Review for paper:
"Multiphase MCM/CAPRAM modeling of formation and processing of secondary aerosol constituents observed at the Mt. Tai summer campaign 2014"
by
Y. Zhu et al.

Submitted to Atmospheric Chemistry and Physics

General Comments:
This paper presents a modeling study with a 0D-sophisticated model of the formation and processing of dicarboxylic acids and related compounds (oxo-carboxylic acids and α-dicarbonyls) (DCRCs) in clouds and deliquesced aerosols at the Mt. Tai. Results are compared to observations of aerosols composition analyzed from night and day filters. This study is very interesting and valuable in doing the effort to compare simulated results to observations. However, I have some main concerns detailed below on the definition of the scenario and on the absence of information on the microphysical structure of simulated cloud.

Overall recommendation:
I recommend that the paper should be accepted for publication in Atmospheric Chemistry and Physics after major and specific revisions listed below.

Major Comments:
1 – About the simulations set-up:
I found that the conditions used in simulations (meteorological conditions, emissions, initial chemical concentrations, aerosol parameters) are very confused. I list below some of my main concerns:

- No value is given for meteorological conditions contrary to that it states page 5, line 148. I did not understand why the meteorological values along the trajectories are not directly used to drive the air parcel. For instance, in Zhu et al. (2018), WRF simulations and HYSPLIT back-trajectories are mentioned: I guess that typical trajectories to Mt. Tai could be extracted from these runs.
- With regard to scenarios (cloud or cloud-free), in my opinion, a third series of simulation without aqueous chemistry at all should be of interest in assessing the contribution of aqueous pathways to the formation of secondary aerosol constituents. Especially since the ideal solution hypothesis biases the results for aqueous chemistry inside deliquesced aerosols.
- For biogenic emissions, you should precise, which inventory you used to extract biogenic emissions: is-it MEGAN-MACC, CAMS-GLOB-BIO? Also, why did you consider biogenic emissions only for isoprene and pinenes whereas a lot of other species are available from MEGAN-MACC or CAMS-GLOB-BIO? I suggest that the biogenic and anthropogenic emission values be separated in Table S1.
- Where values for deposition velocities come from?
- In Table S3 and S4, the source of each value (literature or urban CAPRAM scenario) should be indicated. Why measured observations of VOC analysed from stainless steel canisters (Zhu et al., 2018) are not used to initialize the model?
- I do not understand aerosol parameters in Table S4. Although, the unit of ng/m3 or μm/m3 is used in the article, aerosol species composition is given in mixing ratio (g/g) in the Table. No initial value is given for aerosol number concentrations.

For all these reasons, I found the simulation set-up questionable.

2 – About the results:
In my opinion, some important information is missing. No results are reported for the microphysical structure of simulated clouds and how they compare to observations.

<u>Specific Revisions:</u>

Introduction:

- The recent following review paper should be cited: Shrivastava, M., Cappa, C. D., Fan, J., Goldstein, A. H., Guenther, A. B., Jimenez, J. L., Kuang, C., Laskin, A., Martin, S. T., Ng, N. L., Petaja, T., Pierce, J. R., Rasch, P. J., Roldin, P., Seinfeld, J. H., Shilling, J., Smith, J. N., Thornton, J. A., Volkamer, R., Wang, J., Worsnop, D. R., Zaveri, R. A., Zelenyuk, A. and Zhang, Q.: Recent advances in understanding secondary organic aerosol: Implications for global climate forcing, Rev. Geophys., 2016RG000540, doi:10.1002/2016RG000540, 2017.
- The citation of following paper should be added in the paragraph lines 52 to 64: Mouchel-Vallon, C., Deguillaume, L., Monod, A., Perroux, H., Rose, C., Ghigo, G., Long, Y., Leriche, M., Aumont, B., Patryl, L., Armand, P. and Chaumerliac, N.: CLEPS 1.0: A new protocol for cloud aqueous phase oxidation of VOC mechanisms, Geosci. Model Dev., 10(3), 1339–1362, doi:10.5194/gmd-10-1339-2017, 2017.

Part 2:

- The sampling period of observations should be given here. A discussion about the known sources of DCRCs deduced from Zhu et al. (2018) should be done.
- 2.1:
    - The limitation of SPACCIM due to the assumptions of ideal solutions concerns deliquesced particles. This should be specified.
    - Microphysical processes include in SPACCIM should be listed. Also it should be mentioned that cloud particles size distribution is spectral.
    - Does SPACCIM include aerosols? If yes, it should be specified how: which processes are considered for aerosols: microphysics processes (nucleation, aggregation, sedimentation), chemical aging, nucleation and impaction scavenging by cloud particles? Also the method to represent their size distribution should be indicated. Do you use thermodynamics equilibrium to partition inorganic and organic species between gas phase and particles?
    - Could you please indicate if recent findings on isoprene and aromatics gas phase chemistry are included in MCM? As the reference papers for MCM are from 2003, it is probably not the case and could lead to other limitations in the results.
- 2.2: Could you please indicate the reason to exclude days of the campaign influenced by biomass burning?
- 2.3: You should use the proper ECCAD address; https://eccad.aeris-data.fr/. Note that you have to acknowledge ECCAD and to reference the dataset citation (see metadata page of the inventory that you used). Why did you use urban CAPRAM scenario for missing values? I suggest to indicate also initial gas-phase conditions in mixing ratio (ppbv or pptv), which is the usual quantity used for representing observations of trace gases.

