Reviewer #2

In the submitted manuscript, the authors present an analysis of selected field experiments and a model study based on data of the SEAC4RS 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 k, 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.

Response: We thank the reviewer for his/her constructive comments. We address them in detail below. Line numbers refer to the revised manuscript without track changes.

We would like to point out that we redid some of the calculations as we noticed discrepancies between the parameters in Table 1 as compared to those reported by Shingler et al. (2016).

1) We realized that we had only listed the masses from the SMPS (D < 320 nm) whereas Shingler et al reported masses for the full size range (up to 850 nm). The resulting total masses are considerably higher and, thus, the resulting R values are much smaller. However, the trends for the various air masses are the same as before.
2) In the previous simulations, we had calculated the initial κ value based on the aerosol fractions in Table 1. However, the resulting values were all significantly higher than those derived by Shingler et al. (2016) based on growth factor measurements. Several factors may have contributed to this discrepancy:
   (i) The growth factors by Shingler et al., (2016) were measured for discrete sizes whereas our calculations were performed for the bulk aerosol composition. It is likely that the size-dependent values differed from the bulk values.
   (ii) We assumed that all initial organics had κ = 0.1. However, fresh organics might not be hygroscopic and, thus, the kappa for the organic fraction might be smaller, in particular in fresh air masses.
   (iii) Related to (ii), several studies have shown that κ for organics at sub- and supersaturated conditions can differ significantly, with the former values being smaller. Thus, while κ_{org} = 0.1 might be appropriate close to CCN activation, the values measured at RH < 100% might be smaller.
   We cannot assess which of these reasons contributed most to the discrepancy. In order to be consistent with the measurements, we adapted the kappa values by Shingler et al. (2016) as initial bulk values.
   We redid all simulations using the lower (measured) initial κ values. Accordingly, Figures 2, 4, S1 and S2 changed.

General comments:

1) 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.

Response: The reviewer is right that the title question cannot be answered unambiguously. The conclusions of our study include exactly this message (l. 527)

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 always a clear signature of chemical cloud processing on aerosol. The extent to which aerosol properties are modified by chemical processes in clouds depends primarily on the initial aerosol mass, particle number concentration and sulfate and aqSOA precursor gases, as quantified by the mass ratio R_{tot}.

We think that exploring our model results and comparing them to previous studies helps to identify scenarios where an aqueous phase signature can be expected. The ratio R can be used to estimate a priori whether an aqSOA, sulfate or overall cloud signature might be likely to detect when ambient experiments are planned.

2) 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.

Response: We apologize for this confusion. The masses listed in Table 1 were based on the SMSPS data only, i.e. up to ~320 nm. The model input included 'stitched' size distributions from both the SMPS and UHSAS (cf. Section 2.1.1). The full size range results in the total masses as reported by Shingler et al. (2016). The masses and resulting R values were accordingly corrected in Table 1.

3) The authors have introduced a new mass ratio Rtot 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 SO2 to sulfate formation (RSO4) 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.

Response: We respectfully disagree with the reviewer that the parameter R is not a needed parameter. We are not aware that such a parameter has not been explicitly defined before in the literature. While we stated already in the conclusions that R_{tot} is dominated by R_{sulf}, we added this information now also in the abstract (l. 31):

As the formation processes of aqSOA are still poorly understood, the estimate of R_{aqSOA} is likely associated with large uncertainties.

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

Response: The reviewer is right that κ is a volume-based parameter. We think that the general trends in volume or mass increase will not differ much as they only differ by the density of the aerosol constituents. Given the differences of less than a factor of 2 in density and given all other uncertainties in the current estimates (e.g. aqSOA yield), we think that using mass- or volume-based parameters can be used interchangeably.
The O/C ratio is an atomic ratio; however, several measurements have shown that it is related to the OM/OC mass ratio and, thus, can be related to aerosol mass (e.g. Aiken et al., 2008). Thus, while not strictly a mass-based parameter, the O/C ratio can be considered being a proxy for oxidized organic aerosol mass (e.g., aqSOA).

4) 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.

Response: We restructured the conclusion section and shortened text where possible.

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.

Response: The reviewer is right. We added ‘chemical’ where appropriate.

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

Response: Changed

Page1 line 28: It should be noted in the abstract that the calculated Rtot is almost exclusively dominated by the contribution of the expected SO2 to sulfate formation (RSO4). 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%

Response: We added (l. 29/30)

R_{tot} is dominated by the addition of sulfate (R_{sulf}) in all scenarios due to the more efficient conversion of SO_2 to sulfate as compared to aqSOA formation from organic gases.

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 Rtot 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 SO2 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 Rtot 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 Rtot is definitely not the right means.

Response: R_{tot} differs in nature with the evidence provided by tracer compounds as it is a mass-based parameter rather than a qualitative marker for cloud chemistry. The reviewer is right that R_{tot} (or R_{sulf} or R_{aqSOA}, respectively) is not a direct measure of hygroscopicity. However, a high R_{tot} value points to an efficient mass increase in the range of the particle distribution that has been modified by cloud processing, and thus, qualitatively to an increase of CCN sizes, hygroscopicity and change in radiative properties.

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.

Response: Given the rather long introduction and the fact that we refer to several key references for both airborne and hill cloud experiments, we did not add any text. The detailed description of the two types of experiments is not essential to the following discussion.

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

Response: Changed as suggested.

Page1 line 17: Replace "aqueous phase" by "aqueous-phase"
Page2 line 52: Replace "aqueous phase" by "aqueous-phase"
Page2 line 57: Replace "aqueous phase" by "aqueous-phase" and "gas phase" by "gas-phase"
Page5 line 144 and 145: Replace "gas phase" by "gas-phase"
Page6 line 179: Replace "gas phase" by "gas-phase"
Page6 line 194: Replace "aqueous phase" by "aqueous-phase"
Page7 line 219: Replace "aqueous phase" by "aqueous-phase"
Page7 line 233: Replace "aqueous phase" by "aqueous-phase"
Page11 line 360: Replace "aqueous phase" by "aqueous-phase"
Page14 line 470: Replace "aqueous phase" by "aqueous-phase"
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"
Page16 line 524: Replace "aqueous phase" by "aqueous-phase"
Caption of Table1: Replace "aqueous phase" by "aqueous-phase"

Response: We changed 'aqueous phase' to 'aqueous-phase' and 'gas phase' to 'gas-phase', respectively, throughout the manuscript wherever it is used as an adjective.

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 "

Response: We added 'chemical' to cloud processing in the title and at several places throughout the manuscript

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

Response: The general terminology used by the PTRMS team that provides these data is to just list that measurement as "monoterpenes". The definition of this parameter in their archived read-me file is "Sum of all monoterpene isomers". Therefore, we thought it would be useful to just put in parenthesis this definition after the first time we introduce monoterpenes. Added text (l. 108):

"…for selected species, including MACR, MVK, monoterpenes (sum of monoterpene isomers), isoprene, and acetonitrile…"

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 SO2 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).

Response: The reviewer raises a good point. Many marine regions that aircraft have access to near coasts are certainly not pristine but influenced by anthropogenic pollution. For the sake of consistency with past work using the SEAC^{4}RS dataset that used the same air mass categorization titles and criteria (Shingler et al., 2016; Aldhaif et al., 2018), we prefer to keep the label as Marine but to note in the text that the marine air masses sampled were not truly pristine. Added text (l. 120):

It is further noted that the marine category is still impacted by anthropogenic pollution owing to transported continental pollution and ship exhaust and thus should not be regarded as representing pristine marine air masses.

References:

Shingler, T., Crosbie, E., Ortega, A., Shiraiwa, M., Zuend, A., Beyersdorf, A., Ziemba, L., Anderson, B., Thornhill, L., Perring, A.E., Schwarz, J.P., Campazano-Jost, P., Day, D.A., Jimenez, J.L., Hair, J.W., Mikoviny, T., Wisthaler, A., Sorooshian, A., 2016. Airborne characterization of subsaturated aerosol hygroscopicity and dry refractive index from the surface to 6.5km during the SEAC(4)RS campaign. J Geophys Res-Atmos 121, 4188-4210.

Aldhaif, A.M., Stahl, C., Braun, R.A., Moghaddam, M.A., Shingler, T., Crosbie, E., Sawamura, P., Dadashazar, H., Ziemba, L., Jimenez, J.L., Campuzano-Jost, P., Sorooshian, A., 2018. Characterization of the Real Part of Dry Aerosol Refractive Index Over North America From the Surface to 12km. J Geophys Res-Atmos 123, 8283-8300.

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

Response: The change was made as suggested.

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

Response: We changed ‘Mt.’’ To ‘Mount’

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

Response: We made the change as suggested.

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.

Response: We added the reference but did not include the equation as the parameter is commonly used in the literature.

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

Response: The space has been removed.

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.

Response: The reviewer is right that in cloud water both compounds are likely hydrated. However, as organic aerosol mass, including aqSOA, is determined in dried particles, the compounds will dehydrate and thus their O/C ratio will be 1 and 1.5, respectively.

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 m0 value is an important parameter in the paper and the linked ratio Rtot. If the m0 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?).

Response: Please refer to our response to the main comment 2) above. The masses in Table 1 have been corrected.

Page6 line 179: Please correct "aerosl"

Response: Corrected (We assume that the reviewer referred to line 186.)

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.

Response: We added (l. 198)

On the other hand, loss reactions of organic acids might be underestimated, such as the photolysis of iron-dicarboxylato complexes (Weller et al., 2014).

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.

Response: The text was changed as follows (l. 207):

'…over the course of the 1-hr simulations, with the parcel spending about 40 min in the cloud.

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

Response: Commas were added.

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?

Response: We added (l. 214)

'…where a similar chemical mechanism was applied

Page6 line 205: Replace "SO2 depletion" with "SO2 oxidation"

Response: 'Depletion' was changed '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?

Response: The rates reported here are an average over the 40 min in-cloud time.
The sulfate formation pathways considered in the current study are the oxidation of S(IV) by H_2O_2 and O_3 with the former being predominant due to the moderate to low pH in the cloud water. Other

pathways have not been considered as many studies have shown that these pathways will be the dominant ones in many regions of the world. In addition, data such as metal ion concentrations (Mn, Fe) were not available from the current data set.
We would like to compare the formation rates to other studies; however, formation rates are not commonly reported.

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".

Response: We removed the sentence.

Page7 line 237: Please compare the calculated changes in k with observed changes in the field in this subsection (see e.g., Henning et al. 2014).
Henning, S., Dieckmann, K., Ignatius, K., Schafer, 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.

Response: We thank the reviewer for this idea. We added the following discussion (l. 259ff):

Similar trends in an increase of the hygroscopicity parameter κ have been observed previously; for example, Henning et al. (2014) demonstrated an increase of $< 0.1 < \Delta\kappa < \sim 0.3$ in a forest site in Thuringia (Germany). However, in a marine cloud no distinct difference in hygroscopicity of particles due to cloud processing was detected (Swietlicki et al., 1999) since the pre-existing particles consisted mostly of ammonium-sulfate particles and the added mass was sulfate. In the Amazon, during the biomass burning season, the increase in particle size and hygroscopicity was small due to atmospheric processing but still more significant than in the dry season (Rissler et al., 2006). In that case, mostly organic material was added to the pre-existing particles. These trends in the various scenarios are in qualitative agreement with the findings from our model studies where the largest change in hygroscopicity is predicted to occur in biogenic areas.

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

Response: Space was added.

Page8 line 276: Remove "B".

Response: 'B' was removed. (Please note that the preceding sentence was removed as well.)

Page9 line 283-297:
In general, the Rtot ratio itself is a nice idea, but particularly the RaqSOA 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.

Response: We agree with the reviewer that the assumed yield for aqSOA is very uncertain. However, since our current study is very explorative at this point and not many lab experiments have been targeted to determine these yields, we don't think that additional model studies using different yields will lead to different conclusions. We highlighted the complexity of the aqSOA yield and the need of more experiments that refine this parameter by adding the following text (l. 308):

This parameter might be higher for aqSOA formation from oxygenated compounds but is not a conservative value over time due to the possibly efficient decrease of aqSOA products due to oxidation. Therefore, targeted experiments should be performed in order to refine this value for a variety of (oxygenated) VOCs.

Page9 line 299: Correct the values of Rtot "0.2.0"

Response: Since all R values have changed (cf introductory paragraph to this response), the value was corrected accordingly.

Page9 line 299: "Rtot" has to be subscript: "Rtot"

Response: Rtot was corrected to R_{tot}.

Page9 line 307-311: Please discuss the contribution of RSO4 and RaqSOA to Rtot 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%

Response: We refrain from adding lines to Table 3. However, we added text to the abstract and discussion, respectively, as follows to clarify the dominant role of sulfate over aqSOA (l. 29 and 323):

Abstract: R_{tot} is dominated by the addition of sulfate (R_{sulf}) in all scenarios due to the more efficient conversion of SO_2 to sulfate as compared to aqSOA formation from organic gases.

Section 3.1.4: The contribution of aerosol processing by organics is highest in the biomass burning cases where R_{aqSOA} is 20% and 6% of R_{tot}, respectively.

Page9 line 310/ and Page10 line 314/342 and Page11 line 360: "R" should be "Rtot". Please check carefully the whole manuscript for missing indices.

