Response to Martin Gysel

We thank Martin Gysel for the review, constructive comments and suggestions for improvement of our manuscript. Detailed responses to the individual comments (including additional information and figures from the revised manuscript) are given below.

(Referee comments in *italics*, the responses in plain font)

Comments and suggestions:

1. The concept of describing the results of monodisperse CCNC measurements in the form of hygroscopicity distributions is certainly not yet wide spread and it may possibly be called new. However, this is definitely not true for hygroscopicity distributions obtained from HTDMA measurements. Stolzenburg and McMurry (1988) introduced the concept of describing inverted HTDMA measurements as a normal distribution of growth factors with their TDMAinv algorithm. Adapted versions of the TDMAinv algorithm, which describe the growth factor PDF (GF-PDF) as a superposition of multiple Gaussian distributions, have been used by many groups. Recently Gysel et al. (2009) have developed an algorithm which inverts HTDMA data and describes the GF-PDF as a piecewise linear function. The code of this algorithm also contains a function to convert a GF-PDF into a kappa-PDF and it is available on the web (http://people.web.psi.ch/gysel/restricted/). In 2008/2009 HTDMA measurements have been made during a whole year at several sites across Europe as part of the EU-funded project EUCAARI. The inverted GFPDF data of these studies are available in the form of GF-PDFs on NILU's EBAS database. Kammermann et al. (2010) showed in a hygroscopicity-CCN closure study how such GF-PDF data can be used to consider the size-resolved particle mixing state for CCN predictions. Equation (6) of this manuscript is essentially equal to equation (2) in Kammermann et al. (2010), except for describing the mixing state in kappa- instead of GF-space.

Responses and Revisions

We included the work of Stolzenburg and McMurry (1988) and Kammermann et al. (2010) in the introduction:

Page 2 line 47-51:

"Early and recent HTDMA studies have already presented distributions of diameter growth factors, which are also related to particle hygroscopicity, and addressed the relation to aerosol mixing state (Stolzenburg and McMurry 1988; Swietlicki et al., 2008; Kammermann et al., 2010)."

Comments and suggestions:

2. The concept of reporting mixing state resolved HTDMA or CCNC data as kappa distributions is generally applicable for any kind of mixing state found in the atmosphere. Unfortunately the theoretical concept remains confined to bimodal lognormal kappa distributions as the most complex example explicitly given in this study. Bimodal lognormal kappa distributions may often be sufficient to describe the properties of atmospheric aerosols but there are certainly many cases with more complex kappa distributions. What about the example given in Fig. 1, is it possible to represent it accurately with a bimodal lognormal distribution? How would you calculate the mean kappa for these examples? In order to make this paper a complete and general reference for future studies I encourage the authors to provide the basic equations for deriving integral parameters such as (geometric) mean, (geometric) standard deviation, etc. from a whole distribution of any shape as well as for sub-ranges of the kappa distribution (possibly in an appendix). The latter may for example be of interest in the case of distinct modes. Equivalent equations for GF-PDFs instead of kappa-PDFs are given in appendix C of Gysel et al. (2009). Direct integration of (interpolated) distributions can make your life much easier when it comes to determining mean kappa values of many individual distributions of a large HTDMA or CCNC data set. The detour through fitting multimodal (log-)normal distributions can be very tedious work.

Responses and Revisions

Good suggestions. We added more equations and explanations in the revised manuscript including the general expression for multi-mode distribution and characteristic distribution parameters such as (geometric) mean and (geometric) standard deviation, etc.

These revisions can be found in **Sect. 2.1.**

Comments and suggestions:

3. The authors use both the cumulative hygroscopicity distribution, N(κ), and the normalized cumulative hygroscopicity distribution, n(κ) throughout their manuscript. I recommend that the unnormalised forms of cumulative distribution function (CDF) and probability distribution function (PDF) are completely avoided, and that only the normalized forms of CDFs and PDFs are used. Furthermore hygroscopicity *distribution data, be it from HTDMA or from CCNC measurements, should always be reported in the normalised form (information on the total number of measured particle counts can always be separately added). Reasons for my strong opinion are:*

