Review of "Is there an aerosol signature of cloud processing? " by Ervens et al. (2018)

In the submitted manuscript, the authors present an analysis of selected field experiments and a model study based on data of the SEAC^{4}RS field campaign to explore whether there is a clear aerosol signature of cloud chemistry processing. The analysis focuses on trends of changes in mass, hygroscopicity parameter κ, and oxygen-to-carbon (O/C) ratio due to chemical cloud processing.

In my opinion, the paper under discussion is often well structured, however, partly a bit lengthy. It contains some interesting information, which can provide a basis for future works on this important topic. The topic will be of interest to the journal's readers and might support future studies examining the potential role of chemical cloud processing and its impact on the CCN processing.

However, the paper in its present forms need major revision. After addressing my comments/questions/suggestions given below, this paper might be suitable for publication in ACP.

General comments:

Although there are interesting aspects, the whole purpose of the paper and what the authors wants to tell us, does not open to me completely. The main question of the paper, if there is an aerosol signature of chemical cloud processing, is in the end not really answered. So, does this not help anyone? The authors should discuss in the revised manuscript if at all a clear and universal answer to such a general question can be given due to the huge dependence on the specific parameters and conditions.

In the modelling section, I don't understand why there are huge differences in the input aerosol masses between the present study and the data given in Shingler et al. (2015). Moreover, the concentrations of the applied scenarios need to be discussed. Are the applied values realistic? For example, 1.25 µg m^{-3} as an initial mass in the urban case seems to me very low.

The authors have introduced a new mass ratio R_{tot} in order to predict the potential to extent to which aerosol properties are modified by chemical processes in clouds. However, the simple ratio is mainly dominated by the contribution of the expected SO_2 to sulfate formation (R_{SO4}) and is limited to the present aqSOA formation knowledge (individual mass yields, etc.) as well as the incomplete characterization of the OVOCs (aqSOA precursors). Therefore, to my point of view, the simple ratio does not provide much more information and does not represent a breakthrough and needed parameter.

Furthermore, the authors have outlined in the paper that not only mass-based parameters have to be considered but also parameter such as κ and O/C ratio. However, the new mass ratio R_{tot} is then purely mass-related. So, is it possible to conclude from R_{tot} alone whether cloud processing will be detectable, as it is proposed in the abstract and elsewhere?

To my point of view, the conclusion section is lengthy and too little structured. I would suggest to restructure and condense this section to better present the main issues.

Further Comments/Questions/Suggestions:

Page1 line 1: Is the title fitting to the topic addressed in the manuscript? "cloud processing" includes also microphysical cloud processes! Therefore, please replace "cloud processing" by "chemical cloud processing" to be more precise.

Page1 line 10: Replace “Colorado“ by “CO“

Page1 line 17: Replace “aqueous phase” by “aqueous-phase”

Page1 line 28: It should be noted in the abstract that the calculated R_{tot} is almost exclusively dominated by the contribution of the expected SO_2 to sulfate formation (R_{SO4}). See the Table below. This finding should be also discussed in more detail in the paper.

	Marine	Urban	Biomass Burning	Agric. Biomass Burning	Background	Biogenic
RSO4	5.1	1.8	0.1	0.5	0.7	7
RaqSOA	0.005	0.15	0.03	0.08	0.05	0.16
total	5.105	1.95	0.13	0.58	0.75	7.16
%RSO4	100%	92%	77%	86%	93%	98%
%aqSOA	0%	8%	23%	14%	7%	2%

Page1 line 29: The authors have mentioned in the abstract that already “tracer compounds give evidence that aqueous phase processing occurred, they do not reveal the extent to which particle properties have been modified in terms of mass, chemical composition, hygroscopicity and oxidation state.” Please, outline if the calculated parameter R_{tot} leads to an improvement with regard to the prediction of a chemical cloud processing signature and help to predict the extent to which particle properties can modified in terms of mass, chemical composition, hygroscopicity and oxidation state. Please explain in detail why such a ratio, which basically only relates the gaseous SO_2 budget with the already existing particle mass, represents a breakthrough and needed parameter.

