

Notes: Line numbers refer to the original document, and may have changed in formatting.

Comments from Referee #2

While the data and conclusions are interesting and the study timely, I do have significant concerns related to the manuscript and find that it needs major revision. In particular the reference for the error treatment (Irwin et al. 2010) is not available and the description of the error treatment in the current manuscript is inadequate. The manuscript is difficult to read; the notation is not always well explained and should be checked for consistency. I have a number of suggestions and comments which I hope will be helpful to the authors in improving the manuscript.

We'd like to thank the referee for their useful comments and understand their concerns with the manuscript relating to the treatment of error propagation and consistency of terminology within.

To address this concern, we have removed all references to *Irwin et al. (2010)*, and have expanded on the treatment of measurement uncertainty and propagation of errors in both the main text and supplementary material.

Major Comments:

A correct error treatment and propagation is an essential element of this reconciliation study, and the error treatment has been expanded upon in the text in addition to the supplementary material and figures. We have put the majority of the error propagation description into the supplementary material so as to not detract from the focus of this paper.

The reference for Jones et al. (2010) has been correctly assigned.

Abstract: *It says that hygroscopic growth factors were measured and critical supersaturating simultaneously derived – this is confusing – does “derived” here mean based on the GF’s or on measurements using a ccn-counter?*

“Derived” here means that the critical supersaturations were based on measurements of the number of activated droplets measured as a function of size using the DMPS-CCNc combination of instruments. Critical supersaturation is not directly measured by any instrument and so is a derived product. However, for clarity, ‘critical supersaturation simultaneously derived’ has been changed to ‘CCN activity measurements [made]’, and we have amended the abstract for clarity:

Aerosol physical, chemical and hygroscopic properties were measured in a range of airmasses during COPS (Convective and Orographically-induced Precipitation Study) ground-based in June and July of 2007 at the Hornisgrinde mountain site in the Black Forest, Southwest Germany. Non-refractory aerosol composition was measured with an Aerosol Mass Spectrometer, simultaneous to hygroscopic growth factors at 86% relative humidity and CCN activity measurements for particles of dry (< 20%) diameters 27 to 217 nm, with particle water uptake exhibiting substantial variability with time and with particle size.

Variability in the measurements of hygroscopic growth factor and critical supersaturation for particles of similar sizes indicates significant compositional impact on particle water affinity. Critical supersaturation prediction using a single parameter hygroscopicity approximation derived from measured HTDMA mean growth factors deviate, beyond measurement uncertainties, from critical supersaturations derived from CCN measurements. These led to differences averaging around 35% in the number of CCN (N_{CCN}) for the most reliable measurements depending on averaging methodology, often very much larger for individual time periods. This indicates aspects of water uptake behaviour unresolved in this experiment by the single parameter representation which, depending on its origin, may have important consequences on its generalised use.

Page 17075 line 21: *“The Köhler equation can be . . .” This is a very long and complicated sentence. Could be written more clearly.*

This sentence has been split into two to aid readability:

“The Köhler equation can be envisaged as the competition between two effects, namely the Raoult effect and Kelvin effect. The Raoult effect is defined by the water activity and drawing water into the growing droplet by virtue of the soluble material therein. The Kelvin effect is defined by the resistance to growth resulting from the increased saturation vapour pressure of water with increasing curvature of smaller particles by virtue of the energy associated with the creation of the droplet surface.”

Page 17076: *. . .it has been assumed that they may play a role in determining cloud activation (Abdul-Razzak and Ghan, 2004) – this has been shown before 2004 and it would seem appropriate to cite a more original reference.*

Reference changed to (e.g. Novakov and Penner, 1993; Saxena et al., 1995; Shulman et al., 1996; Abdul-Razzak and Ghan, 2004).

The first part of page 17076 (lines 1-19) *is not well structured and difficult to read and I suggest it be re-written. For example: “such an effect would results in an increase in the number of CCN” – compared to what?*

We understand that some of this paragraph was written in a passive manner, and as such was rather non-specific.

We have changed: “it has been assumed that they may play a role in determining cloud activation (e.g. Novakov and Penner, 1993; Saxena et al., 1995; Shulman et al., 1996; Abdul-Razzak and Ghan, 2004). If it were to occur, a change in surface tension would play a more important role as the saturation ratio increases (Wex et al., 2008),”

to:

“it has been assumed that organic components may play a role in determining cloud activation (e.g. Novakov and Penner, 1993; Saxena et al., 1995; Shulman et al., 1996; Abdul-Razzak and Ghan, 2004). A change in surface tension would play a more important role as the saturation ratio increases (Wex et al., 2008), though it might be more likely that some other instrumental or physical reason is responsible for discrepancies in reconciliation studies such as this.”

Page 17078: *What sizes of PSLs were used for calibrating the DMAs? What kind of bubble flow meter was used to calibrate flows?*

A Gillibrator bubble flow meter was used. PSL sizes used were 81 ± 2.7 nm, 199 ± 6 nm, 299 ± 6 nm and 499 ± 5 nm.

