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Atmospheric Chemistry and Physics Discussions

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

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Firstly we would like to thank the referee for their detailed comments, they are much appreciated.

- General comments:

- 1) It would be preferable to move some of the system description...

A table has been added in section 2.1 outlining the temperatures, residence times and sheath type. A more detailed description of each system is then given in the supplementary material to which the reader is guided in the text. Some small changes

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are made in section 3 to reflect the details added in 2.1.

- 2) Reading the paper it was not really clear what different experiments were done...

Additional sections now numbered 2.2 (Measurements unseeded experiments) and 2.3 (Measurements seeded experiments) are added to distinguish between the measurements made during the seeded and unseeded experiments. Section 3.1 is renamed (HTDMA results: un-seeded experiments) and an extra sentence is added at the start of section 3.6 to further clarify. Table 2 lists the experiments presented.

- Specific comments:

- 1) Page 22621 row 27:

The first point: I would dispute this comment, 22622 row 1 states clearly that “we cannot state if the water activity coefficient changes significantly” i.e. whether there is a change in non-ideality, not whether the solution is ideal.

The second point: the final assertion is correct, what we are saying it that because of the differences in the HTDMA we cannot say. Taking a HTDMA in isolation could lead to a conclusion about any change in the activity coefficient.

"due to the differences in the HTDMA data" is added to the final sentence of the abstract to clarify the point.

- 2) Page 22626, line 5:

This has now been corrected

- 3) You describe a number of possible explanations for the difference in H-TDMa results...

None of the instruments differ from those described in Duplissy et al 2009. The overview of the instrument design in the supplementary material now gives the reader extra information. The fact the instruments are all closed loop is now stated in the text and included in the new table (now Table 1).

All 3 HTDMAs utilise closed loop DMAs. This hopefully minimised any repartitioning. Open sheath lines drawing their air from the chamber itself so changes in the chamber are matched quickly in the DMAs would perhaps be an even better solution. Though this might not be practical in all cases as the chamber is of finite volume (i.e. the available sample volume is a limiting factor).

- 4) For the seeded experiments, ...

We believe the reviewers comment should read: "For the unseeded experiments, the kappa values of the SOA changed with time, is this time dependency included in the seeded experiments?" and is answered assuming that is the case.

This dependency is not included as the humidograms used in the ADDEM could only be captured after the growth factor had stabilised. The time dependency has a small effect in these cases due to the fact that the inorganic fraction is large compared to the inorganic fraction during at the start of the experiments when the change in growth factor with time is strongest. This is compounded by the fact the change in the organic growth factor with time is fairly small compared to the differences in the organic and inorganic growth factors.

- 5) Page 22626 line 7

Corrected

- 6) Page 22627, line 3:

I agree this sentence is not clear and is reworded as follows:

The seeded experiments are better suited to the monodisperse sampling mode because the presence of the seed results in a relatively slow increase in the mode of number size distribution throughout the experiment. Therefore over a $\sim$20 minute CCN measurement cycle the mode of the distribution will remain below the size selected. As

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the critical supersaturation of the seed is known a-priori, the initial supersaturations to be set by the CCN counter are known and the Sc can be tracked throughout the experiment without downtime searching for the correct settings.

- 7) Page 22627, line 5:

To clarify the initial definition is reworded slightly to say:

“The CCN counter was operated in two different modes; polydisperse and monodisperse.”

However I believe the confusion arises as it is stated in a section dealing with the mono-disperse measurements alone. So the sentence is simply changed to:

“The supersaturation set point was increased in a series of 5 steps over ∼20 minute periods to build up an activation spectrum.”

- 8) Figure 1, right panel:

Each HTDMA measured at a different dry size, this is clarified in the text. The theoretical line includes the Kelvin effect for a 150nm particle dry diameter, the 100nm (and hence the 105nm) curve is virtually indistinguishable from it. So the values can be compared to the line shown, as the instrument uncertainty is much larger than the theoretical Kelvin effect.

- 9) Page 22628, line 8: “relatively unimportant”.

Added.

- 10) Page 22628, line 16:

The graph was designed to focus on the comparison of the instruments at higher RHs, giving a clear visualisation on the measurement uncertainty and inter- instrumental comparison at the same set RHs. Humidograms showing the full RH range are shown in Duplissy et al 2009 which is cited in the manuscript.

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These points are now added. The Manchester HTDMA gives a bimodal distribution as it crosses the deliquescence point because the RH increases slightly as the scan progresses so both dry and deliquescence particles are present. These transient points are highlighted on the graph.

- 11) Why are you using the parameterization of Suwanee river Fulvic acid? ...

This is the crux of the problem. It is difficult to estimate the surface active properties of the SOA material. We decided to use a surfactant representative of atmospherically-isolated organic material (in this case HULIS). The objective was to show the possible extent of the surface tension suppression using a strong atmospheric surfactant followed by a demonstration of impact of the bulk-to-surface partitioning. Ideally we could have created an a-pinene surface tension parameterisation based on the results however, as stated in the manuscript, such a parameterisation would be instrument specific.