Response: We checked the manuscript and added indices where necessary.

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.

Response: Most of this text refers to a study performed by one of the corresponding authors describing Figure 3 that contrasts wet vs dry conditions. In order to complement the list of other cloud processing studies, we complemented the text at the end of the paragraph (l. 392):

Similarly, tracers of aqSOA formation were detected in fog in the Po Valley (Gilardoni et al., 2014).Cloud-processed particles were observed in many targeted field experiments. For example, increased mass in large particles was detected during the HCCT experiment where cloud processed aerosol was analysed (Henning et al., 2014).

Page11 line 381: Please revise "Figure 32"

Response: Corrected.

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.

Response: We added g(RH) when 'growth factor' is first used which is indeed at the end of section 2.1.2.

Page13 line 431/432: Do not separate "-" and "3"

Response: This separation cannot be changed due to the used word processor. It will be corrected in the copy-edited version of the manuscript.

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.

Response: We added these references.

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

Response: We added the following references (Häkkinen et al., 2014; Nah et al., 2018)

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.

Response: We added the following references reflecting lab, field and model studies (l. 487) (Volkamer et al., 2006; Perri et al., 2010; McNeill et al., 2012; Marais et al., 2016)

Page15 line 514: Replace "and thus" by "and, thus,"

Response: Commas have been added.

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

Response: 'Chemical' was added.

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."

Response: We thank the reviewer for these thoughts. We agree that the droplet mode is probably still the best indicator for cloud processing – whether by chemical or physical processes. We extended the paragraph as follows (l. 531):

Size-resolved measurements can provide evidence whether a droplet mode exists that is formed from the addition of cloud-derived mass. Our model results show that this droplet mode can be expected to be mostly comprised of sulfate whereas a modification of aerosol properties due to aqSOA formation is likely to be small.

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.

Response: We added (l. 531):

In addition, parameters such oxidant levels, cloud water pH and life time will also affect in-cloud mass formation rates.

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 Rtot. As mentioned in the comment above, the extent to which aerosol properties are modified depends also on other parameters.
Furthermore, the current "Rtot" is almost exclusively related to the complete conversion of SO2 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 Rtot. Therefore, I'm not convinced that Rtot represents a substantial process or breakthrough to the proposed question.
If the main outcome of Rtot 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.

Response: Given that we tried to shorten the conclusions, we did not add a further discussion of these referee comments at the end of the section. We think that R_{tot} (or R_{sulf} and R_{aqSOA}) are useful parameters to estimate the potential of air masses to introduce efficient modification of aerosol by cloud-processing. As pointed out in our responses above, Rtot does not reflect a quantitative estimate of changes in hygroscopicity or other parameters. However, it is useful as a first-order estimate for the characterization of air masses whether cloud processing can be detected or not.

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.

Response: We changed the references accordingly.

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

Response: We added the doi number.

- 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.

Response: We corrected the formatting of the doi numbers accordingly

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

Response: The reference was replaced.

-Page21 line 838: Please correct "SEAC⁴RS:"

Response: Corrected

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

Response: Corrected

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

Response: We decreased the size of the legend boxes to avoid this.

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

Response: Eq was replaced by Equation

Caption of Figure 2: Put a dot at the end.
Caption of Figure 4: Put a dot at the end.

Response: Both captions were corrected.

Caption of Figure 5: Please use “k” in the caption and as axis label of the y-axis.

Response: ‘kappa’ was changed to ‘κ’

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

Response: GF-derived was changed to growth-factor-derived and the figure was revised.

Supplemental Information:

- Add a parenthesis “log ([absolute mass increase / g m-3])”.

Response: Please note that we show the absolute mass increase on a linear scale. The unit was corrected accordingly.

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

Response: The period at the end was added.

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.

Response: The period at the end was added.

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

Response: We changed the captions of Figure 2, S1 and S2.

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Is there an aerosol signature of chemical cloud processing?

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Abstract

The formation of sulfate and secondary organic aerosol mass in the aqueous phase (aqSOA) of cloud and fog droplets can significantly contribute to ambient aerosol mass. While tracer compounds give evidence that ~~aqueous~~ 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. We analyse data from several field experiments and model studies for six air mass types (urban, biogenic, marine, wild fire biomass burning, agricultural biomass burning and background air). We focus on the trends of changes in mass, hygroscopicity parameter κ, and oxygen-to-carbon (O/C) ratio due to chemical cloud processing. We find that the modification of these parameters upon cloud-processing is most evident in urban, marine and biogenic air masses, i.e. air masses that are more polluted than very clean air (background air) but cleaner than heavily polluted plumes as encountered during biomass burning. Based on these trends, we suggest that the mass ratio (R_{tot}) of the potential aerosol sulfate and aqSOA mass to the initial aerosol mass can be used to predict whether chemical cloud processing will be detectable. Scenarios where this ratio exceeds R_{tot} ~ ~~2~~ 0.5 are the most likely ones where clouds can significantly change aerosol parameters. R_{tot} is dominated by the addition of sulfate (R_{sulf}) in all scenarios due to the more efficient conversion of SO_2 to sulfate as compared to aqSOA formation from organic gases. As the formation processes of aqSOA are still poorly understood, the estimate of R_{aqSOA} is likely associated with large uncertainties. Comparison to R_{tot} values as calculated for ambient data at different locations ~~confirm~~ validates the applicability of the concept to predict a chemical cloud-processing signature in selected air masses.

1 Introduction

Clouds and, in particular, aerosol-cloud interactions represent one of the largest uncertainties in our current understanding of radiative forcing (Stocker et al., 2013). Thus, representing cloud chemistry in models is challenging,

as the prediction of aerosol mass production in clouds is inherently impacted by the uncertainties in the description of cloud properties (e.g., liquid water content (LWC), drop size distribution, cloud lifetime, geographical location, altitude and cloud density), in addition to uncertainties in the chemical mechanisms and precursors (Ervens, 2015). Airborne chemical measurements in clouds can be used to study cloud processing, but such measurements are relatively sparse and usually only represent snapshots of a few seconds of an aircraft transect. Several studies have been performed on mountain tops where hill capped clouds cover the summit for extended period of times (Choularton et al., 1997; Herrmann et al., 2005; Li et al., 2017). While in "hill cloud" experiments more continuous data sets can be collected, they are limited in their geographical coverage and their interpretation is complicated by variable advection of various sources and air masses. Many studies show enhanced concentrations of sulfate, oxalate and related organics in cloud-processed air as compared to cloud-free air (Crahan et al., 2004; Sorooshian et al., 2006a; Sorooshian et al., 2007; Wonaschuetz et al., 2012). It has been recognized for several decades that globally a major fraction of sulfate is formed in clouds (Roelofs et al., 1998; Barth et al., 2000) and to a smaller extent also in deliquesced aerosol particles (Sievering et al., 1991; Alexander et al., 2005; Zheng et al., 2015). More recently, it has been shown that also secondary organic aerosol (SOA) mass can be formed by chemical reactions in cloud and aerosol water (aqSOA) (Surratt et al., 2010; Ervens et al., 2011; McNeill, 2015; Xu et al., 2015; Marais et al., 2016). However, SOA formation in clouds is not always observed~~, however~~. For example, Wagner et al. (2015) systematically analysed vertical profiles in the SOA-dominated Southeast US, and found that SOA formation in the fair-weather cumulus clouds was statistically insignificant.

The formation processes, precursors and conditions for aqSOA formation are more poorly quantified than for sulfate. Tracer compounds such as oxalic acid that are dominant products of ~~aqueous~~ aqueous-phase processes have been identified but usually only contribute a few percent to the total aerosol mass (Shen et al., 2012; Wang et al., 2012) and, thus, they do not reveal the general role of aqSOA formation to modify aerosol properties. In addition, oxalate might have additional, less dominant emission sources such as biomass burning (Narukawa et al., 1999; Falkovich et al., 2005; Zhang et al., 2017) and other ~~others~~ sources (Huang and Yu, 2007). Bulk properties of OA have been shown to be modified differently by ~~aqueous~~ aqueous-phase processes than by surface or ~~gas~~ gas-phase reactions. These properties include the oxygen-to-carbon (O/C) ratio which is often higher in aqueous-phase derived products (Ervens et al., 2011; Sorooshian et al., 2011; Waxman et al., 2013; Chakraborty et al., 2016) or hygroscopicity (Shingler et al., 2016). However, pathways that produce aerosol with high O/C via gas-phase reactions are also possible (Chhabra et al., 2011; Ehn et al., 2014; Krechmer et al., 2015), which needs to be taken into account in the interpretation of case studies. Several laboratory studies have shown that organics that are formed in aqueous-phase reactions might absorb light (e.g., (De Haan et al., 2010; Powelson et al., 2014; Laskin et al., 2015)). However, these products only comprise a very small fraction of the total organic carbon and are likely only formed in evaporating cloud droplets, i.e. on short time scales and when solute concentrations become sufficiently high.

The addition of mass in clouds only occurs on activated particles and often leads to a distinct droplet mode that separates unactivated particles from activated ones (Hoppel et al., 1994). A similar effect of mode separation might be achieved by collision/coalescence within clouds (Feingold et al., 1996); however, these physical processes do not lead to a distinct change in chemical composition such as the production of ~~aqueous~~ aqueous-phase tracer compounds.

While this size separation might be the most unequivocal microphysical tracer of chemical cloud processing, also the change in bulk and/or size-resolved (physico)chemical properties of the aerosol population might be used to identify cloud-processed aerosol. Not only total aerosol mass, but also its distribution throughout the particle population is important since particle size and composition determine particles' atmospheric lifetime by dry and wet deposition (Maria et al., 2004) and the aerosol direct and indirect effects on climate (Lin et al., 2014). Thus, it is important to identify and quantify how cloud-derived products affect aerosol loading and properties.

~~Many current model parameterizations for sulfate and aqSOA formed in clouds apply empirical expressions to distribute mass throughout the aerosol size distributions (Ervens, 2015, and references therein). However, such approaches might lead to inaccurate representation of time dependent mass evolution and consequently of particle lifetime.~~

In the current study, we apply a combination of model simulations and observations to explore a possible signature of chemical cloud processing in aerosol. Unlike other studies that focused on single parameters, such as modification of size distribution (Eck et al., 2012), aqSOA tracer compounds (Kawamura and Ikushima, 1993; Kawamura and Yasui, 2005; Agarwal et al., 2010), and O/C ratio (Chakraborty et al., 2016), we compare all of these properties in different air masses, from ~~very~~ clean (background air) to heavily polluted (biomass burning) as they were identified using highly instrumented aircraft data from SEAC^{4}RS. Trends in model results are compared to those from other observational data sets, in order to draw conclusions on a possible ~~cloud~~ cloud-processing signature in different air mass types.

2 Data Sets

2.1 Data Sets and Air Masses

2.1.1 SEAC^{4}RS (Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys) aircraft field study results as input to model

A rich set of airborne data collected on the NASA DC-8 is used from SEAC^{4}RS based out of Houston, Texas in August-September 2013 (Toon et al., 2016). SEAC^{4}RS was a multi-platform field campaign addressing issues associated with atmospheric composition over North America. It included two test flights and 21 research flights with the DC-8 covering altitudes from the surface to above 10 km. Data from this campaign were used to initialize model simulations that will be discussed subsequently.

Owing to the broad range of conditions sampled, a variety of criteria used by Shingler et al. (2016) for the same dataset, were applied to define the following air mass types:

- Biomass Burning (BB) – Wildfire: Acetonitrile > 250 pptv or (when acetonitrile unavailable) CO > 250 ppbv in non-urban areas;
- Biomass Burning – Agricultural: Same as BB - Wildfire, with additional visual confirmation;
- Biogenic: Isoprene + monoterpenes + methyl-vinyl-ketone (MVK) + methacrolein (MACR) > 2 ppbv and acetonitrile < 250 pptv;
- Marine: in planetary boundary layer (PBL), over ocean, and more than 40 km from the coast;

- Urban: in PBL; spatially over Houston (30.50°N, - 94.60°W to 29.00°N, -96.10°W) or Los Angeles (34.17°N, -117.00°W to 33.44°N, -119.75°W);
- Background/Mixed: in PBL; did not fit into first five categories.

Relevant instruments used to obtain data to apply the criteria above included a Proton-Transfer-Reaction Mass Spectrometer (PTR-MS) (de Gouw and Warneke, 2007) for selected species, including MACR, MVK, monoterpenes (sum of monoterpene isomers), isoprene, and acetonitrile. Isoprene levels in biomass burning plumes represented upper limits owing to interferences from other species such as furan. Furthermore, isoprene levels are higher in the Biomass Burning – Agricultural category as compared to the Biomass Burning – Wildfire category owing to the aircraft having sampled the former much closer to its source as compared to the more aged plumes of the latter. The MVK and MACR data also are vulnerable to an interference (ISOPOOH), which is most relevant in lower NO regions. As the corresponding NO and NO_2 levels (measured by NOAA NO_yO_3 instrument) in ***Table S1*** are not very low, this potential interference is considered to be minor, except for the biogenic cases, where it is known to be substantial. Data for CO were obtained from a folded-path, differential absorption mid-IR diode laser spectrometer (Sachse et al., 1987). Water vapour data were used from the Diode Laser Hygrometer to identify the height of the PBL (Diskin et al., 2002). ***Table S1*** also lists the concentrations of the following gases: HCHO (NASA In-Situ Airborne Formaldehyde (ISAF) instrument), SO_2 (Georgia Tech Chemical Ionization Mass Spectrometer (CIMS)), H_2O_2 (Caltech CIMS) and O_3 (NOAA NO_yO_3 instrument). It is further noted that the marine category is still impacted by anthropogenic pollution owing to transported continental pollution and ship exhaust and, thus, should not be regarded as representing pristine marine air masses.

An Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-AMS) (DeCarlo et al., 2006; Canagaratna et al., 2007; Dunlea et al., 2009) was used for non-refractory composition of submicrometer particles, including the O/C ratio of OA. Given that the HR-AMS, as operated and analysed for SEAC^{4}RS, did not quantify refractory and semi-refractory species, submicron sodium chloride and nitrate in the marine BL are not included in the AMS results.

Black carbon (BC) data were obtained with a Humidified-Dual Single-Particle Soot Photometer (HD-SP2) (Schwarz et al., 2015). Aerosol size distribution data were used from the Langley Aerosol Research Group Experiment (LARGE) instrument package from a Scanning Mobility Particle Sizer (SMPS; TSI, Inc, model 3080/3010; mid-point D_p between 11 and 316 nm) and an Ultra-High Sensitivity Aerosol Spectrometer (UHSAS; Droplet Measurement Technologies, Inc.; mid-point D_p between 63 nm and 891 nm). Sizing calibrations were performed frequently during the measurement period using polystyrene latex spheres and monodisperse ammonium sulfate particles for the SMPS and UHSAS, respectively. The two distributions were stitched together at the upper diameter bound of the SMPS, above which the UHSAS data were used (cf ***Section 3.2***).

2.1.2 Data sets for identifying cloud processing

Data are analysed from several other campaigns. More specifically, the following datasets are used:

(i) Water-soluble anions and cations from a particle-into-liquid sampler coupled to off-line ion chromatography (PILS-

IC, Brechtel Mfg. Inc.; (Sorooshian et al., 2006b) deployed on the Center for Interdisciplinary Remotely Piloted Aircraft Studies (CIRPAS) Twin Otter during the Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS) mission between August and September 2006, based in Houston, Texas;

(ii) Size-resolved aerosol composition from a micro-orifice uniform deposit impactor (MOUDI, MSP Corporation (Marple et al., 1991)) at three ground sites in Arizona (Hayden, Tucson, ~~Mt~~Mount~~.~~ Lemmon; (Sorooshian et al., 2012; Youn et al., 2015) and in Marina, California (Maudlin et al., 2015; Braun et al., 2017); and

(iii) Size-resolved aerosol hygroscopic growth factors g(RH) as measured by a humidified tandem differential mobility analyzer (HTDMA; Brechtel Manufacturing Inc. (BMI) Model 3002; (Wonaschütz et al., 2013)) for samples collected at a ground site at Mount~~t.~~ Lemmon in Arizona.

2.2 Model

2.2.1 Model Description

A parcel model is used to simulate cloud-processing in a transect of an air parcel along a prescribed trajectory through a cloud (Feingold and Kreidenweis, 2000; Ervens et al., 2004). ~~Gas-~~Gas-phase chemistry occurs during the full simulation; the chemical scheme is based on the NCAR Master mechanism (Kim et al., 2012). ~~Gas-~~Gas-phase precursors for aqSOA include isoprene, toluene, xylene, and ethylene whose oxidation products (glyoxal and related compounds) are taken up into the aqueous phase and further oxidized (Ervens et al., 2004). These precursor compounds and SO_2 are not replenished during the simulation, ~~in order~~ to simulate emissions into a cloud away from emission sources. AqSOA formation from these compounds and sulfate formation by SO_2 oxidation with H_2O_2 and O_3 have been described previously (Ervens et al., 2014; McVay and Ervens, 2017). Aerosol mass formation outside clouds or on/in interstitial particles inside the clouds is not included to focus only on aerosol modification due to ~~aqueous-phase processes~~ chemical processes in cloud droplets. We do not include non-oxidative aqSOA formation pathways in our model (e.g. IEPOX formation) as they have been shown to (i) occur on longer time scales and (ii) are most effective in wet aerosol as compared to cloud droplets (Woo and McNeill, 2015). ~~They likely occur on longer time scales than the rapid oxidation reactions.~~ Thus, overall the predicted total aqSOA mass might represent an underestimate while the formation rate might be overestimated. ~~–~~Particle growth is assumed to only occur via chemical mass addition; ~~it is assumed here that in stratocumulus clouds~~ collision/coalescence processes ~~processes do not greatly contribute to a change in mass and composition~~are neglected~~le~~.

It should be noted that we do not aim to reproduce observational results but rather seek trends in aerosol properties (O/C ratio, ~~κ,~~ hygroscopicity, mass) over a wide range of conditions in different air masses. The volume-weighted hygroscopicity parameter κ is calculated based on the equations ~~as~~ given by Petters and Kreidenweis (2007), considering ~~These values change over the course of a simulation due to the addition of sulfate and aqSOA mass (mass and κ) and individual aqSOA constituents (O/C ratio). The hygroscopicity parameter κ is calculated as a volume-weighted value of~~ the individual aerosol fractions multiplied by ~~(~~κ_{sulf} = 0.7; κ_{aqSOA} = 0.5, κ_{NH4} = 0.6, κ_{NO3} = 0.55, κ_{org} = 0.1, respectively~~)~~. κ_{org} refers to the initial organic aerosol fraction before cloud processing; this organic fraction is likely composed of both SOA and primary organic aerosol (POA). This estimate is based on measurements during

SEAC^{4}RS where particles with high organic content exhibited κ ~ 0.1 (Shingler et al., 2016). The organics that are added by chemical reactions in the cloud water are referred to here as aqSOA. The hygroscopicity parameter for this added aqSOA mass (κ_{aqSOA} = 0.5) is assumed to be the upper range of oxalate salts (Drozd et al., 2014) since oxalate/oxalic acid is one of the major constituents of cloud aqSOA (Ervens et al., 2011). ~~Using this high value for aqSOA, seems an appropriate assumption to represent the hygroscopicity of organics in their dissolved state, i.e. in cloud water. The initial bulk κ values for each air mass are estimated based on the volume fraction of each species (sulfate, nitrate, organics, chloride, ammonium, black carbon, ***Table 1***) using the ZSR approximation (Petters and Kreidenweis, 2007).~~ The initial κ values at t = 0 are the values that were determined from growth factor measurements during SEAC^{4}RS (Shingler et al., 2016). The change in κ during the course of the simulation is calculated after each model time step (1 s), i.e. by taking into account the newly formed sulfate and aqSOA masses that are added to the initial mass.

The O/C ratio is molecular-based and its evolution is calculated according to aqSOA products (O/C(glyoxal) = 1; O/C(glyoxylic acid) = 1.5, O/C(oxalic acid) = 2, etc) that are added to the initial organic fraction. While these compounds might by hydrated in cloud water and have O/C = 2, in the dried aerosol phase, they are likely present in their dehydrated state. The bulk O/C ratio is calculated by summing the total number of oxygen atoms across all organic species and dividing by the total number of carbon atoms. The evolution of particle sizes in 30 size classes (11 nm < aerodynamic diameter < 860 nm) is tracked.

2.2.2 Model simulations

The model simulations are initialized with air-mass-specific aerosol and gas-phase compositions for the six air masses. The cases differ in their initial concentrations of aerosol mass, mass fractions, particle number concentrations and initial κ, O/C ratio (***Table 1***) and ~~gas~~ gas-phase mixing ratios (***Table S1***). It is assumed that the aerosol is internally mixed and particles of all sizes have the same composition, which is supported by the AMS size distributions for most cases, except some fresh biogenic plumes. For simplicity, we consider the same trajectory for all air masses in the parcel model where an air parcel spends about 40 min of the 1-h long simulation time in the cloud (between ~450 s and 1100 s and 1800 – 3600 s, respectively). Cloud chemistry occurs only when a minimum total liquid water content, LWC > 0.01 g m^{-3}, is exceeded. When RH drops below 100% cloud droplets evaporate, together with some volatile organics. Even though organic acids (glyoxylic, oxalic, pyruvic) have relatively high vapour pressures, it is assumed that they stay in the particle phase as they contribute to aqSOA in form of salts and complexes. ~~–~~The low pH value of ~~aerosl~~aerosol water as observed during SEAC^{4}RS might ~~also~~ lead to evaporation of organic acids with low pK_a values (Häkkinen et al., 2014; Nah et al., 2018). However, the fact that these acids are present in aerosol found during the campaign suggests a complex set of equilibria of acid gas/condensed phase partitioning and salt and complex formation of partially dissolved carboxylates. However, ~~also~~ additional formation pathways may be missing from our model studies so that the production rate of organic acids (Lim et al., 2015) is, on the one hand, underestimated. On the other hand, loss reactions of organic acids might be underestimated, such as the photolysis of iron-dicarboxylato complexes (Weller et al., 2014).

All initial size distributions show already some evidence of cloud processing (***Section 3.2***); however, our model exercise intends to show the extent to which such somewhat aged aerosol populations will be further altered due to ~~aqueous~~ aqueous-phase processing. In the following, we discuss both the modification of bulk and size-resolved parameters.

3 Results and Discussion

3.1 Bulk Parameters

3.1.1 Mass increase

Figure 1 show the predicted increase of sulfate and aqSOA mass (left axis), respectively, over the course of the 1-hr ~~cloud~~ simulations, with the parcel spending about 40 min in the cloud. The in-cloud time is marked by the black lines at the top of each panel in

Figure 1. In all cases, sulfate increases very rapidly and stays constant after all SO_2 has been consumed. The increase in aqSOA is slower as it is formed in multiple oxidation steps from precursors (e.g. isoprene → glyoxal → glyoxylic acid → oxalic acid). ~~The in-cloud time is marked by the black lines at the top of each panel in ***Figure*** 1.~~ In the time period between the two cloud passages (~1100 – 1750 s), the lines are horizontal as no mass is added during that time and, thus, the aerosol mass and properties remain unchanged. These different time scales are in agreement with previous findings on the comparison of sulfate vs OH-initiated aqSOA formation in clouds (Ervens et al., 2004) where a similar chemical mechanism was applied and in aqueous aerosol (El-Sayed et al., 2015). Rapid SO_2 ~~depletion~~ oxidation within clouds and fogs has been observed previously (Husain et al., 2000; Reilly et al., 2001). Our predicted sulfate formation rates (~10^{-8} – 10^{-5} M s^{-1}, depending on the air mass) are in general agreement with those as found at Mount Tai, China, for moderately acidic and neutral cloud water (Shen et al., 2012).

The relative proportions of sulfate and aqSOA to total in-cloud mass addition depend on the air mass: While there is clearly more aqSOA than sulfate in the biomass burning and biogenic scenarios (

Figure 1***c, d, and f***), the mass formed in cloud in the urban and marine scenarios are more sulfate-dominated, even though the total SO_2 in these scenarios is less than the total VOC mixing ratios (cf ***Table S1***). While SO_2 is completely converted to sulfate (other sulfate precursors are not considered) on a short time scale, aqSOA mass yields from in-cloud VOC oxidation are much lower (≤ ~10%) as in each oxidation step, volatile compounds are formed (e.g. HCHO, CO_2) that do not contribute to aqSOA (Ervens et al., 2008) but evaporate from the droplets.

The absolute mass increase seems quite large (0.2 - 10 μg m^{-3} depending on air mass type). However, it should be remembered that our predictions might exaggerate real conditions as neither physical (deposition) nor chemical (oxidation of organics to volatile compounds in cloud water) sinks for aerosol mass are included in our model in order to tease out the clearest signature of ~~aqueous~~ aqueous-phase processing possible. The predicted increase in sulfate in clouds has been observed in many previous studies for a variety of air masses~~, e.g.~~ (e.g., Table 1 in Ervens, 2015).

Cloud residues at Mount Tai, China, exhibited large fractions of sulfate and water-soluble organics (Li et al., 2011). In the latter study, both sulfate and aqSOA were found internally mixed in the droplet mode, which suggests that both were formed in clouds. Increasing organic mass with altitude in clouds (which can be considered being analogous to processing time) have been observed in several previous field studies focused on marine and urban air masses, e.g., (Sorooshian et al., 2007; Wonaschuetz et al., 2012). *Erreur ! Source du renvoi introuvable.* compares the distribution of individual organic acids to the total organic acid content in various air masses, as measured by the PILS-IC method on the CIRPAS Twin Otter during the 2006 GoMACCS campaign. ~~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.~~ The comparison of the oxalic acid contributions below, in and above cloud suggests that these three air masses were connected and mass was transported vertically while it was processed in cloud leading to an increasing oxalate fraction. Often times, air above clouds might not be cloud-processed but transported horizontally, which may lead to erroneous interpretation of the role of cloud processing (cf ***Section 4***). While the increase in oxalate clearly points to in-cloud mass formation due to ~~aqueous-~~aqueous-phase processes, in-cloud aerosol measurements are likely associated with some uncertainties, in particular due to difficulties of sampling cloud droplets vs interstitial particles, and issues associated with cloud droplet impacts on inlets, e.g. (Murphy et al., 2004). In contrast to the GoMACCS and other measurements, no clear aqSOA signature was observed in an SOA-rich biogenic region (Wagner et al., 2015).