- *A HTDMA provides only information on the normalised hygroscopicity distribution. Additional effort such as an extra CPC behind the first DMA, a parallel SMPS, or a very accurate characterisation of TDMA kernel (including losses in the dryer and humidifier) would be required to infer the correct factor for obtaining the unnormalized hygroscopicity distribution from the normalised form. Actually, this fact is withheld in the statement "Then a second DMA is used to measure the size distribution of the equilibrated wet particles, n(Dw) and to calculate the cumulative wet particle size distribution function, N(Dw)." made on p. 1010, line 4.*
- *A priori the CCNC delivers via the monodisperse activation spectra the normalized form of the hygroscopicity distribution. In this case it is possible to infer the correct absolute values of the unnormalised form from the CPC data. However, it is much easier to get rid of concentration units immediately by directly using activated fractions for inferring the hygroscopicity distribution functions.*
- *Hygroscopicity distributions are an intensive quantity. Therefore it is natural to use the normalised form of the hygroscopicity distributions. Absolute concentration values become only relevant, when it comes to calculating total CCN number concentrations from size dependent hygroscopicity distribution data from a HTDMA or CCNC combined with size distribution data from an SMPS. For this calculation, it is natural to have the information on absolute particle concentrations in the CN number size distribution (an extensive property), while using the normalised form of the hygroscopicity distribution to describe the mixing state (an intensive property). See also main item 4 for my request to provide the equations for this calculation.*
- *Reporting unnormalised hygroscopicity distributions with absolute concentration values is very susceptible to errors because units are often ambiguous (see main item for an example from within this manuscript). A typical error is a factor of ln(10) in absolute values (from using ln instead of log). The authors actually state that "we apply the same terminology and formalisms as used by Seinfeld and Pandis (2006)." However, the latter uses ln, whereas log is used in this study.*

Responses and Revisions

We agree with Martin and use only the normalized definitions in the revised manuscript.

Comments and suggestions:

4. For completeness I suggest that equations are added, which describe how the total CCN concentration at a given SS can be obtained from measured number size distribution data (SMPS) combined with a complete set of size-resolved kappa distribution data (HTDMA or CCNC). These equations are readily obtained by adapting equations (2) and (3) from Kammermann et al. (2010) (i.e. replace GFPDF by kappa-PDF, GFcrit by kappacrit, etc.).

Responses and Revisions

Nice suggestion, we add the following new equation:

Page 10 line 271-276:

$$N_{\mathrm{CCN}}(S, D_{\mathrm{d}} \to \infty) = \int_0^{\infty} n(D_{\mathrm{d}})(1 - H(\kappa_{\mathrm{c}}(S, D_{\mathrm{d}}), D_{\mathrm{d}}))dD_{\mathrm{d}} \qquad (33)$$

Comments and suggestions:

5. In general, and especially for the above request it is necessary to explicitly indicate which parameters are size dependent, i.e. always write NCCN(Dp), NCN(Dp) κ_{cri}(Dp), etc. (SS dependence may also be added explicitly). This may seem tedious and an unnecessary complication of the equations. However, it is to be remembered that the dependencies of parameters on other variables is by far not always obvious for those, who have not derived the equation on their own. Omitting these dependencies can easily lead to errors if such incomplete equations are used by other groups in their studies.

Responses and Revisions

We took this suggestion and always included the dependence of variables.

Comments and suggestions:

6. The notation is ambiguous: "n" is used for both n(κ) and n(Dw), while n(Dw)/=n(κ(Dw)). The same applies to N(κ) and N(Dw).

Responses and Revisions

To avoid such ambiguity, we adopted new symbols 'H' and 'h' for normalized hygroscopic distribution and used 'N' and 'n' for particle size distribution only.

Comments and suggestions:

7. The units of N_{CN} are not unambiguously defined. It can be concluded from equations 3 and 6 that NCN is meant to be NCN=ˆnlog CN(Dp)= d ˆNCN dlogDp (Dp), where ˆN CN is the cumulative CN number size distribution, i.e. ˆNCN(D_p) is the total number concentration of particles with diameter smaller than D_p, and d ˆNCN/dlogDp (Dp) is one common way of describing particle number size distributions. The same is true for the units of NCCN. The definition of NCCN and NCN given in Table 2 is definitely too sloppy: "The number concentration of CCN (CN) in one size bin". For an experimentalist it would be much more natural to interpret this definition as "CCN (CN) number concentration measured with the CCNC (CPC) behind the DMA", which also has the unit of an inverse volume, as indicated in Table 2 for NCCN and NCN. It is very easy to show that this interpretation is different from the correct one: NCCN and NCN would then become dependent on the flow ratio set in the DMA. Thereby equation 6 would become inconsistent because the far left and far right part would change with changing flow ratio, while the centre part remains constant.