Furthermore, the authors should discuss in the paper that also a small mass production (low R_{tot} values), due to cloud chemistry, can be important and significantly influence the aerosol properties (e.g., CNN, hygroscopic and radiative properties). For example, when surfaces of mineral dust or BC particles are modified even by a small mass addition, this can lead to significant changes in their properties. In such cases, the parameter R_{tot} is definitely not the right means.

Page2 line 40: I can somehow understand the limitation of **“**hill cloud**”** experiments in terms of their geographical coverage, however, the limitations with regards to complicated interpretation due to variable advection of various sources and airmasses needs to be explained in more detail. Why should various sources and airmasses restrict the interpretation of field experiments? Maybe other limitations of hill cloud experiments can be addressed here.

Page2 line 47: Please begin the sentence with “However, SOA formation in clouds….”.

Page2 line 52: Replace “aqueous phase” by “aqueous-phase”

Page2 line 57: Replace “aqueous phase” by “aqueous-phase” and “gas phase” by “gas-phase”

Page3 line 76: Replace “signature of cloud processing” by “signature of chemical cloud processing”

Page3 line 83: Replace “possible cloud processing signature” by “possible chemical cloud processing signature “

Page3 line 97: Please specify the term “monoterpenes” and list the single compounds considered here.

Page3 line 99: Here or somewhere in the text it should be mentioned that such a definition of a marine regime might include also ship emissions and urban influence. Please discuss the chosen value of 40 km. In the paper of Kummu et al. (2016), coastal continental zones are defined to be <100 km from the coast. So, I would suggest that the continental influence on the marine regime would be at least in the same range. Furthermore, the flight paths shown in the paper of Toon et al. (2016) shows just a few flights over the Gulf of Mexico, which is most likely a region with a lot of anthropogenic influence (incl. marine traffic, etc.). Furthermore, the initialized SO_2 concentration of 0.42 ppb is also quite high for a marine environment suggesting an anthropogenically influenced air mass. This issue should be mentioned in the manuscript. The obtained data over the ocean are maybe not representative for a pristine open ocean (marine environment). The term "Marine" is maybe not fitting here, but, has been taken over from a former study (Shingler et al., 2015).

Page4 line 114: Replace “Table S1 also lists …” by “Table S1 also lists the concentration of …”

Page4 line 140: Please use a uniform nomenclature; “Mt. Lemmon“ or “Mount Lemmon”, Mt. Tai etc.

Page5 line 144 and 145: Replace “gas phase” by “gas-phase”

Page5 line 151: Replace “aqueous phase” by “in-cloud” if processes in clouds are meant here.

Page5 line 159: The hygroscopic parameter needs to be introduced with a calculation formula and the corresponding reference.

Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos. Chem. Phys., 7, 1961–1971, doi:10.5194/acp-7- 1961-2007, 2007.

Page5 line 170/171: Please do not separate the value “1” and the unit “s”

Page5 line 172: In cloud water solutions, the glyoxal and glyoxylic acid should be predominantly present in their hydrated form (gem-diol form). Thus, their O/C ratio should be 2.

Page6 line 178/179: I have compared the aerosol mass concentration given in Table 1 with the values in the cited paper of Shingler et al. (2015). There is a huge difference in the values. For example, the average total aerosol mass of the agric. biomass burning aerosol is 116.1 µg m^{-3} (see Shingler et al., 2015; Figure 1) and 12.1 µg m^{-3} in the present work. Please explain this difference because the m_0 value is an important parameter in the paper and the linked ratio R_{tot}. If the m_0 values would be larger, the calculated relative mass additions due to cloud processing would be significantly lower and, thus, the cloud signature less significant than proposed by the present model runs.