3.1.2 Changes in bulk hygroscopicity

The initial κ is in all air masses lower than that of sulfate (κ_{SO4} = 0.7) and in most cases even lower than that assumed for aqSOA (κ_{aqSOA} = 0.5) (***Section 2.2.1*** and ***Table 1***). The predicted κ values (blue lines in

Figure 1**,** first right axis) increase immediately due to the rapid sulfate addition and then drop when aqSOA mass is added to the processed particles, corresponding to the changes in absolute masses and mass ratios (***Section 3.1.1***). It should be remembered that the simulations are set up such that they represent the decay of precursor gases without any replenishment during the simulation time. If mixing of additional gas-phase precursors occurred continuously into the cloud, the changes in κ might not be as temporally resolved as predicted in ***Figure 1.*** In such a case, the distinct temporal changes in κ due to sulfate and aqSOA addition, respectively, might be more obscured, e.g. when other secondary organics are added simultaneously to the particles. The time scales of aqSOA formation might be different for other aqSOA formation processes, i.e. those that are not initiated by the OH radical which would also change the slope of the mass and κ evolution in ***Figure 1***. In addition, in the ambient atmosphere the predicted trends in κ could be additionally obscured due to mixing with other air masses into the cloud. ~~The~~ Overall, the changes of κ in the biomass burning cases (Figure 2***c*** and ***d***) are overall very small (Δκ ≤ 0.1) except during the sharp peak at the beginning when ~~aqSOA (κ_{aqSOA} = 0.5)~~sulfate is added.

Similar trends in an increase of the hygroscopicity parameter κ have been observed previously~~,~~; ~~F~~for example, Henning et al. (2014) demonstrated an increase of < 0.1 < Δκ < ~0.3 in a forest site in Thuringia (Germany). However, in a marine cloud no distinct difference in hygroscopicity of particles due to cloud processing was detected (Swietlicki

et al., 1999) since the pre-existing particles consisted mostly of ammonium-sulfate particles and the added mass was sulfate. ~~(2008)~~ In the Amazon, during the wet season, the increase in particle size and hygroscopicity was small due to atmospheric processing but still more significant than in the dry season (Rissler et al., 2006). In that case, mostly organic material was added to the pre-existing particles. These trends in the various scenarios are in qualitative agreement with the findings from our model studies where the largest change in hygroscopicity is predicted to occur in biogenic areas.

3.1.3 Changes in bulk O/C ratio

The oxygen-to-carbon (O/C) ratio only reflects the composition of the organic portion of the aerosol (OA). The orange lines in

Figure 1 (second right axis) show the predicted bulk O/C ratios as calculated based on predicted aqSOA formation (***Section 2***). In all cases, the O/C ratio increases close to the beginning of the simulations, with the lines following the same trends as predicted for the aqSOA mass increase (***Section 3.1.1***). The increase in O/C ratio continues still in the second passage of the parcel through the cloud. This increase is caused both by oxidation of dissolved VOCs and by the further oxidation of aqSOA products that have been formed in the cloud water (e.g. oxidation of glyoxylic to oxalic acid). Similar to the findings for the mass increase and κ, the largest increase in O/C ratio can be seen for the urban, marine and biogenic cases with $\Delta(O/C) \leq 0.4$. For the biomass burning cases, the changes are rather subtle with an increase of $\Delta(O/C) \lesssim 0.1$. It should be noted that this change might even represent an overestimate as we neglect numerous physical and chemical processes that could lead to a weaker increase in Δ(O/C) or even to its decrease. Such processes include non-oxidative reactions that lead to aqSOA which will produce less-oxygenated aerosol. It was discussed that IEPOX might contribute significantly to aqSOA in wet aerosol (Budisulistiorini et al., 2017) or non-photochemical processes ~~occur~~ in fog (Sullivan et al., 2016). Wet deposition or further oxidation of oxygenated and highly soluble aqSOA constituents might lead to a removal of highly soluble organics and thus to an overall decrease of the bulk O/C ratio.

There are not many studies that focus on modifications of the O/C ratio in the aqueous phase. Gilardoni et al. (2016) found an increase in O/C ratio of $\Delta(O/C) \sim 0.2$ upon fog processing in a biomass burning plume. The increase upon processing was similar to the predicted one with $\Delta(O/C) \sim 0.2$ (

Figure 1***c, d***). During the Whistler Aerosol and Cloud Study (WACS 2010), Lee et al. (2012) found that in a biogenically-influenced background site, the O/C ratio was clearly enhanced upon cloud processing, similar to the O/C ranges as shown in

Figure 1***e and f***. However, they pointed out uncertainties in translating the f_{44} signal from unit-mass resolution AMS measurements into O/C ratio, as the relationships determined by Aiken et al (2008) and Canagaratna et al. (2015) might not be generally valid for all species and ranges of O/C ratios. ~~The largest change in κ and O/C ratio is predicted for the urban, marine and biogenic air masses (***Figure 1a, b, f***) whereas the changes in the biomass burning cases (~~

~~***Figure* 1*c, d*) and background air (**~~

~~***Figure* 1*e*) are smaller. B**~~

3.1.4 The ratio of potential added mass from precursor gases to initial aerosol mass

~~Biomass burning scenarios are characterized by high aerosol mass loadings and high – mostly organic – trace gas mixing ratios. The background/mixed case has a higher initial mass (3.86 µg m^{-3}, ***Table 1***) than the marine, urban and biogenic air masses whereas the precursor gases are approximately on the same order of magnitude as in these three air mass types (***Table S1***).~~ In order to significantly change the bulk properties of initial aerosol by additional ~~SO_2~~ sulfate and aqSOA mass, the newly-formed mass has to comprise a substantial fraction of the total mass so that the volume-based κ and the molecular-based O/C ratio are significantly changed. Based on this idea, we calculate an initial potential added mass due to aqueous processing of precursors-to-pre-existing mass ratio for each air mass:

$$R_{tot} = \underbrace{\frac{[SO_2]\cdot 98/64}{m_0}}_{R_{SO4}} + \underbrace{\frac{Y_{aqSOA}\cdot[aqSOA\ prec]}{m_0}}_{R_{aqSOA}} \quad [\mu g\ m^{-3}\ /\mu g\ m^{-3}] \qquad \text{Equation-1}$$

Where [SO_2] is the mass concentration of SO_2 [µg m^{-3}], the factor of 98/64 accounts for the mass difference of H_2SO_4 vs. SO_2, and [aqSOA prec] is the total mass concentration [µg m^{-3}] of all VOCs that may act as precursors for aqSOA (***Table S1***). These precursors include isoprene, methyl vinyl ketone, methacrolein, toluene, xylene and ethylene. The numerator is the potentially added mass, i.e. the mass that would be added to the initial mass m_0 [µg m^{-3}] due to cloud processing, if the precursors were completely consumed. The VOC mixing ratio is multiplied with an approximate effective mass yield factor Y_{aqSOA}, in order to account for the facts that (i) only part of the VOCs mass will be converted into aqSOA and (ii) aqSOA species can be further oxidized to CO_2 and thus – unlike sulfate – it is not a preserved mass. An effective yield of 10% is assumed in the remainder of this study, based on model studies that have shown that the aqSOA yield from isoprene is at most 10%, depending on cloud and NO_x conditions (Ervens et al., 2008). This previous model study might not have included all aqSOA precursors and formation pathways so that the mass yields reported there might represent an underestimate. If more updated information on yields for specific precursors becomes available, the value of Y used in Equation 1 can be updated accordingly. This parameter might be higher for aqSOA formation from oxygenated compounds but is not a conservative value over time due to the possibly efficient decrease of aqSOA products due to oxidation. Therefore, targeted experiments should be performed in order to refine this value for a variety of (oxygenated) VOCs.

In

Table 2, the R_{tot} values for all six air masses are listed. The highest value (R_{tot} = ~~5.2~~0.97) is shown for the marine scenario followed by the values for the biogenic (R_{tot} = ~~0.2.0~~0.31) and urban (R_{tot} = ~~2.0~~0.21) cases. The lowest values are shown for the biomass burning cases (R_{tot} = 0.~~012~~ 04 and R_{tot} = 0.~~56~~ 14 for the wildfire and agricultural burning, respectively) with a similar value for the background case (R = 0.~~72~~07). While the VOC mixing ratios in the biomass burning air masses are relatively high, the inefficient conversion into aerosol mass (as compared to sulfate) and the high pre-existing aerosols lead to an overall low R_{tot} value. This is in agreement with previous studies that showed that in biomass burning plumes large fractions of organic material reside in the particle phase as compared to the gas

	Marine	Urban	Biomass Burning	Agric. Biomass Burning	Back-ground	Biogenic
SO2 [µg m-3]	1.1	1.5	0.66	3.8	1.7	1.5
aqSOA precursors [µg m-3]	0.16	1.9	2.9	9.8	1.9	11.5
m0 [µg m-3]	1.75	11.69	35.4	119.9	11.99	11.21
RSO4	0.96	0.20	0.03	0.13	0.05	0.21
RaqSOA	0.01	0.02	0.008	0.008	0.02	0.10
Rtot	0.97	0.22	0.04	0.14	0.07	0.31

phase (Heald et al., 2008; Cubison et al., 2011). Even though the agricultural biomass burning air mass contains the highest SO_2 mixing ratio among all six air masses, the added sulfate is not sufficient to alter the properties of the initial aerosol mass m_0, which is also the highest among all cases (***Table 1***). All R_{SO4} values are higher than the R_{aqSOA} values for the same air mass. This trend suggests that generally the addition of sulfate to an initial aerosol population might more efficiently change the initial aerosol population than the addition of aqSOA. The contribution of aerosol processing by organics is highest in the biomass burning cases where R_{aqSOA} is 20% and 6% of R_{tot}, respectively. The trends in ***Table 3*** give some guidance for which air masses a cloud-processing signature may be expected: The higher the ratio R, the more susceptible the pre-existing aerosol mass is to be substantially enhanced by in-cloud mass formation.

Air masses in the Southeast US are usually categorized as biogenic, but yet only little evidence of cloud processing was observed which was mostly ascribed to sulfate addition (Wagner et al., 2015). Applying the concept of the ratio R to these air masses, it can be shown that the initial mass of ~10 µg m^{-3} was relatively high whereas the precursor concentrations were comparably low ([SO_2] ~ 0.3 ppb, [Isoprene] ~ 1.5 ppb, [Aromatics] < 1 ppb) (Lu et al., 2015; Wagner et al., 2015), resulting in R_{SO4} = 0.5, R_{aqSOA} = 0.008 and R_{tot} = 0.6, respectively.

In contrast, above Houston, cloud processing was observed (Wonaschuetz et al., 2012). The air masses there contained lower aerosol mass but higher precursors (m_0 ~ 5 µg m^{-3}; [SO_2] = 1.5 ppb; [Aromatics] ~ 8 ppb,

[Isoprene+MVK+MACR] ~ 4 ppb), yielding R_{SO4} = 0.5, R_{aqSOA} = 0.8 and R_{tot} = 1.3, respectively, slightly lower the result for the urban air mass in the current model study (Table 3).

3.2 Changes in size-resolved parameters

Bulk properties do not allow any detailed conclusions about the effect of cloud processing on individual particles and, thus, on their resulting composition and size. While being more complex both in terms of measurements and model simulations, only size-resolved measurements and model studies permit such conclusions and are discussed subsequently. Chemical processes in cloud droplets might significantly change the properties of the droplet residuals. Depending on the activated fraction, this modification might change the bulk properties of the total aerosol population to different extents. It has been discussed by Ervens et al. (2014) that in small droplets, i.e. in particles with a relatively high surface-to-volume ratio, more efficient aqSOA formation can be expected as oxidation rates might be enhanced due to efficient oxidant and precursor uptake. The size of cloud droplets is not a strong function of the size and/or composition of the CCN but it is mostly determined by the growth history and competition for water vapour within the cloud. As size-resolved composition measurements from SEAC^{4}RS are very noisy, any conclusions based on this data might be inconclusive.

3.2.1 Size-resolved mass increase

Many studies have discussed the formation of a droplet mode upon cloud processing, which is caused by mass addition to activated particles only. Such predicted evolution of the aerosol size distribution is shown for the six air masses in ***Figure 2***. ~~The black symbols and lines denote the aerosol size distribution that was used as model input (black symbols are mostly covered by colored symbols).~~

~~Upon cloud processing, the predicted separation of the cloud processed particles from the smaller sized particles is different in the six air masses.~~ Processed size distributions in ~~***Figure 1***~~***Figure 2*** are overlaid on the initial size distributions (black symbols) and color-coded by the relative mass increase, i.e.

$$\text{Relative mass increase [\%]} = \left(\frac{\text{Mass after cloud processing}}{\text{Initial mass}} - 1\right) \cdot 100\% \qquad \text{Equation -2}$$

This relative mass increase is similar to the parameter R as defined in ***Equation 1*** in the sense that it shows the resulting mass increase upon complete processing of the precursors after cloud processing. In agreement with the trends as identified for the bulk masses (**Section 3.1.1**), the two biomass burning scenarios show the smallest relative mass increase with largest values of ~~10~~12% and ~~17~~30%, respectively. In all other cases, the mass of some particles might double (relative mass increase ~100%). ***Table 3*** summarizes the maximum relative mass increase for individual sizes, together with the particle size range that is mostly affected by cloud processing. In the two biomass burning scenarios, only particles with diameters > ~250 nm show any processing. Due to the high particle number concentration in these cases, the maximum cloud supersaturation is suppressed because the numerous particles act as an efficient condensation sink for water vapour. Consequently, only a small fraction of the aerosol population is activated into cloud droplets. This small activated fraction explains the rather small changes in bulk κ and O/C ratio (

Figure 1). Cloud processing often leads to the separation of unactivated and activated particles within the aerosol size distribution due to the 'Hoppel minimum'. In ***Figure 2a, b, e, f*** the particles around 100 nm are affected most strongly and also show some sign of this separation into a droplet mode. Thus, it is predicted that cloud processing leads to a shift to larger particle sizes and a narrowing of the size distribution (Feingold and Kreidenweis, 2000). In the biomass burning cases (***Figure 2c, d***), the most affected particles are near the maximum of the main size mode and the shift to larger sizes is not as clear.

