Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
https://doi.org/10.5194/acp-2022-147-RC2, 2022

Comment on acp-2022-147

Anonymous Referee #2

Referee comment on "The effect of clouds and precipitation on the aerosol concentrations and composition in a boreal forest environment" by Sini Isokääntä et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-147-RC2, 2022

General comment

The study by Isokääntä et al., investigates the effect of cloud processing and wet removal on aerosols, using airmass history analysis and in situ measurements from a boreal forest in northern Europe. The manuscript is interesting and the quality of the analysis is good but the interpretation of their results not always convincing. Additionally, the structure of the manuscript should be improved for clarity. I think this manuscript is within the scope of ACP but the following points should be addressed before I can recommend its publication.

Major comments

Multivariate mixed effect model

A good part of section 2 is dedicated to describing this statistical model but then its results are not really used in the rest paper. There are only a few short parts referring to the model in the main result section. It should be clear what is the purpose of the model and how it contributes to the findings of this paper. I think the paper would be clearer and more concise without the model (which could be used for a separate publication). It is fine for me if the authors decide to keep the model in the paper, but then they should describe its results in a clear way and discuss them coherently with the other findings.

Effect of wet scavenging on aerosol concentration

In line 284 the authors say that the vertical position of the air parcel with respect to the cloud is not considered. So, what if the air parcel is actually above the precipitating cloud? This is a potential drawback which should be addressed to make the analysis more robust and convincing. ERA-interim contains vertically resolved information concerning the cloud fraction and type, so it should be possible to distinguish between an airmass below, inside or above the clouds. I urge the authors to include this type of analysis in their work. With this addition, it should also be possible to compare more directly in-cloud with below-cloud scavenging, and confirm if the first is more efficient than the latter as currently hypothesized in the manuscript.

Effect of wet scavenging on the aerosol composition

Line 357: "SO4 is removed less efficiently than Org and eBC", this is counterintuitive since sulphate particles are more hygroscopic compared to organics and black carbon. Hence, they should activate and be removed preferentially in clouds. The authors draw this observation from the results in Figure 4d, which shows the normalized mass concentration as a function of accumulated precipitation. However, the data in the figure look odd because the organics and eBC normalized mass is less than 1 for an accumulated precipitation value of zero. Can the authors explain this discrepancy? Just by looking at the relative decrease it seems like sulphate is scavenged as efficiently as organics and eBC, so the authors should maybe revise their statement.

Effect of in-cloud processing on aerosol concentrations and composition

The choice of a threshold RH equal to 94% is arbitrary, the authors should do some type of sensitivity study to support their choice. For example, they could explore how the results change when a smaller and larger threshold are used (e.g. 90% and 98%).

Moreover, while reading the manuscript for the first time, I was confused about why the authors decided to give the same weight to every air mass within cluster 3 and did not consider the time spent inside the cloud (I had to read through the entire section before finding an answer).

I think that Figure 8 highlights the effect of cloud processing much better than Figure 5 and 6 because it clearly shows that the sulphate mass increases with time spent at RH>94%. Hence, I would recommend to show the same also for total particulate mass and number concentration and start the discussion from there. If this is done then figure 5 and 6 could probably be removed but I leave the final decision to the authors.

The classification used in this section (WC, WP, CC and CP) is more specific compared to the previous sections, where only warm and cold periods were separated. It is not clear why the authors decided to use two different classification and I would recommend to use

the same classification throughout the manuscript.

When comparing changes between groups it would be important to check if these differences are statistically significant, I would encourage the authors to run a simple statistical test to support their observations (I suggest to use a nonparametric test like the Mann-Whitney U rank test)

Minor comments

Line 62: I would mention that not all particles activating as cloud droplets actually precipitate.

Line 81: I would include also the study of Lamkaddam et al., 2021 as a reference for aqSOA formation, it is an important experimental study.

Line 122: this study is focusing on more than just "the influence of below-cloud scavenging during transport", so this sentence should be reformulated.

Line 280-281: the particle number concentration tends to increase for some bins with an accumulated precipitation above about 30mm, do the authors have an explanation for this effect? Is it just statistical noise or a real signal? It would be interesting to see if the effect persists also when using larger bins.

Lines 311-314: It is difficult to assess if sub100nm particles are really unaffected by precipitation as stated here because of the way the data are shown. I would suggest to show the decrease of particle number in different size bins as a function of accumulated precipitation (something similar to Figure 1b, maybe using larger bins). This additional figure could be included in the supplement.

