

Dear Prof. McFiggans,

please find attached our response to reviews and the revised manuscript for the HCCT-2010 special issue. We answered all arose questions with care and to our best knowledge. We marked the changes or additions in the manuscript text in bold for easy recognition.

We thank you for your work dedicated to our manuscript.

Best regards,

Silvia Henning

Answers to interactive comments on “Influence of cloud processing on CCN activation behaviour in the Thuringian Forest, Germany during HCCT-2010” by S. Henning et al.

We would like to thank both referees for the time invested in reviewing our manuscript. We highly appreciate their comments and hints for improving the paper. In the following we will address all comments and show how we changed the paper accordingly. The reviewers are cited in italic. We attached the changed manuscript text as pdf, where we highlighted the changes in the text in bold.

Answers to Anonymous Referee #1

The authors present two different methods for estimating the error in kappa, and each is based on different estimates of the uncertainty in set supersaturation. The first uses the accuracy in SS derived from repeated calibrations: presumably these were done as part of a separate study (Gysel and Stratmann, 2013), in which case what are the results of the calibration for the present study? The second method describes the error in SS as Gaussian with certain values of standard deviation, and applies Monte Carlo simulations. Could the authors explain where this assumption, and these values of standard deviation, comes from? It is not clear to me why the second approach is better than the first as the first uses an experimentally derived uncertainty in SS, and I would like the authors to please clarify this. As the authors point out, however, the main conclusion has already been tested by rigorous statistical methods, and the choice of error on kappa does not seem to affect this.

Our answer:

You are correct; the calibration was not explained clearly enough and we have improved the explanation. The second method also uses SS values previously derived from repeated calibrations. The assumption of modelling the SS uncertainty by a Gaussian distribution is based on previous experimental results (repeated calibrations) showing that the error in instrumental SS values given by the CCNC is normally distributed. We have observed that the uncertainty of these instrumental SS values with 95 % confidence level is ± 0.014 % for supersaturations ≤ 0.2 % and ± 0.027 % for SS=0.4 %. These uncertainties are absolute values, i.e. SS = (0.1 \pm 0.014) %. According to the properties of the Gaussian distribution, 95 % confidence

level corresponds to 1.96 standard deviations, in which case one standard deviation (σ) is 0.00714 % for $SS \leq 0.2$ % and 0.01429 % for $SS = 0.4$ %.

As an answer to your second question why the second approach to estimate the error in kappa is better, we added the following paragraph in the text:

Using maximum absolute error is a bad way of representing a Gaussian distribution, and since we know that the error in SS is Gaussian, the original error bars are a crude approximation. By assuming a Gaussian distributed SS error we are able to calculate the uncertainty distribution of kappa (by Monte Carlo sampling), and from this distribution it is easy to calculate percentiles with which to represent error bars at desired confidence level. Percentiles, e.g. 95 % confidence intervals are a more correct way to represent the uncertainty in kappa than the maximum absolute error.

Changed manuscript text: Inserted the sentences in **bold**. (also corrections)

second paragraph in section 3.1

In Fig. 3a and b the results are illustrated. The error bars were calculated by assuming a maximum absolute error in SS of $\pm 0.02\%$ for $SS = 0.2\%$ and assuming a 10% relative uncertainty for $SS > 0.2\%$ (Gysel and Stratmann, 2013), and applying Eq. (2) to calculate kappa. Due to the ~~asymmetric~~ **nonlinear** relation between SS and kappa ~~also~~ the error bars are asymmetric and give the maximum uncertainty in kappa. The increase in kappa after the cloud passage in the FCE is obvious, whereas in the NCE the data fall together on the 1 : 1 line. However, the observed effect is within the measurement uncertainty – especially for the lower supersaturations. Therefore, we tested the statistical significance of the change in critical diameters (and thus kappa values) between the stations during FCE and NCE, and re-estimated the uncertainty of kappa by modeling the instrumental error in supersaturation **by a Gaussian distribution**.