The absolute mass increase is in all cases around several ng m^{-3} in the individual size classes that are separated by d(log bin-width) ~ 0.05 (***Figure S1***). Whereas this translates into doubling of particle mass in the cleaner air masses, the relative mass increase in the biomass burning cases is much smaller owing to the initial high particle loading, i.e. low R values (***Equation 1***). Tracers of ~~aqueous~~ aqueous-phase processing have been identified, e.g. by (Cook et al., 2017), in cloud samples that were affected by biomass burning plumes. However, such analyses do not reveal the extent to which the total aerosol population might have been altered in the cloud. Our results show that ~~they~~ the modified particles only represent a small fraction of the total aerosol population.

Many previous studies have identified a droplet mode upon cloud processing. An overview article has been given by (Eck et al., 2012). In ***Figure 3***, exemplary results of cloud processing in urban, marine and remote air masses are shown. The relative mass increase of sulfate and oxalate is examined as tracers for chemical cloud processing. For two sites, data were compared between a moist and dry period; more specifically, data were compared between monsoon months (July – September) and a dry period (June) for the urban area in Tucson, Arizona, and also between a monsoon period and a drier period in November for a remote site in Hayden, Arizona. Finally, data were compared between a fire period and a non-fire period in Marina, California during the summer when there is persistent cloud coverage. A consistent feature for the two Arizona sites was that a peak in the relative mass increase (Monsoon versus other periods) for sulfate and oxalate was between 0.32 - 0.56 µm, which is consistent with the droplet mode. While the fire and non-fire comparison does not contrast periods with varying moisture levels, it contrasts periods with varying amounts of precursors that still reveal the importance of aqueous processing in terms of the greater mass production when precursors are more plentiful. The relative mass increase for the comparison of fire and non-fire conditions in the coastal/marine area with persistent cloud coverage was highest between 0.56-1 µm, in agreement with the larger critical diameter (i.e., smaller activated fraction) in ***Figure 2***. ~~Similarly, a~~Analysis of fog-processed aerosol in Fresno, California, also revealed a clear signature in terms of size distribution and composition changes (Ge et al., 2012). In this latter study, both sulfate and aqSOA accumulated at particle sizes above ~200 nm upon cloud processing. Similarly, tracers of aqSOA formation were detected in fog in the Po Valley (Gilardoni et al., 2014).Cloud-processed particles were observed in many targeted field experiments. For example, increased mass in large particles was detected during the HCCT experiment where cloud processed aerosol was analysed (Henning et al., 2014). ~~(Gilardoni et al., 2014)~~

3.2.2 Changes in size-resolved hygroscopicity (κ)

Figure 4 shows the same parcel model results as in ***Figure 3~~2~~,*** but color-coded by κ instead of the relative mass

increase. Unlike ***Figure 1*** that shows the time evolution of κ, in ***Figure 4***, the model-predicted values after one hour of processing are shown. Conclusions are similar to those in ***Section 3.1.2*** as the smallest changes in κ are seen in the biomass burning cases where only a small fraction of the aerosol population is processed (***Table 3***) and the high initial mass is not increased substantially by the addition of sulfate and aqSOA.

The hygroscopic growth factor g(RH) is a measure of particle hygroscopicity. HTDMA measurements of initial and cloud-processed aerosol can give evidence of cloud-processing as more sulfate and aqSOA mass is added to larger particle sizes, enhancing the hygroscopicity of previously less hygroscopic particles. ***Figure 5*** shows an example of a size distribution of aerosol hygroscopic growth (shown as κ) atop ~~Mt~~Mount~~.~~ Lemmon in Arizona in relation to chemical mass fractions of selected water-soluble species including inorganic and organic acid ions. The size ranges with the highest κ values exhibit the highest mass fractions of sulfate. The results show how it is difficult to isolate the impact of aqSOA. Although the contribution of oxalate to the total organic acid mass is highest for diameters in the range of 0.32-0.55 μm (41%), that same stage exhibited the highest sulfate mass fraction (73%) and inorganic mass fraction (88%). This may have trumped the smaller effect of a change in the functionality of the organic fraction of the aerosol. In a separate study in the marine boundary layer off the California coast, Hersey et al. (2009) measured reduced size-resolved aerosol hygroscopic growth factors above the stratocumulus cloud top as compared to the sub-cloud region as a result of enhanced bulk aerosol organic mass fractions above cloud. However, the air masses were different below and above cloud, with continental free tropospheric air enriched with organics residing above cloud top and more inorganic-rich aerosol below cloud bases. This observation demonstrates that comparisons of below- and above-cloud air should be performed carefully as differences in aerosol properties are not necessarily due to cloud processing. A recent study comparing inflow and outflow aerosol from deep convective storms revealed that although size-resolved κ values may not have exhibited a significant enhancement in the anvil outflows (and sometimes reduced values), the signature of aqueous processing could have been missed as a result of lateral entrainment and mixing of less hygroscopic aerosol mixing with the processed aerosol that entered at the storm cloud base (Sorooshian et al., 2017); this might be also a consequence of different scavenging efficiencies of sulfate and organics, respectively (Yang et al., 2015). A case was profiled where biomass burning aerosol, with low hygrosopicity, entrained into a storm and resulted in a lower mean κ value in the outflow as compared to the inflow. An altitude-dependent entrainment model was applied to their analysis to show that the measured κ value exceeded that predicted for the outflow, revealing that a process, most likely aqueous processing, helped increase the hygroscopicity of the aerosol.

3.2.3 Changes in size-resolved O/C ratio

The same figure as for mass increase and κ change is once more reproduced in ***Figure S2*** showing the change in O/C ratio throughout the aerosol distribution upon chemical cloud processing. In the marine case (***Figure S2a***), the O/C ratio is predicted to increase by about 0.5 units in the activated fraction. As the smallest activated particles are smaller than 100 nm and thus the activated fraction is substantial, this change in O/C ratio is also reflected in the bulk O/C ratio in

Figure 1 and translates into a high R_{aqSOA} value (Equation 1). Changes in the O/C ratio are ~~rather small~~smaller in the

urban case, as the strong increase in mass is mostly due to sulfate which does not affect the O/C ratio. Even though the organic content is higher in the biomass burning cases, the change of the O/C ratio is smallest as compared to the other cases due to the high initial mass. ~~It can be expected that in~~ In biomass burning scenarios, cloud water might contain highly oxidized organics, and thus a high O/C ratio (Gilardoni et al., 2016; Cook et al., 2017). However, as the dissolved mass only comprises a small fraction of the total particle number, this oxidation might not affect bulk aerosol properties to a large extent.

Fog water analysis in the Indo-Gangetic plains revealed higher O/C in small fog droplets with a difference of Δ(O/C) ~ 0.2 between small and large fog droplets (Chakraborty et al., 2016). Model studies explained this difference with the larger surface-to-volume ratio of smaller droplets, which allows for more efficient uptake of oxidants such as OH and aqSOA precursors from the gas phase (Ervens et al., 2014). As OH is assumed to be (one of) the most efficient oxidants of organics in cloud droplets, the resulting higher OH concentration leads to relatively more aqSOA and a higher O/C ratio in small droplets. The fog study by Chakraborty et al. (2016) might not be directly comparable to the model results in ***Figure S 2*** that contrast activated and non-activated particles upon cloud processing. However, the fog studies show that drop size plays an important role for aqSOA formation. Given the high cloud drop number concentration in the biomass burning cases in the SEAC^{4}RS biomass burning scenarios (a few 1000 cm^{-3}, as opposed to a few 100 cm^{-3} or less in the other cases), the smallest cloud droplets might be present in these cases. Thus, it can be expected that the aqSOA formation rates in such cloud droplets are highest (Ervens et al., 2014) due to the favorable total surface-to-volume ratio (McVay and Ervens, 2017). In fact, in both biomass burning scenarios, ~~nearly 10~~several 10s of $\mu g\ m^{-3}$ organic mass are added (***Figure 1c and d***) in agreement with observations of efficient aqSOA formation in cloud-processed biomass burning plumes (Gilardoni et al., 2016). However, this mass is not sufficient to change the properties of the pre-existing aerosol mass (***Section 3.1.4***).

4 Caution in characterizing air near clouds to detect the cloud-processing signature

The previous model analysis suggests that detecting unambiguous evidence of a particle having undergone aqueous processing as compared to clear-air processing is challenging in the ambient atmosphere. Evidence of cloud processing strongly depends on the air mass and its history. This is in sharp contrast to controlled laboratory experiments where conditions can be ~~controlled and~~ optimized to detect an aqueous signature by an increase in O/C ratio, κ or formation of tracer compounds (Lim et al., 2010; Lee et al., 2012). In the ambient atmosphere, several interferences might obscure the signature and/or lead to false conclusions.

(i) Studies with vertically-resolved measurements below, inside, and above cloud have an added complication that clouds can be decoupled from a significant portion of the sub-cloud layer (Wang et al., 2016), or there can be a very sharp temperature inversion immediately above their cloud top that leads to a different air mass above the tops associated with the free troposphere (Dadashazar et al., 2018). Thus, continuity in meteorological parameters, such as temperature and/or relative humidity should be carefully taken into account before conclusions are drawn on cloud processing. Aircraft that fly even within 10 m above cloud top in the entrainment interface layer, such as in subtropical stratocumulus regions, still have influence from free tropospheric air masses (Dadashazar et al., 2018). ***Figure 6***

demonstrates an example of an airborne experiment where particles with higher κ were found above cloud than below and in cloud. However, this trend is coincidental as the air mass above did not originate from the cloud. In other studies, such an increase in κ was correctly attributed to sulfate addition due to chemical cloud processing (Shingler et al., 2016). Similar mixing of air masses from the free troposphere and the boundary layer were observed within the inter-cloud layer in the Southeast US (Wagner et al., 2015).

(ii) While likely the majority of atmospheric oxalate is formed in clouds, it has been shown that oxalate might have additional sources, such as biomass burning (Narukawa et al., 1999; Falkovich et al., 2005; Zhang et al., 2017) or direct emissions (Huang and Yu, 2007). In addition, oxalate and other aqSOA compounds can get further oxidized in clouds, in particular in the presence of iron (Zuo and Hoigné, 1992, 1994; Furukawa and Takahashi, 2011; Kawamura et al., 2012; Sorooshian et al., 2013; Weller et al., 2013). In addition, oxalic acid and other (weaker) organic acids might evaporate from acidic aerosols (Häkkinen et al., 2014; Nah et al., 2018). Thus, the lack of a clear oxalate increase is not necessarily indicative of processing in cloud-free air only. Finding correlations between aqueous organic tracer species and sulfate (Yu et al., 2005; Huang et al., 2006) are not necessarily indicative of causality. Co-variance alone (or the lack thereof) of tracer species (e.g., oxalate) with their aqueous precursors such as glyoxal or glyoxylate (e.g., Sorooshian et al., 2006a; Rinaldi et al., 2011) are not a sufficient indicator to conclude on chemical cloud processing.

(iii) Aerosol composition can be altered during sampling due to possible fragmentation and volatilization of aqSOA products in counterflow virtual impactor (CVI) inlets used to isolate cloud droplet residual particles (Shingler et al., 2012; Prabhakar et al., 2014).

(iv) Although still limited in their ability to provide direct proof, reports of size-resolved field measurements may miss out on the full story of an aqueous signature if only the submicrometer size range (e.g., droplet mode) is examined, as aqueous processing can influence the composition of aerosol in the coarse mode (e.g., Deshmukh et al., 2017).

(v) Not only ~~aqueous~~ aqueous-phase processing in clouds but also in deliquesced aerosol particles can lead to aerosol mass (Volkamer et al., 2006; Perri et al., 2010; McNeill et al., 2012; Marais et al., 2016). While this is rather inefficient for sulfate, many laboratory and ambient studies suggested that aqSOA can be efficiently formed in cloud-free, high relative humidity conditions. Characteristics of this aqSOA mass might be similar to cloud aqSOA (highly oxygenated and functionalized). Correlations of increased aqSOA mass with increasing relative humidity or cloud vs non-cloud scenarios should be interpreted with caution (Youn et al., 2013). ~~RH~~ Relative humidity is usually higher in the morning, when pollution and the boundary layer thickness and mixing are different than in the afternoon. Similar to findings for nitrate (Lee et al., 2003), it can be expected that the temperature increase during the day might lead to a decrease in organic mass due to the volatilization of semivolatile SOA.

