

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.

A. Bougiatioti et al.

mihalo@chemistry.uoc.gr

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We would like to thank the referee for the positive feedback and the very thorough comments. Our responses follow.

General comments

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.

The readability of the figures has been improved.

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 comments below.

The shape factor for NaCl (1.08) was introduced and the closure was re-calculated. All properties used were based on the average column temperature.

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.

CCN closure had actually been done, but not shown, as it contributed little variability to the closure. Not mentioning this was admittedly an oversight. Using the time-resolved WSOC/OC ratio, lead to a $\sim 1.03\%$ variability (compared to using the average WSOC/OC = 0.7). This is now mentioned in the manuscript.

Specific comments

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.

As mentioned in the manuscript, the references cited are in no way meant to be an exhaustive review of the literature. References from a number of groups were also

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included in the introduction. We have however expanded the presentation to a number of closure studies that recently appeared in the literature, including those suggested.

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?)

Good point. "Bulk" (PM₁₀) filters were collected without an inlet for the chemical analysis or aerosol drying. PM₁, PM_{1.3} and PM_{1.3–10} were sampled through a PM₁₀ inlet but without drying as well.

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

Done.

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.)

We thank the reviewer for pointing this out. It has now been accounted for.

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

Done.

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.

All thermophysical properties were evaluated at the median temperature of the column during the time of the measurement. This is now mentioned in the text.

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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.

As the elemental carbon concentrations are too low ($1.8 \pm 0.4\%$ of the total mass concentration) it cannot account for the “gap” described above.

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.

80% of the total particles activate at 0.8% supersaturation, which justifies the qualifier “most”.

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.

The truth is that “aged” has no strict definition. As shown by the study of the activation fraction for each prevailing wind direction, for the higher supersaturations the activated fraction is well above 0.8 for the majority of the geographical sectors (implying that 20% of the particle number is below the $\sim 45\text{--}50$ nm range, given the composition and critical supersaturation of these particles), and corresponds to sampling of an “aged” aerosol most of the time. The large WSOC/OC and long residence times in the atmosphere (away from major pollution sources) also support the characterization “aged”. To ensure that the term is used qualitatively, have refrained from using the term “very aged”.

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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?

The suggestions will be incorporated in the final version of the manuscript. Trajectory plots for Period E are available but not presented, since the dataset during this period is incomplete.

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.

Done.

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.

Done.

page 10314, line 21: Explain in the text what is meant by “values” in “. . . The corresponding values ($dN/d\log D_p$) 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,?

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Good point, and we apologize for the confusion. Concentrations are reported in cm^{-3} , and computed by integration of the average size distribution.

page 10315, line 21: Define “greqs”

Done.

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?

Given that WSOC constitutes a very large fraction of the OC, the densities of WSOC and OC should be similar. The $(\text{O/C})_{\text{WSOC}}$ and $(\text{O/C})_{\text{OC}}$ however is uncertain, which implies that the fraction of water-soluble organic mass to the total organic mass is somewhat uncertain (albeit high). So, instead of computing a weighted average (as suggested), we assume the same density for both OC and WSOC; a closure sensitivity analysis to the density is then performed to account for the variability mentioned. The density is varied based on measurements of ambient data; a lower limit of 1400 kg m^3 is assumed (Cross et al., 2006; Turšič et al., 2006). An upper limit of 1600 kg m^3 is assumed (Stein et al., 1994; McMurry et al., 2002), and a “basecase” of 1500 kg m^3 is taken.

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

All references cited are independent measurements carried out for water-soluble organics isolated from a variety of sources. There are other studies (some of which we

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have included now as well, such as Henning et al., 2005) but most references in the literature refer to the organic fraction of aerosol (and not the water-soluble fraction) or assume that the surface tension is equal to that of water, which of course would bias the inferred molar mass.

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.

Indeed. This will be mentioned in the text.

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).

Agreed. The color scheme will be explained and we will try to improve its representation (this is challenging, given that the closure is so close to the 1:1 line).

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. . . 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.

Indeed, variation of composition for CCN that are activated does not contribute to the prediction error. It is just an indication of what may be going on at smaller sizes; we understand the concerns of the reviewer however and have removed this discus-

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sion. “Size-resolved chemical composition” refers to data obtained from the analysis of samples collected with a 12-stage Small-Deposit-area-low-volume-Impactor (SDI) (Maenhaut et al., 1996). Size-resolved data are unfortunately not available for the measurement period, so we rely on the observed climatology to suggest what the compositional variation with size may be. The suggested change will be incorporated in the final version of the manuscript.

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.

When placed within the context of what constitutes an important CCN prediction error for indirect effect assessments, a 10% CCN prediction error is very small (as it implies at most a 5% error in droplet number, and at most a 5% uncertainty in indirect forcing; Sotiropoulou et al., 2006,2007). After recalculating the calibration curve for supersaturation, the closure improves even more. The time resolved WSOC fraction does not show large fluctuation (average 0.7 ± 0.12), which in terms of predicted CCN values has an impact of +1.03%. There are very few studies in the published literature that provide a sub-1% bias over a range of supersaturations, and with a variance of < 10%; for this, the characterization “excellent” still seems appropriate.

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?

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The uncertainty in the fluctuation of the organic density was chosen as to include all values between 1400 and 1600 kg m⁻³. The uncertainty in the ammonium sulfate mass represents the measurement uncertainty in the analysis, including the potential impact of residual ions.

“The respective closure errors” refer to the comparison of the closure errors between the original calculation and (a) the increased organic density (-2.9±15%) and (b) the increased ammonium sulfate mass (-3.4±14%).

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

Good point. Done.

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%.

After the correction for the shape of NaCl particles, the supersaturations are as follows: 0.21, 0.38, 0.51, 0.66 and 0.73%. Therefore the difference between 0.66 and 0.73 is not large, and can explain the fact that the particles activate at about 0.6%.

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

See relevant discussion above. With the updated calibration, R² = 0.92.

Comments on figures All comments will be taken into consideration and all necessary changes will be made for the final version of the manuscript.

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