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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aerosol cloud activation in summer and winter at puy-de-Dôme high altitude site in France" *by* E. Asmi et al.

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We thank Referee for their excellent and very helpful comments and suggestions. We feel they have greatly improved our manuscript. We have addressed the comments point by point below.

Comment: p.23042 last paragraph / p. 23043 first paragraph: Maybe merge these two paragraphs, as the explanation for the connection between CCN number concentration and CDNC mentioned in the first is given in the second paragraph.

Reply: Good idea, this was done.

Comment: p.23043, l.19: Maybe add some information on the measurement site

p.23043/23044: Sections 2 and 2.1 give very similar information, I think it would be better to merge them in one section. (E.g. in line 26 (p.23043) one is waiting for more details about the campaigns, which is not given until section 2.1.)

Reply: True. These two sections were merged and now there is only section 2.1 where general information on the site and campaigns is given.

Comment: p.23046, l.16: Are the estimated CCNc supersaturations calculated by averaging both values?

Reply: Yes. Because for the temperature difference of 6 the difference in CCNc supersaturation based on calibrations between summer and winter campaigns was within the limits of uncertainties, same value of 0.24 % was used for both campaigns. Measurements at dT12 were only done in summer.

Comment: p.23046, l.20: How did you estimate the larger error?

Reply: We added an explanation about this: "We made sensitivity studies using van't Hoff factor of $\pm$ 0.2 around the preset values and $\pm$5C deviation of temperature which led to standard deviation of supersaturation of roughly 0.02 % and 0.01 %, respectively. In addition, due to higher quantity of doubly changed particles at higher supersaturations (as a result of the shape of atomized distributions) we estimated an additional 0.01 % deviation dT 12C following this."

Comment: p.23047, l.24: Can you explain the large difference in R2 for summer and winter experiments?

Reply: This is a good point. To double check this, we recalculated the R2 values and found a R2 of 76.5% for summer. Thus, the previously reported 44% was an error from our side. We are very sorry for this, and also very grateful for the referee for pointing this out. The new value is corrected in the revised manuscript.

Comment: p.23047, l.26: Maybe mention cut-off size for WAI and INT already here?

Reply: This was done.

Comment: p.23049, Section 2.2.1: aren0t the indices "*" and "2e" indicating the same – wouldn0t one indiced be enough?

Reply: It is clear that the section 2.2.1 needs some revision, and we have done that. Indices * and 2e are not exactly equal, in most cases. Asterisk (*) indicates that a value is calculated for size vector of doubly charged particles. Subscripts 1e or 2e indicate singly or doubly charged particles so that Ni2e is the number concentration of doubly charged particles, which can be calculated for both size vectors Dp or Dp*. However, you are correct that it is a "double notation" when considering Dp or f, not N. We changed the notations in order to be more clear.

Comment: p.23049, Section 2.2.1, point 3.: I don't understand the line Ni*2e + Ni1e – do you have the value of Ni1e? And if, how was it calculated? Or do you want to indicate that you use Ni, which is Ni*2e + Ni1e? Maybe reformulate to make it clearer.

Reply: Ni1e was calculated similarly as N*i2e, following the Wiedensohler et al. 1989. Ni is not equal to Ni2e+Ni1e, since Ni includes all the particles in channel i (after inversion) and Ni2e+Ni1e include only charged particles (which is the case in CCN and CN measurements after a DMA). We have reformulated also this in the revised manuscript version.

Comment: p.23049, Section 2.2.1, point 5., last sentence: Do you assume that Af*2e = Af1e (and why?) or should that read Af1e?

Reply: CCNi1e/CNi1e was used to calculate Af*2e for the next size, i.e. it was interpolated to a size vector * to update the values of Af*2e for the next (smaller) size. More explanation on this was added.

Comment: p.23051, l.16: "Trajectories were started every three hours starting at 00:00 UTC time" – shouldn't this read either "every twenty-four hours" or "at different UTC times"?

Reply: This was slightly modified now saying: "Trajectories were calculated every three hours, the first starting at 00:00 UTC time". In practice, trajectories were calculated at 00:00, 03:00, 06:00, etc. each day. We hope we made this clearer.

Comment: Section 3.1.: I find it sometimes confusing, which measurements refer to the summer and which to the winter campaign. Could be indicated/structured more clearly. (E.g. p.23052, l. 11: I assume this belongs to the summer measurements?)

Reply: We agree. In this specific point, yes, it belongs to the summer, and this is now added there. We also went through the text and tried to specify, whenever needed, the season in question more clearly.

Comment: p.23053, l.4: How do you know that the influence came from biomass burning, from the NO3 mass fractions?

Reply: During these periods, the average organic mass spectra had a significant contribution from m/z 60 and m/z 73. These two m/z signals are used to identify biomass burning in organic aerosols sampled by the AMS (Lanz et al., ACP 2010). We did not have any other measurements (e.g levoglucason) to really confirm this. Correlations with NO3 also show that the increase in organic aerosol particles is linked to primary emissions.

