**Atmospheric
Chemistry
and Physics
Discussions**

# *Interactive comment on* "Cloud condensation nuclei measurements in the eastern Mediterranean marine boundary layer: CCN closure and droplet growth kinetics" *by* A. Bougiatioti et al.

**Anonymous Referee #2**

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The manuscript is a well written and interesting addition to the growing body of data about CCN (Cloud Condensation Nuclei) observed in the atmosphere worldwide. It introduces data that were measured on Crete, concerning atmospheric particle concentrations, size distributions, CCN, and chemical data, which adds valuable data to the dataset of worldwide measured aerosol properties. Besides this, a closure study on CCN is included, showing the ability to derive CCN concentrations from measured number size distributions and chemical information, and also giving some idea about the sensitivity of this closure on uncertainties of the underlying parameters. The manuscript surely will merit publication in ACP once a couple of issues given below will have been addressed.

One of the large requests that I have, which will be easy to address, is to improve the readability of the figures. Most of them have texts and numbers which are too small to be readable. I repeat this request for each figure concerned, suggesting some additional improvements, at the end of the specific comments given below.

Another large open issue is the calibration of the CCNc. The authors do not state, if they corrected the size of the NaCl particles used for the calibration with a shape factor, something that should have been done. In addition to this, I wonder which temperatures were used when deriving the super-saturations from the measured critical diameters. The calibration of the CCNc depends on these two parameters (shape factor and flow tube temperature) and therefore the results of the CCN closure could be affected. I address this issue again in the specific commands below.

Furthermore, the quality of the CCN closure might be improved if the time resolved measured WSOC/OC ratio was used, instead of using an average value of 70%. As it is now, the closure is not yet excellent, but may become so, and it would be interesting to see how sensitive the CCN closure is to the WSOC-fraction. Therefore I strongly suggest doing this improvement.

Other suggestions / requests for improving the wording at some points of the text are given below.

specific comments:

Abstract, line 5: See my comment for your page 10313, line 12 − 13, and adjust the text here accordingly.

page 10308, line 29: There is more literature around, from additional groups, that shows that a surface tension lowering has to be taken into account when examining the CCN properties of organic aerosol particles, citation of which will broaden the scope of your introduction, e.g.:

- Dinar, E., I. Taraniuk, E. R. Graber, S. Katsman, T. Moise, T. Anttila, T. F. Mentel,

and Y. Rudich (2006), Cloud condensation nuclei properties of model and atmospheric HULIS, Atmos. Chem. Phys., 6, 2465-2481.

- Ziese, M., H. Wex, E. Nilsson, I. Salma, R. Ocskay, T. Hennig, A. Massling, and F. Stratmann (2008), Hygroscopic growth and activation of HULIS particles: experimental data and a new iterative parameterization scheme for complex aerosol particles, Atmos. Chem. Phys., 8, 1855-1866.

page 10309, chapter 2.1, "Measurement site": Add a short description of the inlet system through which the aerosol was sampled (e.g. was there a PM10 inlet?) and about the drying of the aerosol prior to the measurements (was this done at all, if yes, how?)

page 10311, line12: For clarification please add "... yielding a CCN spectrum consisting of 5 different super-saturations every 30 min."

page 10311, line 15: Did you consider the shape factor for NaCl? (As your site was close to sea level, 1.08 should be appropriate.) If not, your calibration would be off, which would influence the results of your closure. Here is some literature about the shape factor:

- Kelly, W. P., and P. H. McMurry (1992), Measurement of particle density by inertial classification of differential mobility analyzer-generated monodisperse aerosols, Aerosol Sci. Technol., 17, 199-212.

- Gysel, M., E. Weingartner, S. Nyeki, D. Paulsen, U. Baltensperger, I. Galambos, and G. Kiss (2004), Hygroscopic properties of water-soluble matter and humic-like organics in atmospheric fine aerosol, Atmos. Chem. Phys., 4, 35-50.

- Biskos, G., L. M. Russell, P. R. Busek, and S. T. Martin (2006), Nanosize effect on the hygroscopic growth factor of aerosol particles, Geophys. Res. Lett., 33(L07801), soi:10.1029/2005GL25199.