third paragraph in section 3.2

Next, we estimated the uncertainty distribution of κ with Monte Carlo simulations. **We have previously observed that** the instrumental supersaturation error of the CCNc is Gaussian, with standard deviations of 0.00714 for 0.07 %, 0.1 % and 0.2 % supersaturations and 0.01429 for 0.4 % supersaturation. **These standard deviations are obtained from repeated calibration results showing that with 95 % confidence level the absolute uncertainty for supersaturations ≤ 0.2 % is ± 0.014 % and for $SS = 0.4$ % the uncertainty is 0.027 %.** **The 95 % confidence level corresponds to 1.96σ , from which we can derive the aforementioned standard deviations.** However, due to the nonlinear relationship between κ and the critical diameter, the uncertainty distribution of κ is non-Gaussian. The distribution of κ is simulated for each data point separately by drawing 100 000 random samples from a Gaussian supersaturation distribution ($\mu = 0.07$, $\sigma = 0.00714$) and using Eq. (2). An example of a simulated κ distribution is presented in Fig. 5, showing the 2.5, 25, 50, 75, 97.5 and 100th percentiles. All the analyses were done using R statistical software (R version 2.15.3, 2013).

By applying this statistical approach to the data, it is possible to present more **realistic** error bars. **Using maximum absolute error is a bad way of representing a Gaussian distribution, and since we know that the error in SS is Gaussian, the original error bars are a crude approximation. By assuming a Gaussian**

distributed SS error we are able to calculate the uncertainty distribution of kappa (by Monte Carlo sampling), and from this distribution it is easy to calculate percentiles with which to represent error bars at desired confidence level. Percentiles, e.g. 95 % confidence intervals are a more correct way to represent the uncertainty in kappa than the maximum absolute error. Figure 6a gives single κ values at the upwind station compared to the κ at the downwind station during FCE. The error bars presented in the figure are the **95 % confidence intervals** calculated from Monte Carlo simulations as explained above. All κ values derived for the downwind station are higher than those at the upwind station. The same analysis was again done for the NCE periods (Fig. 6b).

In section 3.3, the authors state: “This estimate is supported by measurements results from other groups during HCCT-2010, who focused on the chemical and isotopic signature of the particle population”. Can the authors please elaborate on this and provide a reference (if available). Is this the “personal communications” referenced later in this section? The conclusions of this section are supported by these results, so it would be useful, if possible, to provide some numbers / figures. I appreciate the data belong to other research groups, so their inclusion may not be feasible, but I would like at least to see some better referencing, and an elaboration of what these results are.

Our answer:

The sentence “This estimate is supported by measurements results from other groups during HCCT-2010, who focussed on the chemical and isotopic signature of the particle population”. is referencing to the following paragraphs. Up to date, we cannot give a better referencing for the AMS measurements than personal communication / papers in preparation, because the findings are not yet published. The findings based on stable isotope fractionation are meanwhile published in ACP and are referenced correctly. We rearranged the paragraph, which hopefully clarifies that the sentence was meant to be an opening statement for the following paragraphs.

changed manuscript text:

This estimate is supported by measurement results from other groups during HCCT-2010, who focused on the chemical and isotopic signature of the particle population; **for example, sulfur isotope analysis of the particulate material was used to investigate the in-cloud production of sulfate.** Combined gas phase and single particle measurements allowed the dominating sulfate production sources to be identified (Harris et al., 2014). Direct sulfate uptake, through dissolution of H₂SO₄ gas and scavenging of ultrafine particulate, was found to be the most important source for in-cloud addition of sulfate to mixed particles (the most common particle type at HCCT-2010), while in-cloud aqueous oxidation of SO₂ primarily catalyzed by transition metal ions (Harris et al., 2013b) was most important for coarse mineral dust. **The isotopic analyses showed that the sulfate content of particles increased following cloud processing at HCCT-2010 by >10-40% depending on particle type (cf. table 5 in (Harris et al., 2014)).**

Minor corrections:

Page 1620, lines 24-26: “were achieved” appears twice in this sentence.

Page 1623, line 12: Remove either "the" or "another".
The above mentioned typos were corrected.