Part 3:

- 3.1.1:
    - Page 6, lines 178-179, it is stated: "The reduction of OH radical is mainly caused by the reduction of the gas-phase formation pathway of the HO2+ NO

    reaction” and page 7, lines 198-200: “Under daytime cloud droplet conditions, OH aqueous-phase concentrations are increased by a factor of 3, mainly due to the increased direct transfer of OH from the gas phase.”. I found these statements contradictory. I guess that a plot showing the total OH concentrations (gaseous + aqueous) would clarify this point.
    - Whereas, the text page 6 line 187 indicates that obtained OH and HO2 gaseous concentrations are compared to available measurements, it is mainly modelling studies that are used for this comparison. Moreover, no details are given on these studies: which model, which conditions (period of simulation, chemical mechanism used for instance). The only observations cited show discrepancies with results, in particular for OH.
    - Whereas some estimations exist of OH concentration in cloud droplets (see Arakaki, T., Anastasio, C., Kuroki, Y., Nakajima, H., Okada, K., Kotani, Y., Handa, D., Azechi, S., Kimura, T., Tsuhako, A. and Miyagi, Y.: A General Scavenging Rate Constant for Reaction of Hydroxyl Radical with Organic Carbon in Atmospheric Waters, Environ. Sci. Technol., 47(15), 8196–8203, doi:10.1021/es401927b, 2013), no comparison is discussed. It seems to me that the simulated OH concentrations in droplets are high in comparison to available estimations.
- 3.1.2: I suggest using mixing ratio for gas-phase instead of concentrations when comparing simulated results with in-situ measurements. As mixing ratio is a relative quantity, it is not dependent on altitude (via pressure and temperature).
- 3.2: As no information is given on how the interactions between aerosols and cloud water are considered, it is difficult to interpret the results. Why on Fig. 3 sulphate remains constant when cloud dissipates whereas nitrate decreases at the same time?
- 3.3.1: I suggest recalling in legend of Fig.5 what Gly, wC2, C2, Pyr, MGly and C3 means. Does this figure show the aerosol mass concentrations as shown in Figure 3? If yes, I do not understand why the text page 11, line 316 refers to aqueous phase concentrations. Does this mean that aqueous phase concentration is the same than aerosol mass concentration? These results are difficult to interpret without knowing if thermodynamics equilibrium between gas phase and aerosols is considered for organics species. For instance, for malonic acid, it should be mainly in the aerosols and not in the gas phase (Limbeck, A., Kraxner, Y. and Puxbaum, H.: Gas to particle distribution of low molecular weight dicarboxylic acids at two different sites in central Europe (Austria), Journal of Aerosol Science, 36, 991-1005, 2005).
    - Dicarbonyl compounds: I find that the remarkable result is that Gly and MGly are very similar concentrations at the end of the simulation considering or not cloud chemistry. In addition, the small increase of MGly in the cloud case in comparison to the no cloud one, seems to be related to its small production inside cloud droplets during night. So, I disagree with this statement: “This might have been caused by the fact that the aqueous oxidation fluxes under nighttime cloud conditions are lower than the ones under daytime”.
    - C2 carboxylic acids: Could you please rewrite this passage, which is not clear, only describes the curves and does not give hypotheses about the observed trends.
    - C3 carboxylic acids: I don’t see an increase of Pyr in the nighttime cloud.
- 3.3.2:
    - As described in Zhu et al. (2018), DCRCs observations are available for daytime and nighttime. Thus, I suggest indicating in Table 3, ratio for day and

  - night. Could you please specify on which simulated period the averages are done (the three days or only the third day)?
  - By this sentence "SPACCIM overestimates the measured ωC2 concentrations, but underestimates the measured C2 ones, suggesting the conversion of ωC2 might be implemented less efficiently into CAPRAM.", do you mean that the aqueous phase oxidation of ωC2 producing C2 implemented in CAPRAM seems to be less efficient than in the field?
  - Page 12, lines 356-362: the hypothesis of missing processes enhancing the partitioning of MGly implies that the model is capable of simulating realistic total MGly concentrations (gas phase + aerosols): is-it the case?
  - I disagree with this statement "The emission data are obtained through model calculations, not field measurements". Emission data comes from inventory, which is developed in part based upon measurements. I guess that the more probable error coming from emission data is due to the horizontal and temporal resolution of inventories used. This point should be discussed.
  - Why do you mean by "The height of Mt. Tai (about 1500 m) also causes its input to be indefinite."?
  - MCM mechanism: I guess you could cite other limitations, in particular in biogenic VOC oxidation as the Mt. Tai is surrounded by deciduous forest.
  - I disagree that ratios are acceptable except for C3. I think that it is an interesting result to show that, even a sophisticated model as the one used in this study, is not able to reproduce DCRCs observations. A discussion trying to assess why the C3 ratio is close to 1 should be interesting.
- 3.4.1:
  - ωC2: I see a low net formation flux during the last night for non-cloud period.
  - C2: Please moderate the last sentence: one of the reasons and not the reason.
  - Pyr: Do you consider the photolysis of Pyr in aqueous phase (Reed Harris, A. E., Ervens, B., Shoemaker, R. K., Kroll, J. A., Rapf, R. J., Griffith, E. C., Monod, A. and Vaida, V.: Photochemical Kinetics of Pyruvic Acid in Aqueous Solution, J. Phys. Chem. A, doi:10.1021/jp502186q, 2014.) ?
- 3.5.1: Green lines on Fig. 7 are difficult to see: could you please use another colour (grey for instance)?
- 3.5.2: Could you please explain how negative and positive RIR values have to be interpreted? It would help the reader to follow the discussion on DCRCs precursors. Page 17, line 519: please suppress As.