	Marine	Urban	Biomass Burning	Agric. Biomass Burning	Background	Biogenic
Shingler et al. (2015)	1.7	11.9	34.8	116.1	12.7	11.2
Present study	0.33	1.25	10.5	12.1	3.86	1.74
ratio	**5.2**	**9.5**	**3.3**	**9.6**	**3.3**	**6.4**

Furthermore, please explain why the total aerosol mass in the urban air mass is only 1.25 µg m^{-3} and about 3.84 µg m^{-3} in the background air mass. I would expect firstly much higher aerosol loadings in both cases and, secondly, lower concentrations in the less polluted background case. Thus, the concentrations of the applied scenarios need to be discussed (Are the values realistic and representative?).

Page6 line 179: Replace "gas phase" by "gas-phase"

Page6 line 179: Please correct "aerosl"

Page6 line 190/191: Here, it should also be mentioned that important sinks of organic acids may be also missing in your model, e.g., the photolysis of metal-carboxylate complexes.

Page6 line 194: Replace "aqueous phase" by "aqueous-phase"

Page6 line 199: "over the course of the 1-hr cloud simulations" should be replaced by "over the course of the 1-hr simulations" because the in-cloud time is only 40 minutes.

Page6 line 203: Replace "and thus the" by "and, thus, the"

Page6 line 204: Is the conclusion "These different time scales are in agreement with previous findings…." trivial since the same chemical mechanism has been applied in the present study?

Page6 line 205: Replace "SO_2 depletion" with "SO_2 oxidation"

Page6 line 205-207: Are the presented sulfate formation rates of ~10^{-8} – 10^{-5} M s^{-1} an average of the first cloud period? Furthermore, a comparison with a single study is not convincing. What is the predicted pH in the different model runs (result should be provided in the SI) and what are the main S6 formation pathways in the different regimes? Are they comparable with key oxidation pathways at Mt. Tai?

Page7 line 219: Replace "aqueous phase" by "aqueous-phase"

Page7 line 227: I don't understand the following sentence, please rephrase: "AqSOA tracer compounds such as oxalate, and its main aqueous precursor glyoxylate, are clearly dominant in clouds whereas in the free troposphere organic acids dominate that significantly originate from clouds".

Page7 line 233: Replace "aqueous phase" by "aqueous-phase"

Page7 line 237: Please compare the calculated changes in κ with observed changes in the field in this subsection (see e.g., Henning et al. 2014).

Henning, S., Dieckmann, K., Ignatius, K., Schäfer, M., Zedler, P., Harris, E., Sinha, B., van Pinxteren, D., Mertes, S., Birmili, W., Merkel, M., Wu, Z., Wiedensohler, A., Wex, H., Herrmann, H., and Stratmann, F.: Influence of cloud processing on CCN activation behaviour in the Thuringian Forest, Germany during HCCT-2010, Atmos. Chem. Phys., 14, 7859-7868, https://doi.org/10.5194/acp-14-7859-2014, 2014.

Page8 line 273: Please put a space between "(2015)" and "might".

Page8 line 276: Remove "B".

Page9 line 283-297:

In general, the R_{tot} ratio itself is a nice idea, but particularly the R_{aqSOA} parameter is somehow quite arbitrarily defined. Furthermore, only 5 VOC precursors are taken into account in the present study.

Direct precursors for in-cloud chemical processing leading to aqSOA should be OVOCs which are only indirectly considered via their emitted precursors (such as isoprene). Furthermore, at the altitude of aircraft measurements, the emitted VOCs such as isoprene are maybe already largely oxidized to their oxidation products such as glyoxal, glycolaldehyde, MVK etc. In this case, the proposed method would require measurements of several VOCs and OVOCs. This issue should be discussed in detail. Moreover, different yields for different precursors should be used instead of a single effective mass yield factor Y which is based on one single model study focusing on isoprene. Are there other studies available which should be mentioned here?

