

Interactive comment on “Widening the gap between measurement and modelling of secondary organic aerosol properties?” by N. Good et al.

Anonymous Referee #2

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N. Good's et al. "Widening the gap" ACPD paper is interesting and relevant for the HTDMA and SOA smog chamber community, as well as for cloud activation predictions from aerosol compositions in general, and should, in my opinion, be published.

The paper investigates the link from measurements in subsaturated (around 90%RH) conditions to cloud droplet activation (by comparing measurements with a CCNC instrument and what was predicted from the subsaturated measurements).

One conclusion by the authors is that the HTDMA measurements cannot be used to distinguish whether for instance surface tension suppression or the water activity changes, to link to the measured activated aerosol.

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My two main objections that I would enjoy seeing addressed in the ACP version are below. A few minor details follows at the end.

The first objection I have is, that, after reading the paper, remain UNconvinced with the general form of the message/conclusions of the paper. This can be remedied with either: additional data on measurement quality assurance, or by reducing the general conclusions to being slightly more specific (for instance: abstract line 22-26 and 4. Conclusions p 22643 line 14-19).

If you would choose to be more precise on the experimental conditions, that would result in a high-quality paper and it would enhance the citation possibilities of this paper, I think.

I detail:

The authors write in Abstract line 24 "...HTDMA data from proven instruments..." and on p 22626 line 8 "quality assurance procedures of..." and on p 22628 lines 13-14 "...Fig 1 (right panel) that all 3 instruments measured ... in good agreement...".

1) How do you define "proven"? Is it, or is not, according to for instance Duplissy et al (AMT 2009)? Include definition of "proven" in future ACP version. (somewhere on p 22626 would be suitable)

2) "quality assurance procedures" - again, I first thought this was related to Duplissy et al. 2009, but do you really mean only data quality assurance here (Gysel et al. 2009, for instance p 139-140 therein)? Please detail for a reader, or leave as is, if meant only data treatment. What quality criteria for the operation of the instruments were then used?

3) Fig 1. "in good agreement":

3.a) Would you please, in text, state values for average measured ammonium sulfate growth factor (GF) for each instrument and at what RH. Please state, for each instrument, up to what RH that accuracy is valid (90 or possibly 92% by judging from Fig

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1).

3.b) Because in Fig 1 right panel, shows Hman about 1.67 at 90%RH and Hpsi 1.76? Is this the "good agreement"? How many data points are in that panel? Do you have substantially more data points available, state in text how many and if this is why you conclude as you do? Please inform the reader in that case. Ofcourse if the accuracy is 0.1 between the instruments, any model comparison will not work (supplementary material calculations could be connected to this accuracy). You should please clarify this. This connects to the definition of "proven" I mention above, was 0.1 in GF the limit chosen for "proven"? Was it +/-0.05 in GF, as recommended in Duplissy et al 2009, page 371?

3.c) For Hqut the same GF measured appears two times at 81 and 84%RH and at 84 and 86%RH. Furthermore a slightly lower value (than theory) is observed above 90%RH, isnt that what might result in the lower "black box" in figure 3 (aw at "highest measured value by each HTDMA")? How do you guarantee that this GF measured is within accuracy, if there is no ammonium sulfate data at that RH?. Do I dare to consider the water activity for Hman and Hpsi to be more reliable, and state, contrary to the authors conclusions, that these two HTDMAs actually measure an accurate average which is about ($aw = 0.97 X_w$) for the unseeded SOA? In short why do you guarantee the quality of Hqut above 91%RH?

3.d) Is the data Fig 1. for the 150 nm diameter? Couldnt you also show the data for the other sizes, or comment in text with values? A short table?

3.e) What are the error bars in right panel of Fig 1? I dont find that, my excuses if it is written already. (should be on page 22628?).

4) In Supplementary material 1. Introduction you write "The measurement uncertainty is shown in Figure 3 of the original manuscript". I suppose you mean Fig 2?. It would be needed to state the uncertainty used, at what relevant RH, for supplementary material figs 1-3. Did you for instance use Hman +/- 0,02 (as mentioned in text) or +/- 0,04?

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as indicated from Fig 2 (at about 90%RH) (resulting in the KHTDMA uncertainty color range)? It would be interesting to see these Figs 1-3 for the uncertainty of each individual HTDMA (that might be the case but hard to find out from text). Please state clearer in supplementary material that it is considering unseeded experiments (...I think).