5 Conclusions and Implications

We have analysed data sets from the SEAC^{4}RS and other field experiments in order to identify various aerosol properties that might show evidence of ~~aqueous~~ aqueous-phase processing of aerosol particles within clouds. In total, three properties, namely mass increase, hygroscopicity (κ) and O/C ratio were explored by means of model studies

for six different air masses (urban, marine, wildfire biomass burning, agricultural biomass burning, biogenic and background). In order to quantify the susceptibility of an aerosol population to be significantly modified by clouds, we define a mass ratio R_{tot}, which is the ratio of possible precursor gases for aerosol mass formation (SO_2, VOCs), i.e. the potential aerosol mass, and the initial aerosol mass.

Model results suggest that in moderately polluted air masses, such as in urban, marine and biogenic scenarios, changes in particle mass and properties can be most easily identified. ~~In order to quantify the susceptibility of an aerosol population to be significantly modified by clouds, we define a mass ratio R_{tot}, which is the ratio of possible precursor gases for aerosol mass formation (SO_2, VOCs), i.e. the potential aerosol mass, and the initial aerosol mass.~~ The biomass burning cases show the lowest values of R_{tot} (0.~~12~~ 0.14 and 0.~~56~~02, respectively) whereas the marine air mass is characterized by the highest value of R_{tot} = ~~5.2~~0.97. In general, R_{tot} is high in clean scenarios whereas it is rather low in scenarios with high initial mass (e.g. biomass burning). ~~Generally, t~~The mass ratio R_{SO4} (ratio of potential sulfate mass to initial aerosol mass) is larger than the values for R_{aqSOA} (potential aqSOA mass versus initial aerosol mass). Thus, sulfate addition likely leads to more aerosol modification during cloud processing than aqSOA addition.

Calculating this ratio for previous experiments in different air masses explains why in some cases (e.g., urban) cloud processing was observed whereas it was not clearly detected in a clean biogenic scenario. ~~Generally, the mass ratio R_{SO4} (ratio of potential sulfate mass to initial aerosol mass) is larger than the values for R_{aqSOA} (potential aqSOA mass versus initial aerosol mass). Thus, sulfate addition likely leads to more aerosol modification during cloud processing than aqSOA addition. Thus~~Since the O/C ratio only characterizes the organic aerosol fraction, ~~the O/C~~it ratio might not change significantly due to chemical cloud processing~~ as it only describes the organic aerosol fraction~~. Other parameters that describe the total aerosol mass, such as mass increase or a change in the hygroscopicity parameter κ might be more useful to detect a signature of chemical cloud processing.

~~Mass addition to initial high particle loadings, as encountered in biomass burning plumes, might not be sufficient to modify total mass and physico-chemical properties to a large extent. All else being equal (e.g. vertical velocity, cloud processing time), the activated fractions in clouds in clean air masses (low particle number concentrations) are higher than under polluted conditions (high particle number concentrations). High number concentration of particles in the biomass burning cases prevents high supersaturations and, thus, only large particles are activated into cloud droplets where processing occurs. As a result, only a small fraction of particles are cloud-processed in biomass burning plumes. As the ratio of activated to total particles is much larger in less polluted air masses, relatively more particles form cloud droplets and undergo addition of sulfate and aqSOA mass.~~

~~While the~~ Previously, the presence of tracer compounds of ~~aqueous~~ aqueous-phase processing, such as hydroxyl methane sulfonate (Munger et al., 1986), oxalate (e.g., Huang et al., 2006; Sorooshian et al., 2010; Wonaschuetz et al., 2012), ~~or~~ oligomers (Mazzoleni et al., 2010) or light-absorbing products (Laskin et al., 2015) have been used to ~~conclude on~~detect the influence of aqueous processing. T~~, t~~hese compounds usually only comprise a small fraction of the total aerosol mass and, thus, give only limited quantitative information on the role of ~~aqueous~~ aqueous-phase processing on the modification of aerosol. ~~Further, tracers~~These tracer compounds might have chemical sinks~~l~~, such as the ~~ike oxalate might have additional chemical sinks, such as to~~ complexation of oxalate with iron or other trace

metals and subsequent photolysis, e.g., Sorooshian et al. (2013) or the decay or oxidation of ~~.~~hydroxyl methane sulfonate (Kok et al., 1986); (Whiteaker and Prather, 2003), respectively. ~~-~~It is likely that water-soluble organic particle constituents (e.g., SOA from sources other than aqueous-phase processes) get oxidized to volatile compounds within cloud droplets and, thus, the total SOA mass might decrease whereas aqSOA material is added. Evaporation of organic acids from aerosol particles at low pH might lead to further decrease in aqSOA. The analysis and interpretation of data sets acquired near clouds should be performed with care, and it should be made sure that air masses in and above clouds are coupled.

~~Therefore, our approach to look at both bulk and size-resolved aerosol properties gives a more comprehensive idea of the role of aqueous phase processes in clouds or wet aerosol on aerosol modification. It should be noted that our model assumptions likely represent overestimates of this signature as we do not include aqueous phase processes that might act as efficient sinks for organic mass. It is likely that water soluble organic particle constituents (e.g., SOA from sources other than aqueous phase processes) get oxidized to volatile compounds within cloud droplets and thus the total SOA mass might decrease whereas aqSOA material is added. In addition, evaporation of organic acids from aerosol particles at low pH might lead to further decrease in aqSOA. The analysis and interpretation of data sets acquired near clouds should be performed with care and it should be made sure that air masses in and above clouds are coupled.~~

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 always a clear signature of chemical cloud processing on aerosol. The extent to which aerosol properties are modified by chemical processes in clouds depends primarily on the initial aerosol mass, particle number concentration and sulfate and aqSOA precursor gases, as quantified by the mass ratio R_{tot}. In addition, parameters such oxidant levels, cloud water pH and life~~–~~time will also affect in-cloud mass formation rates. ~~–~~Size-resolved measurements can provide evidence whether a droplet mode exists that is formed from the addition of cloud-derived mass. Our model results show that this droplet mode can be expected to be mostly comprised of sulfate whereas a modification of aerosol properties due to aqSOA formation is likely to be small. Our findings are expected to provide guidance on future field and model studies targeting the role of cloud processing on aerosol properties and total ambient aerosol loading. The lack of a signature does not imply that no ~~aqueous~~ aqueous-phase processing occurs. In such cases the signature might have been masked by other processes, which include physical and chemical removal processes of aerosol mass.

Data and code availability

All data from DC3 and SEAC^{4}RS are publicly available from the NASA Langley Research Center Atmospheric Science Data Center: https://www-air.larc.nasa.gov/missions/dc3-seac4rs/index.html and https://www-air.larc.nasa.gov/missions/seac4rs/, doi:10.5067/Aircraft/SEAC4RS/Aerosol-TraceGas-Cloud, respectively. CIRPAS Twin Otter data can be found elsewhere (Sorooshian et al., 2017b, 2018). Complete model results are available upon request from BE.

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Table 1: Initial aerosol properties for six air masses during SEAC[4]RS. These data are used as inputs to the box and parcel models in order to simulate ~~aqueous~~ aqueous-phase processing.

	Marine	Urban	Biomass Burning	Agric Biomass Burning	Background	Biogenic
Relative contributions [%]						
Ammonium	10.6	8.1	2.8	2.1	7.4	7.3
Chloride	0.6	0.1	0.3	1.9	0.8	0.2
Nitrate	1.3	1.4	3.8	2.7	2.0	1.6
Organics	21.5	55.8	89.1	90.5	64.0	63.9
Sulfate	64.7	33.6	1.9	2.1	24.8	26.1
Black carbon	1.3	1	2	0.8	1	1
N / cm^{-3}	651	5,551	3,481	9,762	3,377	2,065
Total mass / $\mu g\ m^{-3}$ 1)	~~0.33~~1.75	~~1.25~~11.69	~~10.5~~35.4	~~12.1~~119.9	~~3.86~~11.99	~~1.74~~11.21
κ	~~0.59~~0.38	~~0.41~~0.28	~~0.21~~0.11	~~0.21~~0.12	~~0.37~~0.24	~~0.37~~0.21
O/C	0.92	0.65	0.65	0.48	0.66	0.57

1) Masses are given in standard m^{-3}

Erreur ! Liaison incorrecte.

Table 2: Mass ratios of potential aerosol mass and initial aerosol mass m_0 from SO_2 (R_{SO4}), aqSOA precursors (R_{aqSOA}) and total mass ratios (R_{tot}) (Equation-1).

	Marine	Urban	Biomass Burning	Agric. Biomass Burning	Back-ground	Biogenic
SO_2 [μg m^{-3}]	1.1	1.5	0.66	3.8	1.7	1.5
aqSOA precursors [μg m^{-3}]	0.16	1.9	2.9	9.8	1.9	11.5
m_0 [μg m^{-3}]	~~0.33~~1.75	~~1.25~~11.69	~~10.5~~35.4	~~12.1~~119.9	~~3.86~~11.99	~~1.74~~11.21
R_{SO4}	~~5.1~~0.96	~~1.8~~0.20	~~0.1~~0.03	~~0.5~~0.13	~~0.7~~0.05	~~7.0~~0.21
R_{aqSOA}	~~0.005~~0.01	~~0.15~~0.02	~~0.03~~0.008	~~0.08~~0.008	~~0.05~~0.02	~~0.16~~0.10
R_{tot}	~~5.2~~0.97	~~2.0~~0.22	~~0.12~~0.04	~~0.56~~0.14	~~0.72~~0.07	~~2.0~~0.31

Table 3: Summary of model results describing the aerosol properties upon cloud processing. Δκ, Δm, Δ(O/C), and ΔDiam values denote the largest predicted change as shown in Figures 3, 5, and S1, respectively.

	Size range [nm]	**$\Delta\kappa_{max}$**	**$\Delta m(relative)_{max}$ [%]**	**$\Delta(O/C)_{max}$**	**$\Delta Diam_{max}$ [nm]**
Marine	80-300	0.~~05~~3	~~100~~120	0.~~5~~4	~~20~~60
Urban	100-400	0.~~13~~5	90	0.~~12~~25	~~37~~50
BB	200-400	0.~~04~~08	~~10~~12	0.~~02~~1	~~18~~20
Ag BB	250-~~430~~600	0.~~08~~15	~~18~~30	0.~~17~~2	~~18~~22
Background	~~100~~150-350	0.~~16~~25	~~80~~38	0.~~14~~07	~~45~~50
Biogenic	~~100~~150-~~400~~500	0.~~18~~25	130	0.~~33~~5	~~50~~65

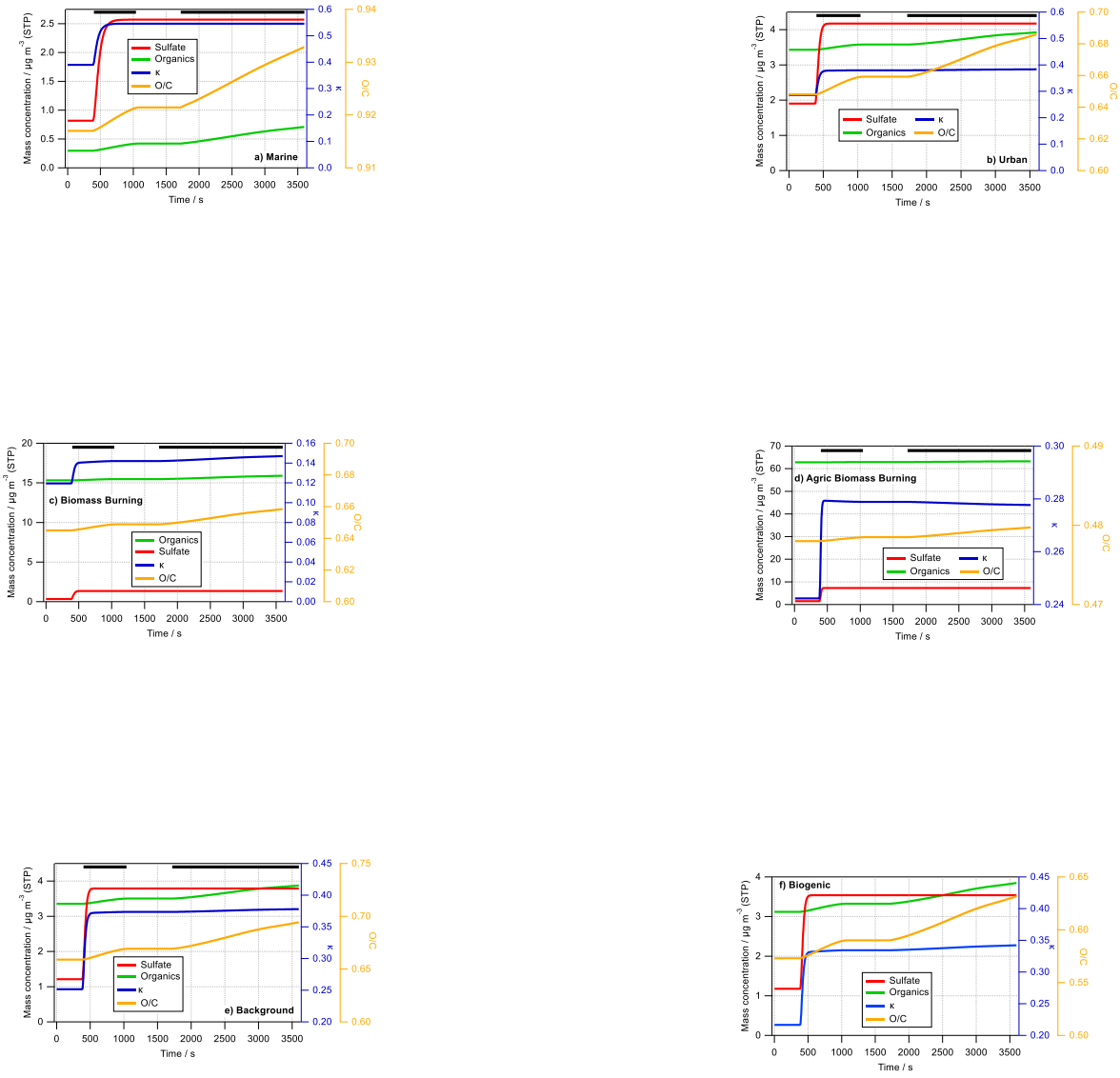


Figure 1: Predicted change in aerosol properties due to cloud processing of six different air masses identified during SEAC[4]RS. Cloud processing simulations are performed for one hour during which a cloud exists for ~ ~~30~~ 40 min. Green and red lines show predicted increases in organic and sulfate mass (left axis), respectively; blue and orange lines represent the change in hygroscopicity parameter κ (first right axis) and O/C ratio (second right axis), respectively. The thick black lines near the top of the panels denote the in-cloud time.