The method applies a sum of all listed VOCs including emitted VOCs such as isoprene and important oxidation products (OVOCs) such as methyl vinyl ketone/methacrolein. If the effective mass yield factor Y is valid for isoprene, is the consideration of its oxidation products adequate?

Furthermore, it would be suitable to mention that there are also other potential precursors, which were not considered in the present study due to lacking measurements, that could contribute to aqSOA. I guess, for example, phenolic compounds can be strongly emitted by biomass burning and can contribute to aqSOA. In the marine case, the oxidation of DMS into methan sulfonic acid might be an important precursor of aqSOA. However, they are not considered in the present study. Thus, this limitation needs to be clearly addressed in the manuscript.

Overall, the assumed mass yield factor Y of 10% is of course very uncertain and the VOC/OVOC sum quite incomplete. Therefore, the authors should perform a small sensitivity study focusing on different Y values and VOC/OVOC sums to reveal the potential impact of these parameters.

Page9 line 299: Correct the values of R_{tot} “0.2.0”

Page9 line 299: “Rtot” has to be subscript: “R_{tot}“

Page9 line 307-311: Please discuss the contribution of R_{SO4} and R_{aqSOA} to R_{tot} in more detail and provide also some numbers in the text. Additionally, the fractions such be considered in Table 3 as shown below.

	Marine	Urban	Biomass Burning	Agric. Biomass Burning	Background	Biogenic
RSO4	5.1	1.8	0.1	0.5	0.7	7
RaqSOA	0.005	0.15	0.03	0.08	0.05	0.16
total	5.105	1.95	0.13	0.58	0.75	7.16
%RSO4	100%	92%	77%	86%	93%	98%
%aqSOA	0%	8%	23%	14%	7%	2%

Page9 line 310/ and Page10 line 314/342 and Page11 line 360: “R” should be “R_{tot}”. Please check carefully the whole manuscript for missing indices.

Page11 line 360: Replace “aqueous phase” by “aqueous-phase”

Page11 line 364-379: I can somehow understand that the authors have included mainly studies from the US, however, there are also plenty of non-US studies focusing on the aerosol-cloud processing which needs to be considered here.

Page11 line 381: Please revise “Figure 32”

Page12 line 386: The abbreviation of the growth factor should be already introduced earlier in the paper (maybe in line 138). Furthermore, in the caption of Figure 6, a different abbreviation is used (“GF”). This needs to be changed or indicate the difference.

Page13 line 431/432: Do not separate “$^-$” and “^{3}”

Page14 line 456/457: Please cite also some experimental studies on this topic such as:

Zuo, Y. and Holgne, J.: Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of iron(III)-oxalato complexes, Environ. Sci. Technol., 26, 1014–1022, 1992.

Weller, C., Horn, S., Herrmann, H.: Effects of Fe(III)-concentration, speciation, excitation-wavelength and light intensity on the quantum yield of iron(III)-oxalato complex photolysis. J. Photoch. Photobio. A, 255, 41-49, 2013.

Page14 line 458: “In addition, oxalic acid and other (weaker) organic acids might evaporate from acidic aerosols.” Please provide some references here.

Page14 line 470: Replace “aqueous phase” by “aqueous-phase”

Page14 line 470: “Not only aqueous phase processing in clouds but also in deliquesced aerosol particles can lead to aerosol mass.” Please add some references here to performed model studies.

Page14 line 480: Replace “aqueous phase” by “aqueous-phase”

Page15 line 504: Replace “aqueous phase” by “aqueous-phase”

Page15 line 508: Replace “aqueous phase” by “aqueous-phase”

Page15 line 511: Replace “aqueous phase” by “aqueous-phase”

Page15 line 512: Replace “aqueous phase” by “aqueous-phase”

Page15 line 514: Replace “and thus” by “and, thus,”

Page15 line 519-520: Replace “signature of cloud processing” by “signature of chemical cloud processing”