Comment: p.23053, l. 25: You conclude that not only size but also particle chemistry has a noticeable effect on the CCN activation, but you do not mention the size distribution here. Was it "normal" as during other times or different, why can you rule out influence from the size distribution?

Reply: Here we say that while high kappa values correlate with high CCN to CN ratio, it indicates that chemistry has a role. Of course, if strong accumulation mode (in relation to nucleation and Aitken modes) is connected with high kappa, then this is not as simplistic. We revised this section completely and replaced the size distribution figure with one which is more precisely showing the individual impacts of 1) size distribution

and 2) kappa on CCN to CN ratio. In fact, it seems that summer aerosol size distributions did not show too much correlation with kappa values while instead, the winter distributions were also very different for different aerosol kappas and thereby aerosol chemistry. Text matching this new figure and this conclusion were added in the revised manuscript.

Comment: p.23054, l.7: "the continental aerosol at our site seems much more aged" – how do you conclude that, based on the hygroscopicity?

Reply: Good point. This was a very simplistic idea that during winter, when aerosol was more continental it also had a higher kappa value and stronger accumulation mode, indicating more aged aerosol. We removed the sentence from this context and discuss this topic in following sections.

Comment: p.23054, l.27: Why should the summer aerosol fit with the continental value, when you mention before that it is mainly influenced by marine air masses?

Reply: True. Actually the "continental" here means aerosol measured in a continental site. This is specified in the revised manuscript.

Comment: p.23055, section 3.3: How do you get to the classification in this section, as you base many conclusions on that? Is it your own classification (and if, can you give more reasoning for it) or is it based on literature references? How representative do you think the classification is, how large would you estimate the variation of it?

Reply: Here we refer to our answer to referee #1 saying: It is not straightforward to define the "impact" of a region (or a square) to a measurement made in a single location. Due to removal processes the near-by squares have a greater impact than squares at further distances. But this does not vary greatly between different trajectories due to relatively constant transport times which make this more of a constant distance dependent factor without too large influence on the results. Instead, the particle and vapour sources are in emitted mass or number per time unit. Therefore, the longer the air

mass spends in a certain square the greater will be its impact on the measured concentration. Here we find this simple linear approximation is well justified, and makes also an impact on the results. Based on these, we decided to use the time and temporal distance in the weighting to get an idea of importance of different regions on measured aerosol quantities. Of course, in reality, the losses are not constant in time as assumed, and depend also on which aerosol quantity is in question (e.g. mass or number). However, without using an aerosol transport model we find this is a realistic attempt to approximate regional impacts and relative differences. Comparing it with an approach where no weighting is used instead, it emphasizes the results obtained when a certain square actually had a possibility (time) to make an impact for the measured result. By no means, however, we consider it representative in comparison to modeled results but do consider it more representative (on average) than an approach without weighting.

Comment: p.23055, l.13: Why is there a difference in the sized squares between summer and winter?

Reply: This was due to the fact that in winter the air masses came from wider longitudal area. Selecting different grid sizes did not affect interpretation of results. However, picture looked better when not too many "NaN"s were in between the grid squares. We added a sentence: "In summer the air masses came was from smaller geographical area which enabled us to use a better resolution grid size with approximately the same statistics per square."

Comment: p.23055, l.20: "to calculate averages" – averages of what?

Reply: Averages of any studied variable in question, in our case e.g. CCN concentration, aerosol kappa and organic mass fraction. We reformulated this part to explain it clearer and added: "In practise, if for example air masses had passed via a specific region (square) five times all together during the campaign but on different days, we assumed that the impact of this region was reflected to our on-site measured aerosol

quantities (such as the CCN concentration or aerosol kappa). Depending on the temporal distance between the region and the measurement site, and the time the air mass spent on that region, weight was given for each of the five individual measurements and average of them was calculated." in the beginning of chapter 3.3.

Comment: p.23056, l.5: How do you get kappa values out of your sectoral data analysis?

Reply: Kappa values are "repsesentative averages" for each region (or square), defined using the assumptions (explained in the beginning of chapter 3.3) that the measurements at our site can be used as an indicative of the history of emissions and losses of different vapours and particles during air mass transport, affecting the kappa.

Comment: p.23056: Figure 7 and Figure 8 are mixed up (text describing Fig. 7 refers to Fig. 8 and vice versa)

Reply: Thank you, this is now corrected.

Comment: p.23056, l.12: Why should the organics in Northern Europe be less frequent or more aged?

Reply: True, we agree this is purely speculative here. The latter figure 8, which shows the aerosol organic mass fraction, explains this more. We removed this and the preceding sentence from here.

Comment: p.23058, l.26: How realistic is it to assume that all inorganic mass was in the form of Ammoniumsulphate, does your data indicate that?

