order process in the model. However, oligomerization is a second order process since two molecules react. In many previous lab studies (e.g. Turpin group) it has been shown that oligomerization rates are dependent on the solute concentrations. Therefore, a first-order rate constant taken from one set of lab studies cannot represent the full range of water content of aerosol particles. This should be more carefully discussed.

b) Several lab studies (e.g. Renard et al, 2014, 2015) have shown that oligomer mass is reduced over time since oligomers get oxidized into more volatile products. Therefore, the accumulation of oligomers is unrealistic. This should be at least mentioned.

3) Comparison to observations

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a) The authors mention briefly that oligomers cannot be measured in ambient aerosol. While I partially agree that measurements are difficult due to the fragmentation of oligomers during analysis, there are a few studies that concluded on oligomer fraction of organic aerosol. In addition, several studies concluded on the fraction of BSOA to total SOA due to various techniques, e.g. positive matrix factorization. How do such measurements compare with the trends in model results?

b) Many studies have used the ammonium/sulfate ratio as a proxy for pH. How do pH ranges compare over the model regions to those values?

c) The most important difference between the kinetic and equilibrium approaches in the model results are the spatial and temporal distributions of BSOA/total OA. How do the predicted trends compare to measurements?

d) Please, give references for the occurrence of deliquescence in the atmosphere. To my understanding, the vast majority of all ambient aerosol particles are in their metastable state as their efflorescence relative humidity is suppressed to very low values due to the complex mixtures of organics and inorganics. Therefore, I think the scenario of dry aerosol particles in the atmosphere is unrealistic.

e) The pH dependent approach was derived based on lab studies with small aldehydes. How well is the aldehyde budget constrained in the model and how does it compare to observations?

f) There is evidence based on observations that SOA formation is not acid-catalyzed (Peltier et al., 2007). In that light, the choice of Eq-1 should be justified and explained.

Minor comments

It should be noted somewhere that oligomerization is only considered in the aqueous phase of aerosol particles, and that chemistry in clouds is not included.

p. 9320, l. 24: SOA is also made up of low volatility organics

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p. 9237, l. 1: Did the study really report that the 'total organic aerosol mass was converted into oligomers' or the precursor mass? I.e. did the organic aerosol mass increase or not?

p. 9239, l. 8: 'Eq (1) alters the solubility ...' is poor wording. Please, reword.

p. 9242, l. 20: I am confused. I thought that ISORROPIA is included in CHIMERE and calculates the liquid water content.

p. 9243, l. 16: Species with 10^{-7} M/atm are not 'insoluble'. For example, in the presence of clouds, they are mostly present in the aqueous phase.

p. 9245, l. 16: 'Discrepancy' implies that one model is 'more correct' than the other. However, I think both parameterizations are very crude assumptions. Wording should express that the current results are all not representative for the atmosphere.

p. 9246, l. 10: 'observed' implies 'ambient measurements'. Is this really meant here or rather 'predicted'?

p. 9249, l. 9: What is meant by 'KH correcting factor'?

p. 9251, l. 3: Again, 'observed' or 'predicted'?

p. 9255, l. 14: Not clear how the 'dependence on RH was removed'.

p. 9256, l. 5: 'Initial' implies that this value might change over the course of the simulation. Is this true?

p. 9256, l. 13: I do not understand this sentence. If only KH were to be used to present oligomer formation, the modules for AQM might be simpler. However, it is obvious that also particle phase reactions need to be added. Such addition, makes such a module quite complex.

p. 9257, l. 2: The study by Wang et al., 2010, referred to nucleation of particles that is enhanced in the presence of organics. This is a completely different scenario than the

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uptake and further processing of oligomer precursors as discussed in the rest of the paper.

p. 9258, l. 9, and l. 23: All the cited studies here refer to bulk aqueous phase experiments. Therefore, they could not give quantitative conclusions about the importance of these oligomerization pathways in the atmosphere. The follow-up study by Ervens et al shows clearly that these processes likely only contribute marginally to ambient SOA. In addition the same study discussed that under atmospheric conditions, likely there is no oxygen limitation.

Figure 3: The indices on the symbols are very blurry in a too small font.

Figure 10: This figure by itself is very misleading. At the very least, it should be noted that it only refers to Eq.-1. Usually KH values increase with increasing pH due to dissociation of acids.

References

Knote, C., Hodzic, A., and Jimenez, J. L.: The effect of dry and wet deposition of condensable vapors on secondary organic aerosols concentrations over the continental US, *Atmos. Chem. Phys.*, 15, 1,1-18, 10.5194/acp-15-1-2015, 2015.

Peltier, R. E., Sullivan, A. P., Weber, R. J., Wollny, A. G., Holloway, J. S., Brock, C. A., DeGouw, J. A., and Atlas, E. L.: No evidence for acid-catalysed secondary organic aerosol formation on power plant plumes over metropolitan Atlanta, Georgia, *Geophys. Res. Lett.*, 34, L06801,doi: 10.1029/2006GL028780, 2007.

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