Page15 line 519-520: “Overall, it can be stated that there is no unambiguous answer to the initial question in the title of this study as to whether there is a signature of cloud processing on aerosol.” From my point of view, the most distinct signature present in the aerosol is still the “cloud mode” and the fact that typical secondary mass contributors mainly formed by in-cloud chemistry such as sulfate are enriched there. This cloud mode and the enrichment of sulfate can be seen, for example, from Figure 5. Thus, a signature of chemical cloud processing in aerosols is there, however, the extent to which aerosol properties are modified by chemical processes in clouds cannot be easily estimated. However, I would agree with the authors if the statement of the sentence is related to the aqSOA: “…that there is no unambiguous answer to the initial question in the title of this study as to whether there is a signature of chemical cloud processing of aqSOA on aerosol.”

Page15 line 521: Please add also other important dependencies to the list such as the budget of oxidants, aerosol composition (important for the cloud pH, etc.), lifetime of clouds etc.

Page15 line 522: The authors conclude that the extent to which aerosol properties are modified by chemical processes in clouds can be quantified by the mass ratio R_{tot}. As mentioned in the comment above, the extent to which aerosol properties are modified depends also on other parameters. Furthermore, the current “R_{tot}” is almost exclusively related to the complete conversion of SO_2 to sulfate and provide no size-resolved information of the possible aerosol modification. The yields of aqSOA are still an issue which requires further investigations and individual yields of aqSOA precursors are uncertain. Furthermore, the size-resolved modification of the aerosol, which is very important, can also not be quantified by R_{tot}. Therefore, I'm not convinced that R_{tot} represents a substantial process or breakthrough to the proposed question.

If the main outcome of R_{tot} is to provide a rough estimate on the question whether a mass signature of chemical cloud processing can be expected at a certain location, I'm not sure that this simple ratio will be a beneficial support for future field and model studies.

Page16 line 524: Replace "aqueous phase" by "aqueous-phase"

Page16 Reference section:

- Between the issue number of the journal and the page number is a space missing in all references. For example: " 10, 13,5839-5858, 10.5194/acp-10-5839-2010, 2010". Please correct this issue in all references.

- The doi number is missing for Aiken et al. (2008).

- The format of the doi numbers in citations is not consistent. Please revise the doi format of the references that they are consistent with the ACP format:

Please see:
https://www.atmospheric-chemistry-and-physics.net/Copernicus_Publications_Reference_Types.pdf

Felder, M., Poli, P., and Joiner, J.: Errors induced by ozone field horizontal inhomogeneities into simulated nadir-viewing orbital backscatter UV measurements, J. Geophys. Res., 112, D01303, doi:10.1029/2005JD006769, 2007.

-Page22 line 854: Please cite the final revised paper published in ACP and not the ACPD manuscript of Wonaschütz et al. 2013.

-Page21 line 838: Please correct "SEAC⁴RS:"

Caption of Table1: Replace "aqueous phase" by "aqueous-phase"

Caption of Table2: Please revise the line break between "(Sorooshian et al., 2007b)" and "."

Figure 1: The axis label of the hygroscopic factor κ is covered in some case on the right y-axis (e.g. in Fig.1b).

Caption of Table 3: "(Eq-1)" should be replaced by (Equation 1) to be consistent.

Caption of Figure 2: Put a dot at the end.

Caption of Figure 4: Put a dot at the end.

Caption of Figure 5: Please use "κ" in the caption and as axis label of the y-axis.

Caption of Figure 6: Please replace "GF-derived" by "growth factor derived" and please use "κ" in the top x-axis label.

Supplemental Information:

- Add a parenthesis "log ([absolute mass increase / g m^{-3}])".

Caption of Table S1: Put a dot at the end.

Caption of Figure S1: Put a dot at the end. Figure S1 contains plots with the predicted relative mass concentration (dm/dlogD) and number concentration (N). Accordingly, please revise the caption or the plot.

Caption of Figure S2: The Figure contains plots of the predicted relative mass concentration (dm/dlogD) and number concentration (N). Accordingly, please revise the caption or the plot.