Page: 17078: *could the 60 s residence time between the humidifier and the second DMA course evaporation of some of the aerosol mass?*

Though the 60 s residence time between the humidifier and the second DMA could cause some evaporation of some of the aerosol mass, it is possibly more likely that there are larger evaporative losses in the drying section of the instrument pre-humidification. The evaporative loss of some of the aerosol mass is dependent on the saturation ratio of the semi-volatile components of the aerosol. As water vapour condenses onto the particle in the humidification section, the saturation ratio of the semi-volatile components decreases leaving fewer soluble particles to evaporate to the gaseous phase. A paragraph has been added at the end of the

discussion section, broadening the discussion, in light of the comments from both reviewers.

Page 17079: *To help the reader it could be explained how the data measured at RH=84-88% were corrected to 86% RH. Line 1-2: “small changes in measurement” – what kind of small changes are addressed here? To help the reader the concept of growth factor probability distribution should be explained in the text.*

Equation S1 and additional text has been included in the supplementary material to better explain the RH correction. $p(GF)$ refers to the probability distribution of the aerosol particle having a specific growth factor, and this has been added to the text. Small changes in measurement refers to changes in all measured parameters, i.e. RH, D_0 , Temperature, flow, number...

In the figure caption (fig 1) it is called growth factor probability density – please use consistent notation.

$p(GF)$ is now used to denote the hygroscopic growth factor probability distribution in all cases.

Experimental: *Was the aerosol dried before entering the DMA? – if so, to which relative humidity? Please explain why was the CCC-counter switched between polydisperse and mono-disperse aerosol? It says in the text that the length of the sample lines from DMA to CPC and CCNC respectively matched – was the sample flow the same in the two instruments? Please provide information about the flow rates through the DMA and through the CPC and CCNC. It must be defined better what is meant by ScD0 and D50S analysis.*

Updated Sections 2.2 and 2.3. The aerosol was dried before entering the DMA, to under 20% RH. The CCNC counter switched modes of operation due to the separate CPC and logging software (alongside the CCNC), sharing the DMA of the DMPS, which had a separate CPC and logging software. The text has been updated to include the sample flows, which were measured daily with a Gillibrator bubble flow meter. “All sample flows were ensured to be the same and were calibrated and checked daily with a bubble flow meter.”

Page 17080: *“The D50S analysis has a smaller associated fitting error resulting from the increase in the number of data points used in each sigmoidal fit” - what does this mean?*

Sections 1.1 to 1.3 and Figure S1 in the supplementary material should help to clarify the updated explanations in the main text. Each supersaturation was measured for 10 minutes, though the first 3 minutes were not used in data processing to ensure temperatures were stable in the column. Section 3.3: The mean of the hygroscopic growth factor is at the same temporal resolution as $p(GF)$, i.e. 1 hour.

If I understand the authors do two things: 1) Plot CCN/CN versus supersaturation (five data points) at a fixed diameter, find D_{cD0} 2) Plot CCN/CN versus dry particle diameter (20 datapoints) at a fixed supersaturation, find $D_{50,S}$. If this is the case this should be described more clearly in the text and examples of the two types of plots should be shown to give a more intuitive idea about the quality of the data. The D_{cD0} based on only five data points must be very uncertain? Also how long time was the CCN-counter measuring at each supersaturation and how long time was allowed for obtaining temperature equilibrium when changing supersaturation ?

Supplementary material and main text should now be easier to follow and provides much more information on the differences between S-step and D-step analysis:

“This function [the sigmoid function shown previously] is used to derive both $D_{50,S}$ and $S_{c,D0}$ for CCNC data. An example of the sigmoidal fitting to D-step and S-step interpreted data is presented in Figure S1. The fitting algorithm outputs a standard error of the x-axis value at $y = 0.5$. This is the error propagated through further calculations of quantities such as D_{thres} and N_{CCN} . S-step analysis is more sensitive to the relative positions of the data as there are only 5 data points (Fig S1a).

Fitting D-step interpreted data with the sigmoidal function results in fit approaching a step function (Fig S1b).”

Page 17081: “resulting in broad agreement with the integrated submicron volume time series from the DMPS “ – this should be explained better.

This has been reworded from:

“The collection efficiency used for the COPS data was 0.5, which is consistent with results from laboratory (Matthew et al., 2008) resulting in broad agreement with the integrated submicron volume time series from the DMPS.”

to:

“The collection efficiency used for the COPS data was 0.5, which is consistent with results from laboratory (Matthew et al., 2008) resulting in broad agreement with the integrated submicron volume time series from the DMPS (i.e. within 20% using an organic density of 1.4 gm^{-3} .”

Page 17083: the definition of cloudy and not cloudy periods is not clear and should be explained better. Explain the notation NC1, NC2, CP3 etc

Changed text to read: “‘Cloud periods’ are denoted ‘CP’ and ‘No-cloud’ periods denoted ‘NC’. Jones et al. (2010) have further detailed the meteorological conditions with the use of cloud camera data for their analysis.’.

3.3 This section is difficult to read – in particularly the authors should specify how averaging was done – with respect to what over which time?