Reply: The largest fractions of inorganic ions detected by the AMS come from sulphate, ammonia and nitrate. If small amounts of ammonium bisulphate or ammonium nitrate were present (which is likely), they should not, however, affect the calculations largely due to the similar hygroscopicity behavior of all the three (hygroscopic growth factors of around 1.7-1.8). We therefore consider this as a reasonable assumption here.

Comment: p.23060, l.10ff: Couldn't negative values also be an indicator that chosing kappa_inorg = 0.61 is not an good option then? Did you vary _inorg to see how the negative values changed?

Reply: Very good point. We varied kappa_inorg during summer between values 0.41 and 0.81, which led to average kappa_org of 0.21 and -0.13, respectively. This does indicate that the method is somewhat sensitive to inorganic kappa. However, we believe that noise and differing time resolutions in AMS data and in CCN data are also both reflected to variability of organic kappa values, and that its variability is not solely explainable by changes in inorganic kappa. Also, a value of 0.61 was independently chosen as the most representative kappa for inorganic aerosol, and it is also possible that organics would actually decrease the aerosol hygroscopicity due to surface effects. Therefore, we left this value as it is, but wrote a couple of sentences on the uncertainties of the inorganic kappa value and effects of that on the results. And finally, what the results clearly show in any case is that aerosol organics are more hygroscopic during winter in comparison to summer.

Comment: p.23060, l. 25ff: Concerning the comparison of the two values for _org, can you explain the differences, which value do you think is more significant?

Reply: The fitting method tends to give more weight to the values observed during highest organic fractions. This method is also less sensitive to noise due to this, and due to the fact that single "outliers" do not significantly affect it. However, as we see that also values obtained when organic fraction is very small or when data is otherwise very noisy, are significant, the pure average seems more justified. While reasoning for both of them can be found, we wanted to present both values in the manuscript.

Comment: p.23061, l.20: Could it also be that different, less hygroscopic organic components are present at smaller sizes?

Reply: Yes, thank you. This is even likely. We added this as a possible additional explanation for the detected differences in kappas between the two SS (and sizes).

Comment: Section 3.6 /Conclusion p.23065, l. 26ff: The conclusions drawn on the CDNC and cloud SS are not mentioned that clearly in section 3.6 as they are in the conclusion section.

Reply: We added a sentence in section 3.6, where the importance of correlation between cloud SS and particle numbers is indicated explicitly. We think this was at least one point, which was not clearly expressed before conclusions section.

Comment: Figure 1 and 2: There is very much information displayed, and the graphics are not very large. Is all this information needed in so much detail (or would it be possible to enlarge them)? Maybe also indicate the different measurement periods / air masses by vertical lines along the graph?

Reply: Very true. However, as the meaning of this figure is solely to give a general view of the data we would not wish to take anything out. Instead, we pay attention to figure resolution and size in the revised version.

Comment: Figure 4: “Dashed lines show the boundaries in within most of the data are centred.” – How did you calculate those lines? (Change to “in which” instead of “in within”)

Reply: These were defined only visually. This is now explained and the figure caption is corrected.

Comment: Figure 13: Through which parameter are the points connected on the x- and yaxis, were they taken at the same time?

Reply: CCN size distributions (and kappas) during summer campaign were measured in turns and so the presented values in x- and y- axis are the closest possible results, but not simultaneous. We added an explanation in section “CCNc measurements and calibrations” where we now specify that CCN measurements at dT6 and dT12 were made in turns and also in figure 13 caption that the kappa values came from consecutive measurements.

Comment: Technical corrections:

p.23042, l. 10/11: “Consequently, the efforts made in modelling the CCN initiating from ..” –Do you mean based on instead of initiating from?

p.23043, l.1: “Upon the particle size and chemistry” – “Next to” instead of “upon”?

p.23043, l.4f: “to which the aerosols can also affect” – remove “to”

p.23043, l.13: “how the particle cloud activation properties” – Please change to “how do the particle..”

p.23048, l. 18: “in a size range of 10 to 500 nm” – Please change to “in a size range from 10 to 500 nm”

p.23048, l.26: "were" instead of "are"

Reply: These were all corrected, thank you.

Comment: p.23049, l.18: Do you mean "Ni" instead of "N* i"?

Reply: No, we really mean N*i, which is referring to a total number of particles in size vector *. This part of the manuscript was modified to make it clearer.

Comments:

p.23054, l.2: “we can suggest that in our measurement site” – Please change to “at our measurement site”

p.23054, l.11: “between the sites” – Please change to “between different sites”

p.23058, l.18: “while” – do you mean “because”?

p.23058, l.28: “remains to be the _” – please change to “remains the _”

p.23059, l.7: The abbreviations LV-OOA and SV-OOA have not been introduced before

p.23062, l.1: “In last part” – please change to “In the last part”

p.23062, l.6: “swithing” – please change to “switching”

p.23065, l. 11: “was good” –maybe change to more quantitative statement?

Reply: Thank you. The technical corrections were done as suggested.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 23039, 2012.