- Niedermeier, D., H. Wex, J. Voigtlaender, F. Stratmann, E. Brueggemann, A. Kiselev,

H. Henk, and J. Heintzenberg (2008), LACIS-measurements and parameterization of sea-salt particle hygroscopic growth and activation, Atmos. Chem. Phys., 8, 579–590.

page 10311, line 28: For clarification please add "... a flow rate of 0.5 lpm and a temperature difference DeltaT = 15K) ..."

page 10311, line 29: For clarification please add "... saturation Sc of the ..."

page 10312, line 11: Which temperature did you use when computing Sc from Dp50? As it gets constantly warmer within the flow tube towards larger super-saturations, this can potentially be important and should be considered, as it influences the value of the surface tension. If you have not accounted for the temperature in the flow tube, check the potential influence. Give the temperature you used in the text.

page 10313, line 3: Do you use the information of the analysis on elemental carbon somewhere in your work? It would be interesting to see if the elemental carbon fraction could explain some of the "gap" between the later described activation of about 80% of all particles, as compared to activating all particles at the higher supersaturation.

page 10313, line 12 – 13: I do not agree with your interpretation "that most particles activate at 0.8%". Your observation rather indicates, that there is only a small number of particles that activate in the range from 0.6% to 0.87%, and that most of the particles that could be activated up to 0.87% had been activated at 0.6% already. Adjust your statement accordingly.

page 10313, line 14 – 17: The average of the activated fraction at the three highest super-saturations only reaches up to roughly 0.8. I wonder why this is. Doesn't this imply, that on average 20% of the particles were not activated, not even at 0.87%. And, in turn, wouldn't this mean that the aerosol might not have been as aged as you argue? Comment on this and adjust your text accordingly.

page 10313, line 18 ff: Period C is better described as "marine aerosol that did not have contact with land during the three days prior to arrival at Crete" (instead of calling

it "the cleaner south"). Period D brought air that originated in North Africa and then touched the Balkans before arriving at Crete, i.e. it was largely marine but somewhat continentally influenced. Modify your text accordingly. Also, is there a trajectory plot for period E?

page 10314, line 12 – 14: The slopes of all the spectra besides the one from the South are similar (drawing horizontal lines at activated fractions of about 0.53, 0.73, 0.8 and 0.86 makes this obvious). But, as all of the samples, besides the one from the South, were continentally influenced, this is a reasonable result. Please adjust your statement accordingly.

page 10314, line 18 – 21: The size distribution from Sept. 21 really differs much from the others but those from Sept. 25 and Sept. 27 are rather similar, besides a somewhat elevated fraction of particles with sizes below 100nm for Sept. 25. Please make this distinction in your text. An indication at Fig. 6 about which of the dates belonged to which of your periods would also be of help.

page 10314, line 21: Explain in the text what is meant by "values" in ". . . The corresponding values (dN/dlogDp) for the aforementioned dates were 7804 . . .". Are these number concentrations obtained from integrating over a certain part of the measured size distributions, or the concentrations in one particular size bin, or those at the maximum, . . .?

page 10315, line 21: Define "greqs"

page 10316, line 3: ". . . density of the insoluble organic (1500 kg m-3 . . ." – One page earlier (page 10315, line 3) you say, that 70% of the organic carbon was water-soluble. Should this not have to be reflected in the average density that you use here, i.e. by using an average from average densities known for insoluble and soluble organics occurring in atmospheric particles?

page 10318, line 8 and 9: You give 4 citations here, all being self-citations (in the

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broader meaning) – there are surely other groups that have published data on this. Also check if all of the studies you mention find a Mo of about 200 independently, or if some of these references are just referencing the others and do not give additional information, as they then should not be mentioned separately.

page 10317, line 10: I assume you integrated over the measured size distribution for diameters larger than the critical diameter at each adjusted super-saturation. This needs to be described here, before you refer to the results shown in Fig. 8.

page 10317, line 11 - 13: Referring to Fig. 8, it seems the lines in different colors belong to the average at each super-saturation. This needs to be explained in the figure caption or in the text here. Also, the lines are hard to see (see comment below for Fig. 8).