Figure 3: for better visualization I would also extract a few representative size distributions, with the colormap is not always easy to appreciate changes (showing for example the average PSD corresponding to 0mm, 20mm and 40mm accumulated precipitation)

Lines 359-361: what is the meaning of "This could indicate that more of the SO4, compared to Org and eBC, is distributed to smaller particles during warmer months which reduces both CCN activation"? Sulphate is more hygroscopic than organics and eBC, so if smaller particles contains a larger fraction of sulphate then they are more likely to activate

as CCN. In general, this study does not provide any evidence that smaller particles contain a larger fraction of sulphate, so I would consider removing this sentence or to back it up with previous studies if available.

Lines 373-374: For me the most striking evidence that wet removal in winter is more efficient compared to summer is the comparison of figure 4d and 4e, so I would start from there. The results of the statistical model are less obvious and I would mention them afterwards (if the authors decide to keep the model in the manuscript).

Figure 4: are panel a,b and c relative to both cold and warm periods? I would mention this in the caption for clarity.

Line 408: what is the meaning of "figs" here?

Lines 414-416: It took me a while to understand why restricting the time window to 24 hours would increase the amount of observations per group. Consider rephrasing or explain this better.

Line 460: include 1 or 2 sentences explaining what were the main findings of Riuttanen et al., 2013, otherwise it is difficult to follow the comparison here.

Lines 473-477: the analysis described here is not very clear for me. The authors are looking at the effect of aqueous phase processing on sulphate production and it should not matter if the sulphate is coming from anthropogenic or biogenic sources, so why making this distinction? Additionally, Figure S17 does not prove anything concerning the effect of marine emissions: it simply shows that cluster 1 is typically made of air masses from the boundary layer whereas air masses in clusters 2 and 3 are more often coming from the free troposphere. This is still an interesting observation but it should just be presented for what it is. Finally, it is important to note that sulphate from DMS oxidation is also mainly added via aqueous phase processing (e.g. Chen et al., 2018; Hoffmann et al., 2016), so there is no simple way to distinguish between sulphate from marine and anthropogenic emissions simply based on the air mass altitude as done here.

Figure 5 and following: why did you decide to show the confidence interval from bootstrap replicates instead of the interquartile range as in Figure 4? I tend to prefer the IQR to provide an idea of the underlying variability.

Lines 504-505: There is probably a mistake here: the oxidation of organics decreases their volatility (e.g. Kroll & Seinfeld, 2008).

Lines 507-514: this paragraph is confused because two different interpretations are mixed together. In particular, the authors first say that aqueous phase production of SOA is negligible and then that the increased mass, produced via aqueous phase, is compensated by reduced production in the gas phase due to lower solar radiation levels. These two things are different and the authors should clarify what is their interpretation of the results. It should be possible to look at the effect of solar radiation by comparing air masses with a similar level of insulation.

Lines 539-540: Could the authors try to calculate a simple mass balance and see if the increase in these size fractions matches with the sulphate increase? This simple calculation could help supporting the conclusions reported here.

Figure 7: I would recommend enlarging the map (reducing the geographical region) for a better visualization.

Figure 8: I would include in this figure also the absolute concentration trends.

Lines 600-603: I would simply say that an increase in the organic mass due to aqueous phase processing was not observed (this study did not differentiate between different types of organics).

Table S1: I would mention in the table if the data are publicly available and provide a direct link if possible.

References

Chen, Q., Sherwen, T., Evans, M., & Alexander, B. (2018). DMS oxidation and sulfur aerosol formation in the marine troposphere: a focus on reactive halogen and multiphase chemistry. *Atmospheric Chemistry and Physics*, *18*(18), 13617–13637. https://doi.org/10.5194/acp-18-13617-2018

Hoffmann, E. H., Tilgner, A., Schrödner, R., Bräuer, P., Wolke, R., Herrmann, H., Hans, E., Tilgner, A., Schrödner, R., Bräuer, P., Wolke, R., Herrmann, H., Hoffmann, E. H., Tilgner, A., Schrödner, R., Bräuer, P., Wolke, R., & Herrmann, H. (2016). An advanced modeling study on the impacts and atmospheric implications of multiphase dimethyl sulfide chemistry.*Proceedings of the National Academy of Sciences of the United States of America*, *113*(42), 11776–11781. https://doi.org/10.1073/pnas.1606320113

Kroll, J. H., & Seinfeld, J. H. (2008). Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. *Atmospheric Environment*, *42*(16), 3593–3624. https://doi.org/10.1016/j.atmosenv.2008.01.003

Lamkaddam, H., Dommen, J., Ranjithkumar, A., Gordon, H., Wehrle, G., Krechmer, J., Majluf, F., Salionov, D., Schmale, J., BjeliÄ□, S., Carslaw, K. S., El Haddad, I., & Baltensperger, U. (2021). Large contribution to secondary organic aerosol from isoprene cloud chemistry. *Science Advances*, *7*(13), 1–11. https://doi.org/10.1126/sciadv.abe2952