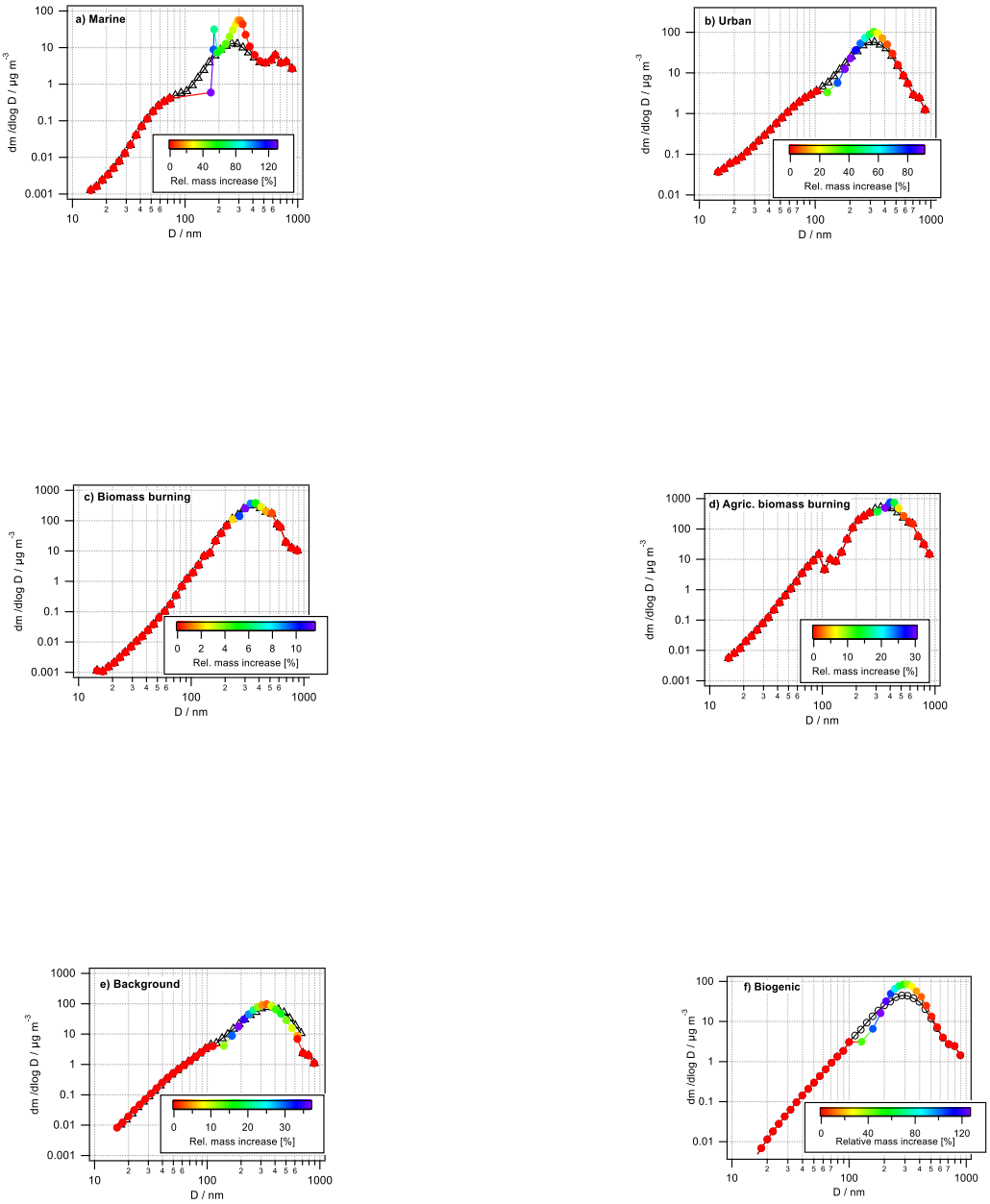


Figure 2: Measured initial (black) and predicted cloud-processed (colored) mass distributions of aerosol particles in six air masses as identified during SEAC^{4}RS. Color-coding refers to the relative mass increase. ~~Predicted relative mass concentration increase due to cloud processing in six air masses as identified during SEAC^{4}RS. Black symbols show the measured, initial size distributions; colored symbols are model results, color-coded by relative mass increase~~ (Equation 2).

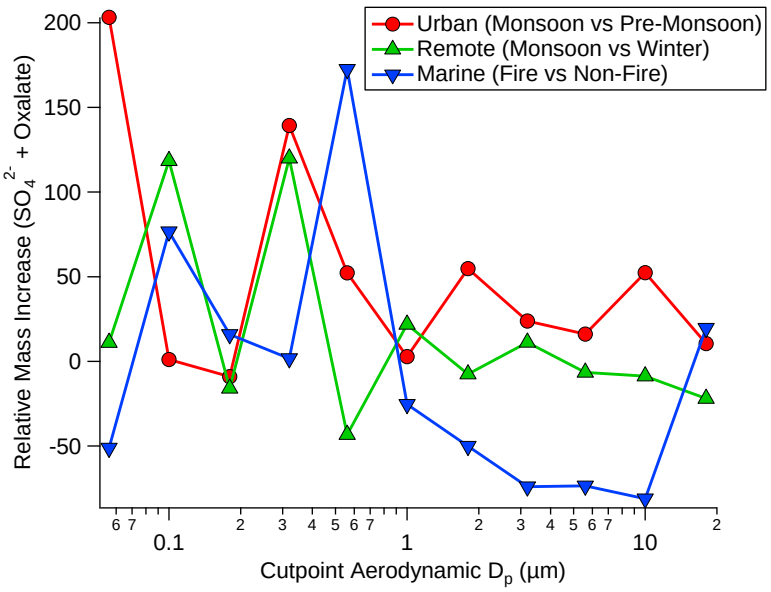
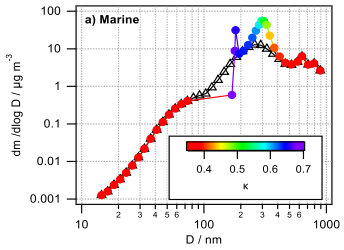
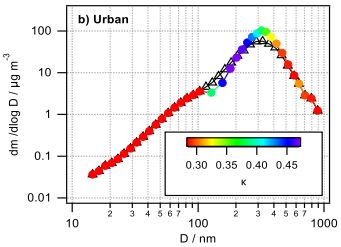
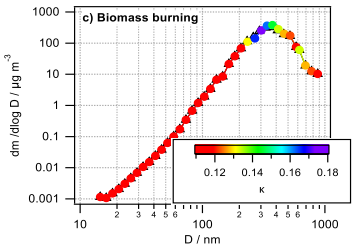
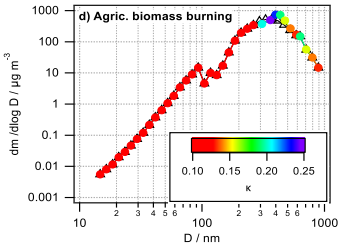


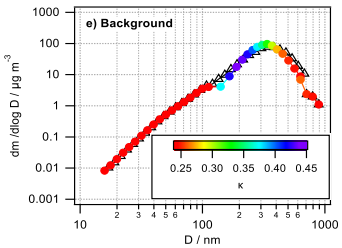
Figure 3: Summary of the relative mass concentration increase for sulfate plus oxalate as a function of dry particle size for three scenarios: monsoon – pre-monsoon changes in an urban area (inner city Tucson, Arizona), monsoon – winter changes in a remote area in central Arizona (Hayden, Arizona), fire – non-fire changes in a coastal/marine area with persistent cloud coverage in July-August (Marina, California).











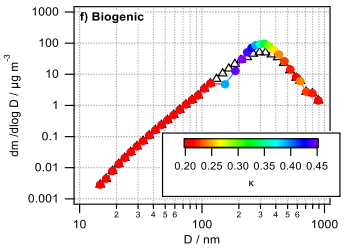


Figure 4: Same as Figure 2 but the processed aerosol mass distribution is color-coded by κ.

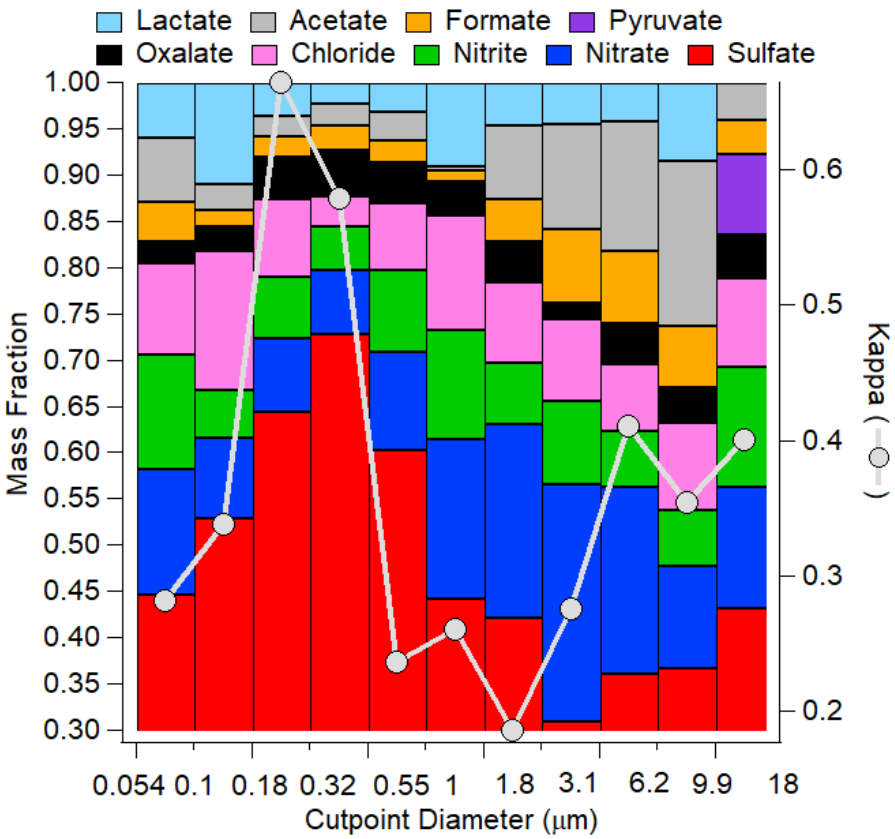


Figure 5: Size-resolved aerosol hygroscopic growth (as ~~kappa~~κ) and chemical mass fractions as a function of dry particle diameter at a mountaintop site (Mount Lemmon, Arizona; February 2010).