page 10317, line 15 ff: Your arguments "i)" to "iii)" all try to describe that your under-prediction is NOT due to different chemical compositions for the different sizes that are activated at the different super-saturations. But different particle composition, with a larger than average hygroscopicity for the particles that activated at 0.2%, can be the reason for the different results of the closure for the different super-saturations (i.e. for the different sizes). You do say that yourself a bit later (beginning of the next page). You say, that ". . . aerosol is internally mixed and composition does not vary between PM1 and PM10 . . ."?, which likely comes from your chemical analysis. But there is still an order of magnitude to go from PM1 to 100nm (and smaller) particles, and surely the composition would differ if one would compare PM0.1 and PM1. (You yourself said earlier (page 10313, line 16): ". . . aged aerosol, where particles are larger in size and practically all contain significant amounts of soluble material.") Therefore, your argument "i)" does not give information about the size range in question for the activation in your study. Also argument "ii)" is misleading for the same reason. Ageing of particles occurs through coagulation or mostly through accumulation of new particulate mass, where it safely can be assumed that this new mass is soluble (acquired by wet phase chemistry while the particle is activated to a cloud droplet, or by condensates

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from the gas phase (e.g. secondary organic aerosols, SOA)). That means that even for size distributions that show ". . . a remarkably constant single lognormal mode . . ." the 500nm particles most likely contain a larger fraction of soluble material than the 100nm particles. This leads to the question, what you mean by "size resolve chemical composition" that you mention in your argument "iii)" – PM1 versus PM10? Or with a higher resolution? Do you have this kind of data for your measurement period? Delete lines 15 to 25 and replace them by a statement, that different particle compositions for the different particle sizes (particles of 100nm as compared to particles smaller than that) that activated at the different super-saturations can be a reason for the different results of the CCN closure.

page 10318, line 5 – 7: As mentioned in the introduction to this review already, there is still some scatter in your data that does not allow to call the quality of the closure "excellent" (average R2 of 0.9). Using the time-resolved information on the WSOC fraction could improve this, and as you have the data it would be a waste not to use it. Also, as you nicely defined the different periods in your work earlier, stressing the different aerosols that you measured during the different periods, using as much time resolved information as possible makes sense.

page 10318, lines 9 ff: As this is an important and interesting section, it would be nice if you added some more details. How did you choose your uncertainties? What do you mean by a 2% improvement of your closure? And for: "The respective closure errors . . ." – does this compare the closure errors for the original calculation and that for an increased ammonium sulfate mass?

page 10319, line 10: ". . . but should all be larger than Dpmin . . ." – explain why!

page 10320, line 10: 0.8 is not "all the particles", and, as said before, there were almost no additional particles that activated above a super-saturation of 0.6%, so change your statement such, that it explains that particles that could be activated at 0.87% almost all had already been activated at 0.6%.

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page 10320, line 13: R2 of 0.9 is not "excellent" but "good" – please change this.

comments on the separate figues:

Fig. 1: As this one figure contains 4 plots with a lot of writing in them, it's hard to see. You might want to delete unnecessary details, e.g. cut away the text boxes below the trajectories.

Fig. 2: Symbols in panel (b) are too small, which is also true for all of the text and numbers in both panels.

Fig. 3: This plot needs improvements to increase its readability: - increase the size of every writing in the plot (legend, tick labels, axis labels, the "periods"!) - please add a small tick for each day on the x-axis - draw thin vertical lines to better distinguish the different periods - the y-axis label rather should be "number concentration", as you depict both, CN and CCN concentrations - try plotting the CN-data as an area-plot underlying the colored CCN-lines – this might improve the plot - Maybe this plot should cover two columns in the final version, even after you have increased the size of the writings – make sure you check this prior to publication

Fig. 4 is a good example for the size that is reasonable for the numbers, labels, . . . . Take this as a "template" for the other plots.

Fig. 5: Again, the size of all labels, numbers, . . . should be increased. The title on the y-axis of panel (b) has to be "activated fraction" (not "ratio").

Fig. 6: Add, which of the given dates belonged to which period.

Fig. 8: Another figure that is hard to decipher. As before, please increase all sizes. Refer to Table 1 in the caption, giving it as the source for the fitting parameters for the differently colored lines, as these lines are hard to see.

Fig. 9: Give a legend! (What is the line? Which data are the base for the symbols?)

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 10303, 2009.

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