Responses and Revisions

We clarify the definition of N_{CN} and N_{CCN} and indicate their dependency in the revised manuscript.

Page 7 line 185-194:

"The cumulative size distribution functions of CCN and CN, $N_{\mathrm{CCN}}(S,D_{\mathrm{d}})$ and $N_{\mathrm{CN}}(D_{\mathrm{d}})$, are defined as the number concentrations of CCN (at S) and CN smaller than D_d, respectively (Sect. 2.1.2; Seinfeld and Pandis, 2006). Differentiation of $N_{\mathrm{CCN}}(S,D_{\mathrm{d}})$ and $N_{\mathrm{CN}}(D_{\mathrm{d}})$ for the dry particle diameter D_d yields the corresponding PDFs of the CCN and CN size distributions: $\partial N_{\mathrm{CCN}}(S,D_{\mathrm{d}})/\partial D_{\mathrm{d}}$ and $dN_{\mathrm{CN}}(D_{\mathrm{d}})/dD_{\mathrm{d}}$."

Comments and suggestions:

8. I suggest to use slightly different notation in order to make things unambiguous and closer to common notation.

- *Use N_{CN}(Dp) and N_{CCN}(Dp) for the cumulative number size distributions of CN and CCN, respectively.*
- *Use nlog CN(Dp):= NCN dlogDp (Dp) and nlog CCN(Dp):= NCCN dlogDp (Dp) for the number size distribution of CN and CCN, respectively.*

• *Use mCN and mCCN for the number concentration of CN and CCN, respectively, measured behind the DMA during a monodisperse CCN measurement. You may think of a better symbol than m but I do not recommend to use N, because the latter is commonly used for the cumulative size distribution function.*
• *Use* a_F *(SS,Dp)=mCCN(SS,Dp)/mCN(SS,Dp) for the activated fraction.*
• *Use c(kappa) for the normalised hygroscopicity distribution. You may think of a better symbol than c but I do not recommend to use n_. "n" is commonly used for number related extensive properties, whereas the hygroscopicity PDF is an intensive property.*

Responses and Revisions

We do appreciate Martin's stimulating comments and make the following revisions:

- Use $N_{CN}(S,D_d)$ and $N_{CCN}(D_d)$ for the cumulative number size distributions of CN and CCN, respectively (Page 7 line 185-194).
- Use $\partial N_{CCN}(S,D_d)/\partial D_d$ and $dN_{CN}(D_d)/dD_d$ for the PDF of CCN and CN distribution (Page 7 line 185-194).
- Use $\Delta N_{CCN}(S,D_d)$ and $\Delta N_{CN}(D_d)$ as the number concentration of CN and CCN (Page 7 line 195-203).
- Use $\frac{\partial N_{CCN}(S,D_d)}{\partial N_{CN}(D_d)} = \left(\frac{\partial N_{CCN}(S,D_d)}{\partial D_d}\right) / \left(\frac{dN_{CN}(D_d)}{dD_d}\right)$ as the activated fraction (Page 7, Eq. 20).
- Use $H(\kappa, D_d)$ as cumulative *h*ygroscopicity distribution function (CDF); and $h(\kappa, D_d)$ as *h*ygroscopicity distribution function (PDF). These functions are always normalized.

Comments and suggestions:

9. It should be briefly mentioned with suitable reference to existing literature that multiple charges are always a potential issue for monodisperse measurements and how this can be addressed. Furthermore, is it possible to state whether either the D-scan or the S-scan mode is to be preferred when it comes to correction of multiple charge effects?

Responses and Revisions

We mentioned it and added references in the revised manuscript:

Page 10 line 281-284:

“The experimental uncertainties depend on various factors like instrument calibration, counting statistics, correction factors, and data inversion techniques (counting efficiency, electric charge, DMA transfer function, particle shape, etc.; Rissler et al., 2006; Rose et al., 2008; Swietlicki et al., 2008; Massling et al., 2009; Mikhailov et al., 2009; Kammermann et al., 2010; Snider et al., 2010).”