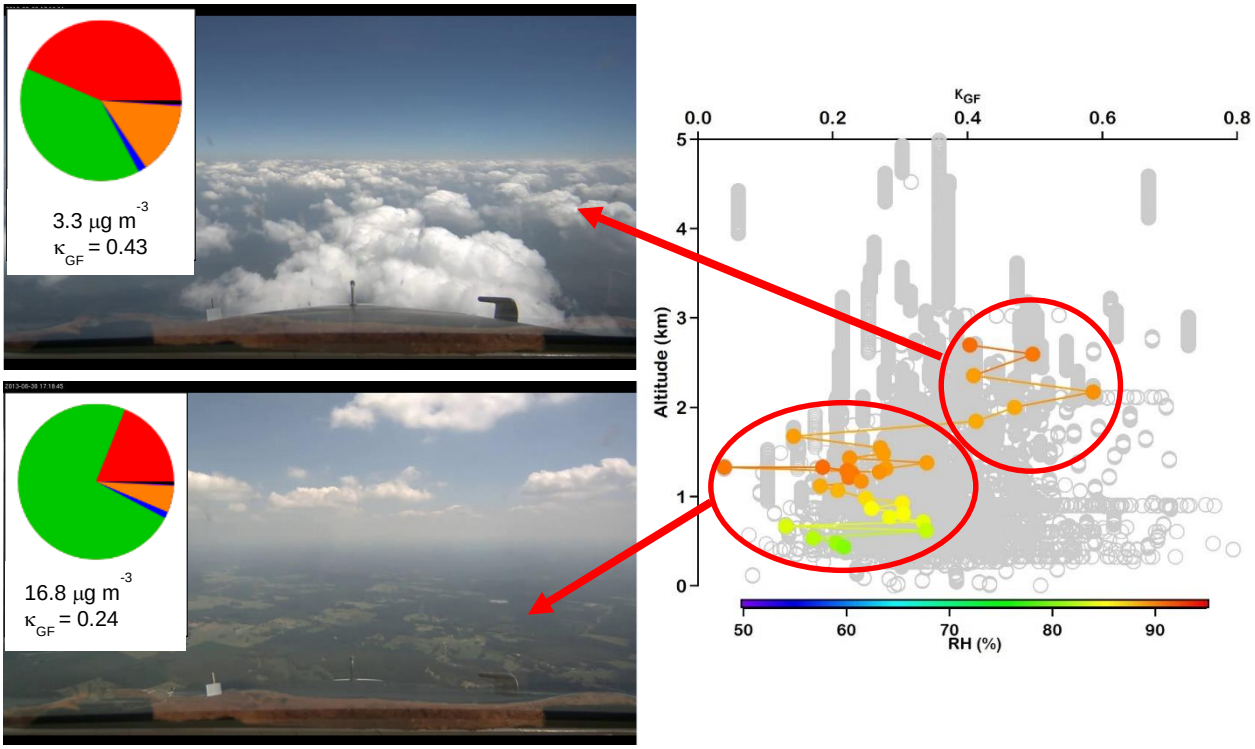


Figure 6: Left: Photographs taken from the NASA DC-8 showing where the aircraft was relative to clouds during a SEAC[4]RS flight on 30 August 2013. The pie charts correspond to AMS chemical mass fractions non-refractory aerosol (green = organic; red = sulfate; orange = ammonium; blue = nitrate) and for black carbon (in black) as measured by the HD-SP2 instrument. The average total submicrometer mass concentrations and ~~GF~~growth-factor-derived κ values are shown below the pies for above-cloud base and sub-cloud base sampling.

Right: Vertical profile of size-resolved GF-derived κ for particles with dry diameters between 180-400 nm with gray being all points during the flight and the colored points being for the specific measurements near the cloud field. While the RH values of the humidified channel of the DASH-SP are shown for each measurement by the cloud field, κ values are shown to allow for a fair comparison regardless of the humidified RH.

Supplemental Information

Is there an aerosol signature of cloud processing?

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This supplemental information includes:

Table S1: Initial ~~gas-~~ gas-phase mixing ratios [ppb] used as input for the box and parcel models. Data are from SEACR[4]S for six different air masses.

Figure S1: Predicted relative mass concentration increase due to cloud processing in six air masses as identified during SEAC[4]RS. Black symbols show the measured, initial size distributions; colored symbols are model results, color-coded by log ([absolute mass increase / μg m^{-3}]).

Figure S2: Predicted relative mass concentration increase due to cloud processing in six air masses as identified during SEAC[4]RS. Black symbols show the measured, initial size distributions; colored symbols are model results, color-coded by O/C ratio.

	Marine	Urban	Biomass Burning	Agric biomass burning	Back-ground	Biogenic
SO_2	0.43	0.56	0.252	1.44	0.64	0.582
NO	0.028	0.2	0.137	0.352	0.112	0.062
NO_2	0.066	1.196	0.311	2.37	0.521	0.283
HCHO	0.883	2.64	4.04	14.4	2.8	4.2
H_2O_2	1.172	2.58	3.72	4.3	2.6	2.8
O_3	27	57	68	63	57	50
Isoprene	0.003	0.14	0.18	1.13	0.147	1.61
Monoterpenes	0.007	0.03	0.098	0.328	0.039	0.123
Methylvinyl ketone [1)]	0.008	0.124	0.113	0.33	0.18	1.1
Methacrolein [1)]	0.008	0.124	0.113	0.33	0.18	1.1
Toluene	0.009	0.07	0.125	0.243	0.041	0.056
Xylene [2)]	0.005	0.035	0.067	0.12	0.02	0.028
Ethylene	0.0486	0.215	0.842	2.68	0.212	0.191

Table S1: Initial ~~gas~~ gas-phase mixing ratios [ppb].

[1)] The total of methyl vinyl ketone and methacrolein was measured by PTRMS. For model purposes, the total was equally split between the two compounds.

[2)] Xylene measurements were not available. The mixing ratio was assumed to be 50% toluene.

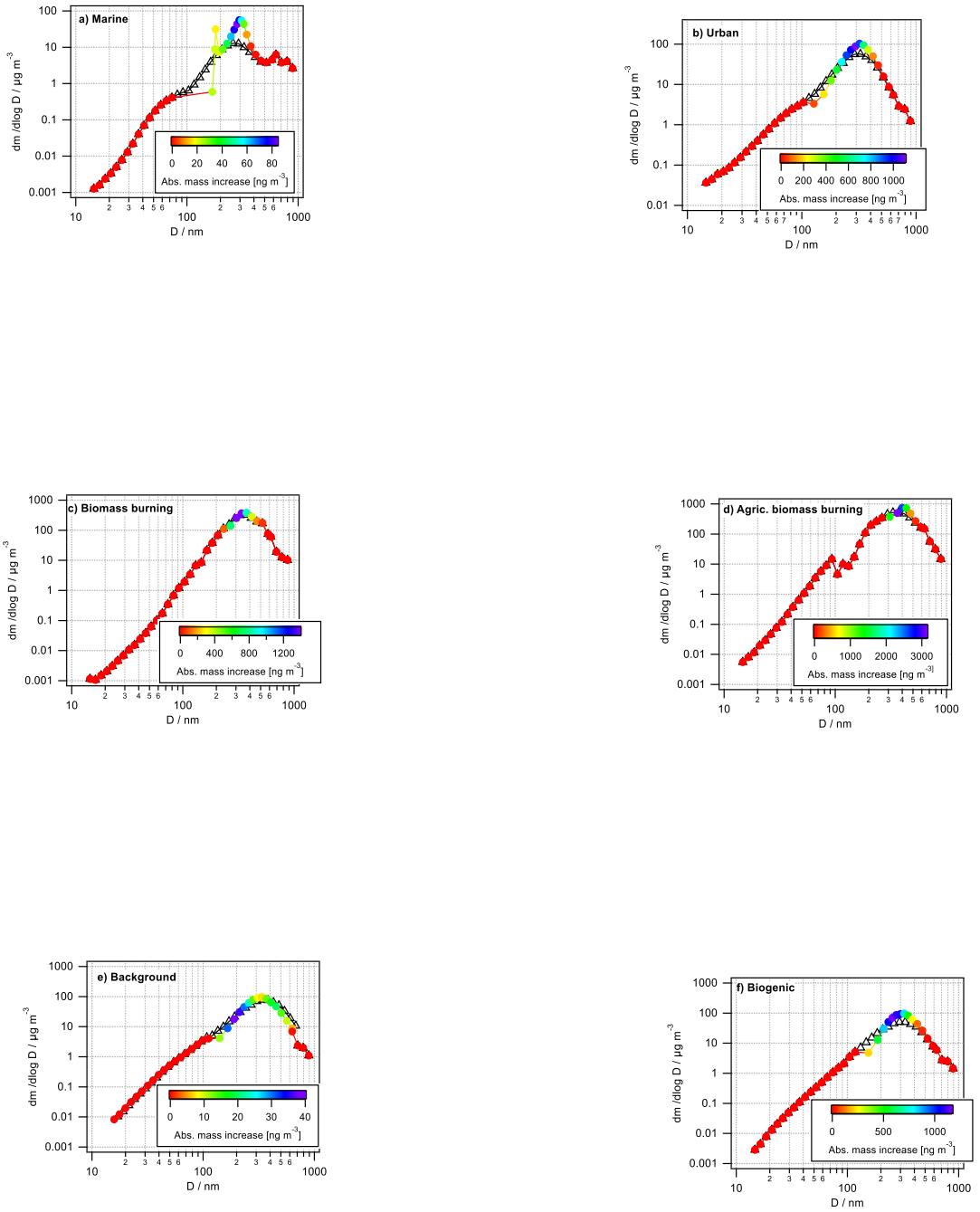

Figure S 1: Measured initial (black) and predicted cloud-processed (colored) mass distributions of aerosol particles in six air masses as identified during SEAC^{4}RS. Color-coding refers to the predicted absolute mass increase [ng m^{-3}].~~Predicted relative mass concentration increase due to cloud processing in six air masses as identified during SEAC^{4}RS. Black symbols show the measured, initial size distributions; colored symbols are model results, color coded by the absolute increased in mass~~

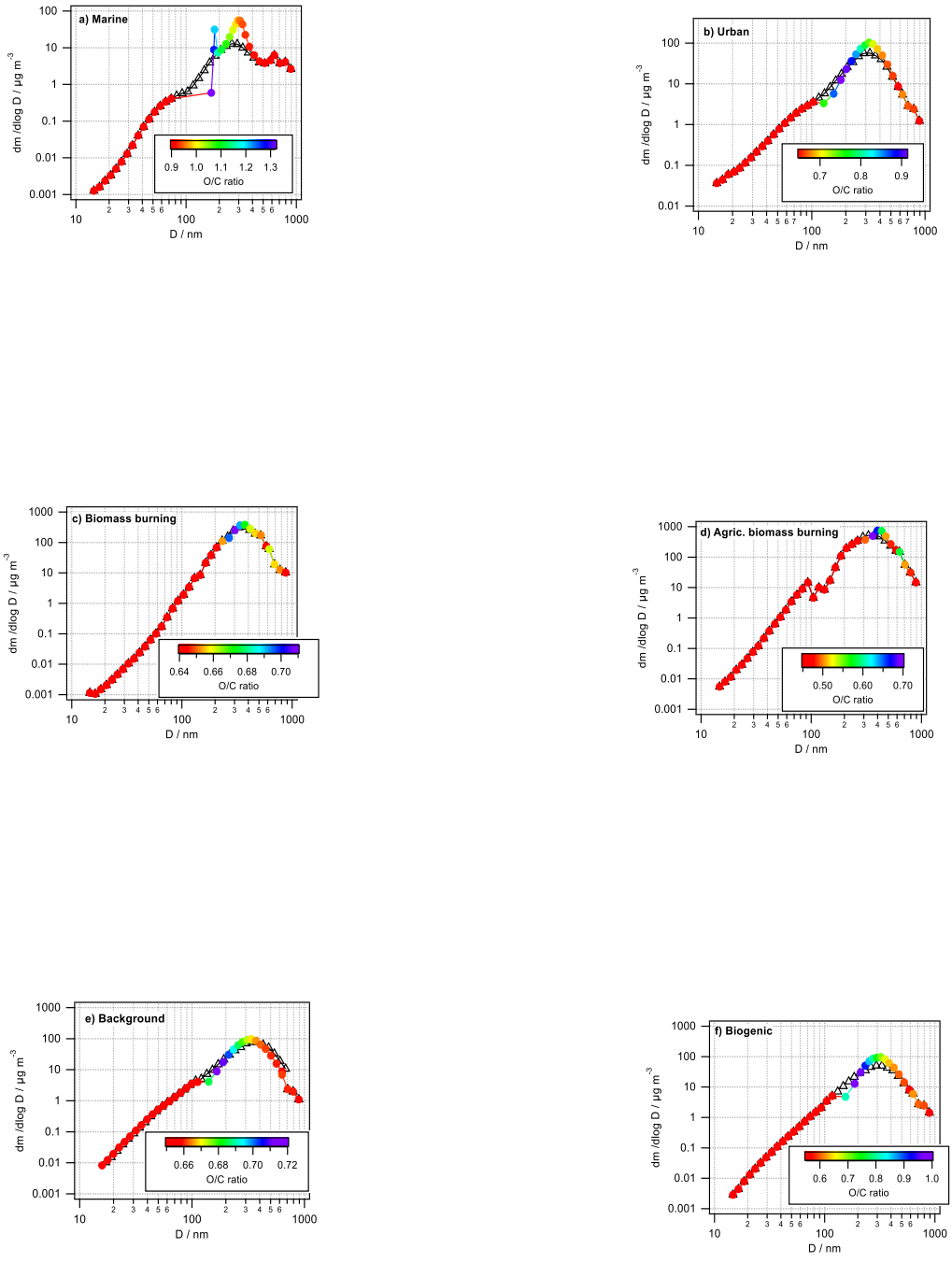

Figure S 2: Measured initial (black) and predicted cloud-processed (colored) mass distributions of aerosol particles in six air masses as identified during SEAC^{4}RS. Color-coding refers to the predicted O/C ratio. ~~Predicted relative mass concentration increase due to cloud processing in six air masses as identified during SEAC^{4}RS. Black symbols show the measured, initial size distributions; colored symbols are model results, color-coded by O/C ratio.~~