**Atmospheric
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Interactive comment on **"Hygroscopic properties of the ambient aerosol in southern Sweden – a two year study"** *by* **E. O. Fors et al.**

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Comments to referee 1:

We thank the referee for the comments, which definitely helped to improve the paper. The specific issues are commented below.

1. The use of two water activity parameterization is unnecessary and simply confuses the reader. The difference between the kappa_R and kappa_P model is simply that in kappa_P the correction term for the non-ideal behaviour is included. In the other case the non-ideality of a model salt is taken into account. How can you be sure that the non-ideality of the measured ambient aerosol is similar to the one of ammonium sulphate? This inserts an unnecessary extra uncertainty in the closure, even if as you

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state this is a small effect. I suggest using only one water activity parameterization (kappa_P) throughout the manuscript.

Good point. The closure has been recalculated, and the kappa_R model has been removed from the paper.

2. Page 6611, description of the closure: I think this paragraph has to be rewritten. I could only follow the text until line 10 ("The particles from one particular DMPS spectrum were then distributed over this surface function"). Then it is not clear anymore how you made your calculations. E.g.: line 11, after which the new surface function was integrated. . . Along which variable? Between what limits? I believe/hope that the made calculations are correct, I think it has to be simply better/correctly explained. For this reason I would like to see the exact equations that you used. One equation tells much more than many sentences.

We have rewritten the model description; hopefully it is now possible to follow the equations.

3. Section 2.5 (Parameterisation of the CCN(s) concentrations): This paragraph for me is a mystery. The title suggests that some kind of parameterization of the CCN concentration will follow. Even though the only thing that is explained is that how one can fit the size distribution with a log-normal function and how then the cumulative lognormal distribution looks like. And then one sentence follows about the definition of the critical dry diameter, where you say if it is known along with the size distribution the CCN concentration can be calculated. For me this paragraph does not make any sense, why do you even need a fit for the size distribution if you have a measurement of it?

The point of this part of the paper was to investigate whether or not the CCN concentration could be well described with averaged log-normal distributions and averaged GF-PDFs (alternatively an average GF(Dp). The point of this is that you need a fit if you want to derive the CCN concentration as a continuous function of the super-

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saturation. If you want to know how many CCN you have a certain supersaturation, you calculate the critical diameter for each mode, using table 8 and then use this on equation 6.

4. The discussion about the CCN data is weak. One could do much more with that data, calculating seasonal/diurnal variations of the CCN concentration or dry activation diameter. Or other CCN properties. I understand if this is out of the scope of this paper and you plan to publish the CCN data elsewhere and you only wanted to show the closure here. Just it would be a pity if the CCN data was not published anywhere.

This is true, and we plan to publish this data at a later point. In this paper, the CCNC data is more a supplement to the H-TDMA data.

Specific comments:

Page 6602 line 8: Define CCN

Corrected

Page 6602 line 24: what do you mean by CCN parameterization?

Maybe parameterisazion is not the best choice of word. The text has been changed to "It was found that although the aerosol is often externally mixed, recalculating to an internal mixture with respect to hygroscopicity did not change the CCN concentration as a function of supersaturation significantly."

Page 6603 line 8-9: the direct aerosol climate effect includes both scattering and ab-Sorption

Corrected.

Page 6604 line 13: the sentence suggests that this is the only or most common classification, please rephrase!

The text has been changed to the following:

"The hygroscopic growth can be subdivided into different classes with respect hygroscopicity. One classification is based on diameter growth factor at 90% RH with respect to ammonium sulphate. For 100 nm dry particles diameter these boundaries are: Nearly Hydrophobic (NH; GF=1.0–1.11), Less Hygroscopic (LH; GF=1.11-1.33), More Hygroscopic (MH; GF=1.33-1.85) and Sea Salt (GF>1.85) (Swietlicki et al., 2008)."