For the two scanning approaches, we added more discussions:

Page 9 line 237 - 271 and a new Fig.6:

“In principle, the two methods are equivalent with regard to probing the surface … because many of the recently reported size-resolved CCN field measurements used this approach (varying D_d at a constant S).”

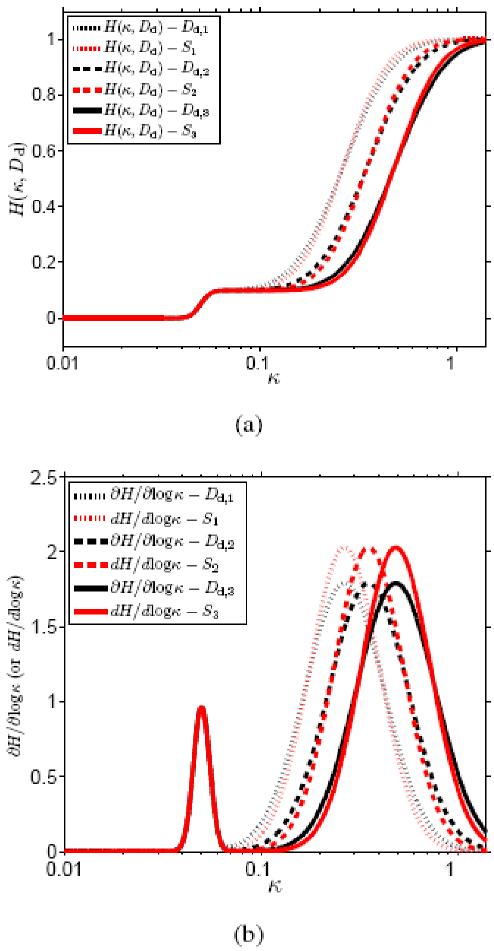

Fig. 6. Cumulative particle hygroscopicity distributions, $H(\kappa, D_d)$ (panel-a), and corresponding logarithmic probability distributions, $\partial H(\kappa, D_d)/\partial \log\kappa$ or $dH(\kappa, D_d)/d\log\kappa$ (panel-b), for the model aerosol of Case C obtained by method I (“S scan” at $D_{d,1}$, $D_{d,2}$ or $D_{d,3}$) and method II (“D_d scan” at S_1=0.86%, S_2=0.26% or S_3=0.067%).

In the current paper, we were still using the correction method proposed by Rose et al., 2008. But we are working on developing a new correction method for multiple charges and other uncertain factors.

Comments and suggestions:

10. It should be emphasized that raw GF distributions measured by a HTDMA must be inverted in order to obtain a valid GF-PDF or kappa-PDF. The least thing to be done with the raw HTDMA data is to correct for the growth factor dependent detection probability. Otherwise the kappa-PDFs derived from HTDMA data will be systematically biased towards the particles with higher kappa-values. Statements such as "From Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA) measurement data, N(kappa) can be directly derived by solving the kappa-Köhler model equation." should be corrected accordingly (see abstract, section 2.2, etc.).

Responses and Revisions

Yes, the HTDMA data need to be inverted and was inverted in our paper. We clarified it in the revised manuscript:

Page 6 line 159-162:

"The HTDMA calibration and data inversion accounted for the counting efficiency of the condensation particle counter (CPC) as well as for the transfer function of the DMA. Further details about the measurement campaign, techniques and conditions are given by Massling et al. (2009)."

Comments and suggestions:

11. State of the art approaches for acquiring D-scan and S-scan data with a CCNC should be referenced (e.g. Moore and Nenes, 2009; Nenes et al., 2010).

Responses and Revisions

The two papers have been included in the revised paper, but Nenes et al., 2010 has been changed to Moore et al., 2010.

References:

Moore, R. H., and Nenes, A.: Scanning flow CCN analysis – A method for fast measurements of ccn spectra, Aerosol Sci. Technol., 43, 1192–1207, 2009.

Moore, R. H., Nenes, A., and Medina, J.: Scanning Mobility CCN Analysis – A method for fast measurements of size resolved CCN distributions and activation kinetics, Aerosol Sci. Technol., doi:10.1080/02786820903289780, 2010.

Rose, D., Gunthe, S. S., Mikhailov, E., Frank, G. P., Dusek, U., Andreae, M. O., and P¨oschl, U.:

Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment, Atmos. Chem. Phys., 8, 1153–1179, 2008.