Conclusion of the above: the above points, make me uncertain that the general form of the conclusions are valid. Please detail whether: your measured HTDMA data is better than can be seen from your Fig 1. (thus your conclusions ARE valid), OR, IF for instance the quality and operation recommendations from Duplissy et al 2009 would be strictly imposed, would it then be possible to use your methodology to obtain information on surface tension etc, in a future measurement geared to that goal?

Please insert in abstract definition of "proven" and "agreement was observed" with a number. "In order to narrow the gap between measurements of hygroscopic growth and CCN activity the processes involved must be understood" - and I suppose in addition you mean: "the HTDMA measurements must be strongly quality assured"? Is it then possible?

Please insert in "Conclusions" p 22643 line 14, for instance, "SOA measurements". Is it specifically SOA which cannot be measured? See comment below on HULIS by Ziese et al 2008. p 22643 line 17 might be better "properties of SOA from smog chambers"? I would not assume as you do on line 19-21 and 25 (Conclusions) that the "SOA from smog chambers" is so directly interchangeable with "natural organics", but would instead recommend you to rephrase this more carefully. Use "synthetic SOA" and "atmospheric organics" or similar, and write clearly when you consider them to be same.

I think you could also mention and compare why your results differ from for instance the ones of Ziese et al 2008. They apparently do succeed with a similar approach (High RH subsaturated measurements - CCNc) with HULIS extracts to estimate σ_c and surface tension. However they also found that HTDMA measurements at a lower

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RH (90-95%) were difficult to use in estimating Sc and understanding surface tension and non-ideality. This is what you conclude p 22642 line 19. A reference to their findings would be well confirming.

Second main point:

P 22634 line 6-9: Do you mean that this temperature difference IS what creates the difference between GF measured Hpsi and Hman/qut?

Did you once measure with the CCNC on same line close to the Hpsi? Should I interpret this as the Hman being the only reliable measurement in the set of three HTDMAs, concerning the issue at high RH (I mention above) for Hqut, thus the Hman being the only one left to link accurately to the measurements from the CCNC, in this study?

What does happen inside the cooled Hpsi; the walls are cooled, some vapors will condense on these walls, the air flow will cool, this will cool the individual aerosol particles. Little by radiation, some by exchange with air molecules, and some possibly by evaporative cooling on the aerosol particle surface. That what evaporates, what would it be? The highest vapor pressure component (if similar vapor enthalpy), which is generally assumed to be the least oxidized, ie the least hygroscopic component. A more hygroscopic aerosol particle would remain. Thus this cooling might explain a part of the higher GF measured by Hpsi. I cannot estimate if this is possible at a temperature difference of 4K. Your discussion of this p 22634 line 14-17 describes this well. Is the conclusion that the Hpsi cannot be used together with the presented CCN data?

Again, this would mean that your outlined methodology could work, if the HTDMAs are exactly at same location as CCNC.

Minor points

P 22625-26 line 1-3: Is the English grammar ok? Or should there be a "and" after "...Meyer et al. (2009)".

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P 22628 line 15-22: You mention the Hman instrument, and then write "...these HTDMA...". Maybe move the last sentence up to line 14?

P 22631 line 20 "detection"

P 22632 line 5 and line 18: Does "later" mean "6 to 8 h"? Please detail. I suppose later means after say 8 hrs? When?

line 16-17: "from about 40% up to about 95%...". Couldnt you here specify up to what RH for each instrument?

Fig 4 x-axis: should be 200 nm to the right, not 2? would, in my opinion, be easier to read... but ok. On P 22636 line 22 you say 3 kappa values but in caption only 2.

Fig 5, 6, and 7: the right hand scales are not the same, it would be maybe easier to spot the differences if they were. Matter of taste. Fig 5 middle panel left scale misses a "3". Fig 6 top panel left scale misses a "2". Fig 7 middle and bottom panel left scale, couldnt it be the same range as fig 5 and 6?

Concerning the temperature in the smog chamber hall laboratory, in table 1 two experiments have a duration of around 24 hrs. On p 22633 line 25-26 you write that the temperature in this laboratory was "...typically in excess of 25°C...". Was this the case for the relevant time of measurements for these longer experiments, during a large hall at night (the 24 h experiments) in Switzerland in August? If so please confirm the "typically", or write a range of temperatures, or add in table 1 the relevant lab temperature. There is surely a suitable temperature sensor which represent the lab temperature with an accuracy of at least +/-2 K.

References

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

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For references below see same in the authors ACPD manuscript:

Duplissy et al (AMT 2009)

Gysel et al (JAS 2009)

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 22619, 2009.

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