"Treatment of non-ideality in the multiphase model SPACCIM-Part2: Impacts on the multiphase chemical processing in deliquesced aerosol particles" *by* Ahmad J. Rusumdar et al.

Anonymous Referee #1

We thank reviewer 1 for the constructive comments to improve the manuscript. The comments of the reviewer are addressed point by point in the sections below. The answers to the reviewer comments are marked as blue text. Furthermore, all changes made in the manuscript are marked in the version with tracked changes. In order to provide a more conceive manuscript and for the sake of clarity, the subsection on the C_3 chemistry has been moved to the supplement.

The study presented in this paper aims to quantify the activity coefficients of species dissolved in deliquescent atmospheric particles. The approach is based on the modeling of two continental scenarios (urban, remote) simulating the chemical evolution in various phases (gas - particle - cloud droplets). The study examines the activity coefficients of inorganic (HOx, SOx, H2O2, metals) and organic (C1-C3) species. The effect of the non-ideal behavior of the species on the dynamic evolution of the system is evaluated by comparing the results obtained when the ideal behavior in the aqueous phase is imposed or not. For the scenarios tested, the budget of key species (S(VI), H2O2, organic acids ...) is substantially modified when the non-ideal behavior of the solution is considered. The results presented are relevant to this journal. The paper is well organized but the writing could likely be more concise.

I have a few comments (see below) that the authors might consider for submitting a revised article to ACP.

1. The description of the two scenarios considered in this study is inadequate. The authors refer to an article by Ervens et al. (2003) (page 7, line 24), but I did not find more detailed information in the article cited. Additional information is necessary to characterize the simulations carried out with the box model (initial conditions, emissions, speciation of organic species, deposition, NOx regime, NH3 level, etc.) and to weigh the simulated behavior of the species (e.g. the accumulation of S(VI) presented in fig.3, page 16 and reaching 90 µg/m3). The details of the simulation conditions could for example be added to the additional material.

Answer to the reviewer comment:
We thank the reviewer for this comment. Unfortunately, the link provided in Ervens et al. (2003) is not up-to-date anymore. Therefore, we have added a link to the CAPRAM webpage, in addition to Ervens et al. (2003). There, initial gas phase conditions, emissions and deposition are provided.

2. The paper examines the effect of the non-ideality of the solution on the condensed phase reactivity but does not discuss its effect on the gas/particle partitioning, as suggested for example page 12, line 4. No result of the non-ideal behavior is presented on the simulated aerosol mass concentrations, their compositions (e.g. inorganic vs organic), their liquid water content… . Adding a section presenting the effects on the overall aerosol properties (mass concentration, composition, water content in particular) would be useful to evaluate the sensitivity of this non-ideal behavior in models dealing with aerosols formation.

Answer to the reviewer comment:

The applied model calculates both the phase partitioning and the occurring multiphase chemistry simultaneously. The latter can substantially affect the budgets of the compounds. Hence, the predicted concentrations in either phase are a result of both the phase partitioning and the multiphase chemistry. Therefore, it is difficult here to discuss the effects of the non-ideality on the gas/particle partitioning and the applied multiphase chemical reactions individually. Due to the focus of the present study on the occurring multiphase chemistry we have not focused on the phase partitioning topic alone and have only cited literature (Cappa et al. (2008)) addressing this issue in more detail.
According to the reviewer comment, we have added a section to the SI presenting additional model results, e.g. total and organic aerosol mass for different model runs/scenarios.

3. The iron activity decreases notably when the non-ideal behavior of the species is considered. The authors show that this decrease in activity is one of the main causes explaining the simulated effects. However, the authors state that the model ignores the "middle range interaction" for Fe and Mg ions, leading to uncertainties about the activity coefficients calculated for these species. This limitation is reminded very regularly in the paper, including in the conclusion of the article (e.g. line 15, page 34). Although clearly mentioned, this uncertainty considerably weakens the conclusions of this study. I think that a test would be necessary to examine the sensitivity of the simulations to uncertainties about the activity of iron. An educated guess could perhaps be made to estimate the effect of the middle range interactions, e.g. using another TMI as a proxy.

Answer to the reviewer comment:
The authors fully agree with the reviewer that the missing middle range interaction parameters for Fe and Mg ions might weaken the conclusions of this study. The authors already thought about this issue quite a bit during the analysis of the modelled data. An educated guess to estimate those middle range interaction parameters was already discussed. For this reason, we have already compared available middle range interaction parameters of different metals. This comparison showed that also similar metals, for example Mg^{2+} and Ca^{2+} (same charge and main group in the periodic table), can be characterized by rather different middle range interaction parameters. Moreover, the use of the Cu^{2+} interactions parameters for Fe and Mn ions can be also difficult as the chemistry of copper is known to be different from those of Fe and Mn. Nevertheless, according to the reviewer comment, we have included a new section in the SI comparing the base model runs with runs where the parameters for Cu^{2+} have been applied for Fe^{2+} and Mn^{2+}. A link to the sensitivity studies in the supplement is now included into the revised manuscript (see Sect. 3.4).