Page 6604 line 14: nearly hydrophobic: this name is misleading. Hydrophobic material is known to repel water. An aerosol particle with GF=1 at high RH means simply that the particle is non soluble at this RH, so it is non-hygroscopic. There is no way to detect hydrophobicity with the H-TDMA technique. Therefore I suggest to use "nearly non-hygroscopic" instead of "nearly hydrophobic" phrase. And be consistent with it throughout the whole manuscript.

Good point. We have changed the term nearly hydrophobic to "barely hygroscopic" and hydrophobic to "non-hygrosciopic".

Page 6605 line 10: Please define OA!

Corrected.

Page 6605 line 12: Delete "that"

Corrected.

Page 6605 line 20-23: monodisperse CCN measurements could give information on the mixing state, reformulate the sentence.

True. The text is changed to "However, when operated as in this study, they do not give any information about the degree of external mixture of the aerosol, something that is essential for a deeper understanding of the atmospheric processes that governs the number of CCN"

Page 6607 line 7: 1:10 is a ratio and has no unit.

Corrected.

Page 6607 line 17: Please mention the residence time in the humidifier already here!

Good point. This has been corrected.

Page 6608 line 5-11: The theoretical values from Tang and Munkelwitz are old and based on a single measurement I suggest to use newer values from e.g. AIM or AD-DEM models.

Since (to our best understanding) both AIM and ADDEM are based on the same electrodynamic balance-measurements and the results are very similar, we prefer to keep the original reference.

Page 6608 line 20 and 21: flow ratio has no unit.

Corrected.

Page 6609 line 15: typo "thesvalues"

For some reason this is only visible in the ACPD-version. We will make sure this is OK in the final version.

Page 6609 line 19: "_ 30 m", change "m" to "min"

Corrected.

Page 6609 section 2.3: how, and how often was the CCNC calibrated?

The following text has been added: "The CCNC was calibrated in a laboratory environment before field deployment using ammonium sulphate particles with a DMA upstream the aerosol flow. The CCNC was set to a fix s, while the DMA selected a span of different sizes, to investigate at which size the selected particles activated. This procedure was repeated when the CCNC was returned to the laboratory during the summer of 2010. For high supersaturations, the old calibration was valid within 2% down to s=0.6. At s=0.25, the CCNC measured 7% higher s than indicated by the instrument, and at 0.2% the error was 14% in the same direction. In the field, the flows of the CCNC were

monitored and checked on a weekly basis, but no salt measurements were conducted."

Page 6610 equation 3: change "a" to "3"

For some reason this is only visible in the ACPD-version. We will make sure this is OK in the final version.

Page 6612 line 2-4: Please rewrite the sentence, I do not understand it.

The text has been changed to the following: "Other possibilities are poor CPC calibration efficiency curves or a badly calibrated DMA flow which will affect the sizing. Problems with DMA sizing will have a more profound effect on lower s values because 1) fewer particles have activated, making the relative error larger and 2) the size limit to which particles will activate is somewhere in the middle of the size distribution. At high s values, a large portion of the size distribution is activated and the relative effect is smaller if you add or remove a few activated particles. In addition to this, there are often fewer particles in the size limit which is relevant to high s ratios. As an example 100 nm particles with a GF of 1.6 activate at around 0.2% s, while 40 nm particles with a GF of 1.3 activate at 1% s."

Page 6613 line 11: "cot"?

For some reason this is only visible in the ACPD-version. We will make sure this is OK in the final version.

Page 6614 line 19: what is FNL?

It is a sub-archive within GDAS (global data assimilation systems). The meaning of the letters is unclear. The text has been changed to "...and meteorological data from the Centre of Environmental Predictions (NCEP) and GDAS (Global Data Assimilation System) archive have been used..."

Page 6615 line 17-18: Is the shift of the more hygroscopic mode at larger diameters only because of the Kelvin effect or is the hygroscopicity changing as well?

It is not only due to the Kelvin effect. The following sentence has been added: "This is not only because of the Kelvin effect, but because of an increased hygroscopicity in the accumulation mode compared to the Aitken mode." This can also be indirectly seen in the diurnal variation of the kappa parameter (Fig. 5b).