- 12) Page 22631, line 20:

Spelling mistake is corrected.

The 50% value for a specific aerosol composition is 3nm. For the 3nm SOA produced in the chamber experiments the value is not derived. Therefore we use the word nominal to denote that the 50% detection cut-off is nominated as 3nm, in reality it could be different. We have added 50% to clarify.

- 13) Page 22631, line 20:

The formation of new particles decreases to zero.

The point is that interpreting the observations using the CPC and SMPS techniques depend upon some knowledge of the nucleation/condensation/coagulation/loss rate. The observed peak in CPC number or SMPS channel will occur when the formation rate equals the loss rate. So the point is that even though nucleation is not linked to wall losses when interpreting the measured number we must consider all these factors.

- 14) Page 22631, line 22:

Split, now reads:

The scanning mobility particle sizer (TSI SMPS, 3080) is was used to estimate the total mass concentration (assuming constant particle sphericity and density of 1300 as measured by alfarra06 for alpha-pinene SOA from photo-oxidation experiments performed previously) . Based on the estimated mass detectable condensation of VOC oxidation products continues for at least 8 hours after nucleation.

- 15) Page 22632 line 4 and below:

This figure has been added.

- 16) After how long time are the SOA humidograms in Fig 2 taken...

Humidograms were collected after at least 6 hours. The dry sizes were 200nm for HMAN and HQUT and 250nm for HPSI . Just a single experiment is shown for each HTDMA and was used to derive the water activity parameterisation.

- 17) Page 22635, line 3:

Since we found that the sensitivity to the molecular weight was relatively small compared to the differences observed for the different models it is difficult to make an informed choice based on our data. Given the difference between the HTDMAs we could have used different values in different cases to get better agreement but this would of course lead to an instrument dependent solution .

- 18) Page 22638, line 17:

Spelling corrected

We agree this is not worded clearly. Really what we were trying to say it this the model predictions do not run exactly parallel to the measurement values. The sentence is therefore re-worded:

“. . .rather each HTDMA’s predictions move slightly towards or away from the measured values with increasing diameter”

- 19) Why does including surface to bulk partitioning increase the predicted critical supersaturation values?

For HMAN and HQUT partitioning always reduces Sc compared to assuming the surface tension of water i.e. in Fig 4. black points are always below the red ones.

For HPSI the partitioning case does increase Sc compared to the pure water case. This is due to the relatively hygroscopic nature of the organic measured by the HTDMA i.e. the removal of solute has a larger impact than the decrease in surface tension. When only surface tension reduction is considered the Sc decreases. The surface tension profile could be altered to make the two lines meet but it is difficult to justify, because the water activity profile derived from HPSI combined with an appropriately modified surface tension isotherm is unrealistic.

- 20) Fig.4:

There are the same number is each case, however some of the values sit on top of each other. Unfortunately, this is a symptom of relying on parameterisations of water activity which are forced to have correct limiting behaviour. At larger sizes it becomes more difficult for the solver to differentiate different critical supersaturations for a relative small change in input parameters. Combined with the highly non-linear behaviour of surface tension parameterisation leads to this effect for the green symbols, the surface tension of water behaving less erratically. This is also illustrated by the fact that this is prominent for the HPSI case where the impacts of ‘unexpected’ water activity profile at very high RH is discussed elsewhere. However, the broad pattern of sensitivities can still be observed. This is a limitation of combining a detailed model with the parameterised behaviour for aw and should have perhaps been mentioned sooner.

- 21) If I understand correctly, no surface to bulk partitioning was used in the seeded experiments, only a parameterization of surface tension. Why is this?

The predictions with the surface tension of water and the surface tension parameterised without partitioning should normally bound the range of predictions. However, as already identified, the bulk-to-surface partitioning for the PSI HTDMA gives the highest Sc, but as explained this is due to the modelling approach rather than a real effect.

- 22) It is unclear why you use 90% RH values for the kappa parameter for the seeded experiments, when the solubility seems to increase above 90%, at least for the PSI system.

We are testing the applicability of the single parameter representation. We showed for the unseeded case the effect of calculating kappa at different RHs. Taking kappa from higher RH will tend to move the result towards ADDEM (assuming the surface tension of water). As you point out whether this improves the result depends on the HTMDA. This effect illustrates the difference between what I sometimes termed an “effective kappa” i.e. one derived from a measurement of growth factor or critical supersaturation and the “intrinsic kappa” defined by equation 2. Ideally we would want to at least identify the intrinsic kappa even though an effective intrinsic kappa might given more consistent results across a range of RHs, so that we can understand the processes involved.

- 23) Figure 4:

To me the plot looks less clear this way. We can expand the panels and enlarge the image though.

- 24) Figure 4:

Yes the black crosses use the Fulvic acid surface tension parameterisation including bulk to surface partitioning. The point we want to make is that is can be achieved with very different assumed behaviour. the sentence is reworded to make this clear. Our responses to points 19 and 20 also discuss the bulk to surface cases.

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

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