4. Minor comments: The term "flux" is used systematically by the authors to define the rate of processes. I think that using "flux" is inappropriate here and should be replaced by "rate" everywhere in the text and in figures 5, 8, 10 and 12.

Answer to the reviewer comment:
The term "flux(es)" has been replaced by “rate(s)” in the revised manuscript.

5. The writing of the chemical formula are often difficult to read for organic molecules. For example in Table 4, OH2CHCH2OH would be more easy to read as CH(OH)2CH2OH to represent hydrated glycolaldehyde. Similarly, C2H4COOH2 would be more easy to read as C(O)OHCH2CH2C(O)OH to represent succinic acid, etc . . . Furthermore, the writing is sometime misleading, like in figure 8 for OHCCHCHCHO (which I guess is for butenedial CHOCH=CHCHO) or, in figure 10, C(OH)2O2COOH which I cannot identify (a typo?) but

understand to be glyoxylic acid from the text. I suggest to use only “conventional” formula in the text, figures and tables.

Answer to the reviewer comment:
The writing of the chemical formulas has been revised.

Page 2, line 20: the word "including" in the context of the sentence is unclear. Change to "leading to"?
Answer to the reviewer comment:
"including" was replaced by "leading to".

Page3, line 16: the paper use both ALWC and ALW. Duplication of 2 similar acronyms could be avoided (ALWC is used only 2 times in paper).
Answer to the reviewer comment:
The ALWC is not used anymore in the revised manuscript.

Page 10, line 26-27: One of the 2 "finally" should be removed.
Answer to the reviewer comment:
One "finally" has been removed.

Page 11, line 22: pyruvic acid is not a simple carboxylic acid (i.e. without another functional group), as suggested in the context of the sentence.
Answer to the reviewer comment:
The sentence has been rephrased and reads now as follows:

“Only carboxylic acids with further substituents and a longer non-polar carbon chain (e.g. pyruvic and butyric acid) show higher activity coefficients, particularly with decreasing RH.”

Page 12, line 18-20. The sentence seems useless in the context of the paragraph and could be removed.
Answer to the reviewer comment:
The sentence has been removed.

Page 13, line 8. I don’t understand the meaning of the word "obstruct" in the context of the sentence.
Answer to the reviewer comment:
The sentence has been rephrased and reads now as follows.

“Mainly, microphysical parameters such as the ALW content pattern pH and ionic strength.”

Page 14, line 5-6: the sentence is obvious in the context of the paragraph and could be removed.
Answer to the reviewer comment:
The sentence has been removed.

Page 15, line 14-16: The sentence is obvious in the context of the paragraph and could be removed.
Answer to the reviewer comment:
The sentence has been removed.

Page 19, line 1: the second processing in "processing of Fe(II) processing aqueous" could be removed.
Answer to the reviewer comment:
The second processing as been removed. The sentence reads now as follows:

"To summarise, the model simulations implicate that the multiphase processing of Fe(II) in aqueous particles is significantly affected by the treatment of non-ideality and the effect depends strongly on the ALW conditions."

Page 19, line 17-31: The reading of this paragraph is tedious. A figure similar to 5, 8, 10 or 12 could be useful.
Answer to the reviewer comment:
For the sake of clarity, we have not included such a Fig. here, but according to the reviewer comment, we have added a similar Fig. for H_2O_2 in the SI (see Fig. S6).

Page 21, line 7: units are missing for OH concentration. Number of significant figures should be consistent for the 2 numbers.
Answer to the reviewer comment:
The unit has been added and the numbers were unified.

Page 24, line 25: I don't understand "formation-substituted" in the sentence.
Answer to the reviewer comment:
The sentence has been rephrased as follows:

"…in-cloud oxidations of C_2 carbonyl compounds such as glycolaldehyde and glyoxal lead to the formation of substituted organic acids (e.g. glyoxylic and glycolic acid),…"

Page 26, line 10-32: The reading of this paragraph is tedious. A figure similar to 5, 8, 10 or 12 could be useful.
For the sake of clarity, we have not included such a Fig. here, but according to the reviewer comment, we have added similar Fig.s for glycolic and glyoxalic acid in the SI (see Fig. S7-8).

Page 31, line 8: Typo in "sSect."
Answer to the reviewer comment:
The typo was corrected.

Page 31, line 14: it is stated that keto malonic acid is the final C3 oxidation product. Figure 12 (page 32) show however a loss process which is not discussed in the text (and not "explained" from the legend in the figure).
Answer to the reviewer comment:
The comment is difficult to understand. Keto malonic acid is the C_3 oxidation product of this reaction chain, subsequent products only include 2 carbon atoms. According to the reviewer comment, the word has been removed from the sentence.

Page 32, figure 12: Only the first 3 processes (dark blue, light blue and pink) can be discerned in the figure. The other processes could be merged in either the "other source" or "other sinks" boxes.
Answer to the reviewer comment:
The Figure has been revised.

References:

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