Page 6615 line 23-24: How clear is this clear increase in hygroscopicity if you exclude the Kelvin effect? It would be actually much easier to interpret the results if you would show kappa-PDFs, I suggest doing so, or including it as a second panel in figure 3.

Figure 3b has been added, showing kappa-PDFs for all sizes.

Page 6618 line 6-7: Have you thought about a chemical composition, hygroscopicity closure for that month when AMS measurement is also available?

Yes, we have done that with a simple ion pairing scheme for 265 nm, the only size which really had a strong enough signal. With a GF of 1.2 for the organics the closure slope was more or less perfect, but the H-TDMA GF varied more than the AMS GF, indicating that maybe the characteristics of the organics is more dynamic than the assumption of a static organic GF. We plan to publish this data in a separate paper.

Page 6618 line 1: Did the Fourier analysis reveal only a daily cycle?

Yes, and "overtones" of the 24 h signal.

Page 6618 line 18: why did you use for the averaging the volume weighted growth factors?

We feel it makes more sense. If you want to calculate the kappa for the entire particle, the 1st moment average is biased, since volume is proportional to r^3. Compare with the ZSR mixing rule: ãĂŰGFãĂŮ_average=âĹŻ($\sum$_$(i = 1)$ⁿε_(s,i) ãĂŰGFãĂŮ_(s,i)^3 ãĂŮ) where ε_(s,i) is the volume fractions of the solute and GFs,i the growth factor of the individual solutes.

Page 6618 line 28: How do you define the amplitude? Difference between minimum

and maximum or average?

Difference between minimum and maximum. The text has been changed to the following for clarification: "...and an amplitude (defined as the difference between maximum and minimum value) of 0.15 while..."

Page 6619 line 7: "three smallest particles", change particles to sizes

Corrected.

Page 6619 line 5-8: for me it seems like, that the 35nm particles are more hygroscopic than the 50 and 75 nm ones. Is this significant, what could be a reason for that?

Yes, the difference is significant with a 95% CI t-test. We are not sure why this is. A possibility is that hygroscopic compounds as e.g. sulphuric acid were involved in the nucleation and that this "core" is somehow diluted with less hygroscopic organics as the particles continue to grow. But we feel that this speculation is a bit of a stretch - we simply do not know. We have added the following text. "It can be noted that the 35 nm particles are slightly more hygroscopic than the 50 and 75 nm particles. The reason for this is unknown."

Page 6619 line 15: the aerosol particles are getting more hygroscopic not the GF-PDF

Corrected.

Page 6619 line 20-22: and you actually see the opposite, the amplitude of the diurnal cycle is higher for the smaller particles.

True, probably the condensation and evaporation of semivolatiles is what is dominating the diurnal cycle of the smallest particles.

Page 6619 line 27-29: it does not matter what kind of organics you evaporate from your particle as long as the overall hygroscopicity of the particle is higher than the hygroscopicity of that organics (which is the case if I am correct). Please correct the sentence!

Good point, The text has been changed to the following: "Evaporation of semi-volatile organics will on the other hand lead to an increased hygroscopicity, since the average hygroscopicity of the particle generally is higher than the organics which evaporates."

Page 6620 line 2-3: for the hygroscopicity the mass (volume) ratio is relevant not the mass itself, so does this diurnal cycle also present if one looks at the mass/volume ratios? Yes the diurnal cycle is still there for mass ratio. The text has been changed to the following: "... confirm strong diurnal cycles in organic mass ratios..."

Section 3.6: The correct calibration of the CCNC is crucial, and this could be also responsible for the not perfect agreement between measured and calculated CCN concentration.

We agree, and as stated in a previous question, the CCNC was indeed measuring slightly higher s than indicated by the instrument, especially for low s values. This may very well account for some of the disagreement. Since there was no salt calibration during the experiment, we prefer not to include any correction for this, as it would be too speculative.