The averaging refers only to the mean of the $p(GF)$, providing a single mean growth factor for any given time. It is not a temporal average.

Page 17086, line 12: what is “low number”?

The ambiguous “low number” now reads “low number concentrations (averaged number concentration of less than 5 particles detected at each D_0)”

Page 17086: the use of the word “calculated” is confusing – these are based on measurements with the ccn-counter?

Changed ‘ S_{c,D_0} calculated’ to ‘derived S_{c,D_0} ’.

Page 17087: Lines 9-10, It says that 300 nm was above the measurement range for both the HTDMA and the CCNc during this experiments – but in Figure 2 the diameter goes up to 600 nm?

This has been changed to read: ‘Particles over 100 nm have an increased organic to sulphate content with a peak at around 300 nm which was above the dry diameter range for HTDMA growth factor measurements and the derivation of critical supersaturation from CCNc measurements during this experiment (see Fig. S4 in supplementary material). Though $F_A(S, D_0)$ data exists for dry diameters above 300 nm, it is not possible to derive S_{c,D_0} from this data, as the fraction of aerosol activated is almost always over 0.5 at the lowest S_{set} .’

Line 19: for the surface tensions different from water – it should be mentioned that surfactant partitioning is neglected.

Added ‘neglecting surface-to-bulk partitioning’.

Page 17088 and figure 4: Could some of the discrepancy between model and experimental data lie in the calibration of the ccnc and HTDMA? For the ccnc the authors apply a dT dependent calibration factor over the range of supersaturations 0.11 to 0.8 %. Was the HTDMA only calibrated with ammonium sulphate of 150 nm? The measurements for ammonium sulphate for a range of dry particle sizes should be shown in figure 4 to compare with the theoretical values.

As the reviewer has indicated, the CCNc was calibrated with ammonium sulphate and the S_{set} calculated through the application of a dT dependent correction factor. The HTDMA was also calibrated using Ammonium Sulphate. The theoretical line in the plot therefore, by definition, corresponds to the values that the two instruments measure.

Page 17089, Lines 16-19: as far as I can see the kappa values discussed are the same within errors at the different organic:sulphate ratios.

We thank the reviewer for bringing this to our attention, and have amended the text accordingly:

“Though the mean κ for both CCNc and HTDMA data appear to vary ($\kappa_{sc} = 0.292 \pm 0.128$, $\kappa_{GF} = 0.181 \pm 0.056$) with increased relative sulphate contribution, possibly indicating a slightly more hygroscopic aerosol than when the organic:sulphate ratio is high ($\kappa_{sc} = 0.283 \pm 0.069$, $\kappa_{GF} = 0.142 \pm 0.036$; Tables 2 and 3), the variability of κ is too large to draw any firm conclusions.”

Page 17090: I agree with the comment by B. Ervans. Figure S4 should be better explained. Why are only two data points included?

We thank B Ervans for the comment, and have changed CDNC to N_{CCN} .

As the critical supersaturations of the aerosol are not known *a priori* to measurement, a fitting function cannot be applied to the data. As such, the best estimate is to fit a straight line between the two points either side of the zero line, to find the intercept is where $D_0 = S_{set}$, defining the physical threshold diameter for activation. Figure S5 is an illustration of the procedure that is applied to the whole dataset.

Figure 1: It is confusing that red is the high number of particle counts and also the average growth factor. I would suggest making the average growth factor white or some other color. What are the normalized counts? They are larger than one? Figure caption: what is the criteria for saying that the GF is “well represented” by the mean growth factor. It is difficult to see that there is an increasing prominence of bimodality with increase of size – this could be shown better I think in a separate figure with some examples.

This figure now has a black line for the mean, which should be clearer for readers. Jones et al. (2010) additionally show HTDMA growth factor data and also discuss the hygroscopic modes. The legend has been adjusted, as the colour scale is normalized to the particle counts in the HTDMA, given by the colour scale of $p(GF)$. The majority of the peak growth bin data falls within 10% of the mean growth factor, and is therefore mostly monomodal and well represented by the mean. A version of Figure 1 focussing on periods NC2 through NC3 is now presented in the supplementary Figure S6, to show better the increasing bimodality at larger dry diameters, and the proximity of the mean to the main hygroscopic mode in the $p(GF)$.

Figure 3: The notation is not consistent with the text: S_c – should it be S_{c,D_0} ? Why is the color scale continuous when five discrete supersaturations were measured??

S_c has been changed to S_{c,D_0} to aid readability. The scale is continuous as the critical

supersaturation is not the supersaturation measurement, S_{set} , rather the derived critical supersaturations, i.e. the results of sigmoidal fits to $F_A(S, D_0)$ vs S_{set} .

Minor: Page 17082 line 11: *I think there is a 0 missing in GFD, RH? (GFD0, RH)* **Page 17087:** *line 14 described → describe* **Page 17087, Line 26:** *Parenthesis after Fig 4 should be removed.* **17095, line 21:** *instrument instrument uncertainty (remove one “instrument”)*

The minor corrections have been made in the manuscript.