Page 6621 line 8-12: you argue that the maximum CCN(s) values at 1% supersaturation reach the values of the integrated DMPS number concentration, and therefore the counting efficiencies of the different instruments cannot be responsible for the observed closure discrepancy. I cannot agree fully with this argument. If someone looks at the points where everything should be activated, due to unavoidable measurement uncertainties some points would be above the one-to-one line and some below. Therefore it is expected that the maximum CCN(s) values are actually higher than the corresponding DMPS number concentration values.

While this is correct, in fact the maximum CCN(s) concentrations are actually sometimes higher than the DMPS concentration, but not more than around 5-10%, which is what can be expected for the reasons you mentioned. Although this is not conclusive evidence, we feel that it is at least circumstantial, and should not be excluded. How-

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ever, the text says "a fact that contradicts the counting efficiency of the CCN as the major problem in the closure". This has been changed to "a fact that contradicts the counting efficiency of the DMPS as the major problem in the closure", as it is more likely that a system counts too few particles, rather than too many.

Page 6622 line 26-29: Could you give an estimate what kind of surface tension value would explain the observed discrepancy?

Roughly 55 mN/m is required. This seems unlikely, as it corresponds to more or less pure HULIS, while in reality we definitely have a lot of inorganic salts mixed in the particles, which would push the surface tension at the point of activation significantly higher.The following text has been adeded: "When altering the surface tension, it was concluded that a surface tension of $\sim$55 mN/m is required to reach a perfect closure"

Page 6623 line 14-15: Why do you need a fit if the direct measurement can be used for the calculation? The fitting introduces only unnecessary error. As it can be seen in Figure 9, the fit is not perfectly matching the measured data.

The reason for using a fit is to describe the aerosol with as few parameters as possible. You can use the full dN/dlogDp-data , but if you want to e.g. describe the aerosol by a model, you want to be able to simplify without losing too much information.

Page 6624 line 19-21: How often?

This is a good question, but a very hard one to answer. To really say something about this, we would need to do modal fits of the GF-PDFs. The problem is that there is no automated robust routine available for this as we know of. Going through the entire dataset manually would be too time consuming. However, looking at the contour plots of the GF-PDFs over time, it is evident that the aerosol is externally mixed. Even though we unfortunately cannot quantify it, we feel that it is relevant information at prefer to leave it in the text as a general remark.

Figure 1: Please add the information on at which dry sizes (or RH) were the measure-

ments performed, or were both varying during the calibration experiments? Please include the number of measurement points at each water activity value.

The figure has been changed according to the suggestion below about density functions. The number of points has also been included and the RH (always 90%) specified.

Figure 2: increase the size of the figure annotation, I suggest to include it only once (but bigger) since it is the same for all panels.

Done

Figure 4: Adding the monthly average GFs to the graph would be good. And please use more colors for this plot not only 8.

Monthly averages have been added. However, we prefer to keep the number of colors.

Figure 6: this figure contains a lot of points and therefore significant part of the plot is just grey. One cannot really see where the highest density of them is. It would be much more informative if you would not show every single point, but rather the density of points per area, or something similar. Do it for all graphs where you show similar amount of points.

The figure has been changed to a density plot. The figure caption has been changed to "Growth factor data as function of water activity and particle diameter from automated salt scans for the complete data set. The data was collected at 90% RH. The graph shows the density of measurement points, based on 451 days of measurements for all dry sizes. In all 4392 measurement points. The density is based on a grid of $\triangle$aw=0.0016 and $\triangle$GF=0.01. The black line is based on data from Tang and Munkelwitz (1994) and Potukuchi and Wexler (1995). Dotted lines represent $\pm$1.2%RH from this line, which is the instrument uncertainty (Nilsson et al., 2009)."

Figure 7: Too many overlapping points here as well. I suggest to show rather the different percentages of the ratio distributions.

We actually prefer to keep this plot as it is, since the statistics are already included in table 5.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 6601, 2011.