Answers to Anonymous Referee #2

"General comments

The manuscript presents a novel method to study cloud processing of aerosol particles, as well as interesting results from a study at Mt. Schmücke in Germany. Cloud processing significantly increase the CCN activity of aerosols. Ground-based cloud experiments are excellent in these type of studies, in order to collect sufficient amount of data to achieve results and conclusions of high statistical significance. Measurements were performed upwind and downwind of a cloud experimental site during periods both with clouds present at the mountain summit and without clouds. The manuscript is very well written, novel methods are used, relevant scientific questions are addressed, the results are sufficient to support the interpretations and conclusions, and substantial conclusions are reached. I recommend publication in ACP after minor revisions."

Thank you.

"Specific comments

Section 2 "Experimental design and setup": How is LWC measured?"

Our answer:

LWC is indeed an important measure in the FCE and NCE classification. It was measured by applying a Particulate Volume Monitor (PVM-100, Gerber Scientific Inc., Reston VA, Gerber, 1991).

added in section 2

LWC was measured by applying a Particulate Volume Monitor (PVM-100, Gerber Scientific Inc., Reston VA, Gerber, 1991).

"Section 2.1, page 1623, line 21: What is $\delta^{34}\text{S}$? Section 2.1, page 1623, lines 16- 23 (last paragraph of section 2.1): It is not describe how sulfur isotope analysis can be used to study cloud processing of aerosols. The paragraph need a few more sentences to describe the purpose of the described measurements."

Our answer:

Your are correct, the explanation how isotope analyses can be used for the cloud processing interpretation was missing. We improved the text concerning this, but we still did not want to explain all the details on isotope analysis in the manuscript as we used the data only as additional information to our CCN data.

$\delta^{34}\text{S}$ is a measure for the isotopic composition of a sulfur sample, given as the permil deviation of the ratio of a heavy isotope (^{34}S) to the most abundant isotope (^{32}S) in the sample compared to a standard, which is the international sulfur isotope standard, Vienna Canyon Diablo Troilite (V-CDT), which has a isotopic ratio of $^{34}\text{S}/^{32}\text{S} = 0.044163$. (e.g. Harris et al., 2012)

$$\delta^{34}\text{S}(\text{‰}) = \left[\frac{\left(\frac{n(^{34}\text{S})}{n(^{32}\text{S})} \right)_{\text{sample}}}{\left(\frac{n(^{34}\text{S})}{n(^{32}\text{S})} \right)_{\text{V-CDT}}} - 1 \right] \times 1000$$

with n the number of atoms.

Stable sulfur isotopes fractionate during reactions, so the isotopic composition of a product is not equal to the isotopic composition of the reactant. Fractionation factors can be characteristic for different reactions, and can be used to model and quantitatively assess the relative contributions of the major atmospheric SO₂ oxidation pathways on a regional and global scale (Harris et al. 2013).

Using previous measurements of sulfur isotope fractionation factors characteristic for different oxidation pathways (e.g. oxidation by OH, H₂O₂ or transition metal ion catalysis, Harris et al., 2012, Harris et al. 2013), the isotopic analyses made during HCCT-2010 allow dominant sulfate production pathways to be determined and resolved for different particle types, as described in Harris et al. 2014.

changed manuscript text, section 2.1

Combined scanning electron microscopy (SEM) and NanoSIMS measurements were used to determine **the isotopic composition of particulate sulfur samples ($\delta^{34}\text{S}$ fractionation factors) of the samples. Stable sulfur isotopes fractionate during reactions, so the isotopic composition of a product is not equal to the isotopic composition of the reactant. Using previous measurements of sulfur isotope fractionation factors characteristic for different oxidation pathways (e.g. oxidation by OH, H₂O₂ or transition metal ion catalysis, Harris et al., 2012, Harris et al. 2013), the isotopic analyses made during HCCT-2010 allow dominant sulfate production pathways to be determined and resolved for different particle types, as described in Harris et al. (2014).**

"Section 2.2, second paragraph (page 1624, lines 12-28): It is mentioned that the CCNc is either used to measure saturation scans or diameter scans. However, it is not clear if both methods are used in this study, or only one of them. A discussion of advantages and/or disadvantages of the two methods might also be relevant. I suppose both methods can be used to obtain the requested results. It seems that the sentence

*"The CCNc can be used either to measure saturation scans,...
, or to measure diameter scans,..."*

would be better. Also, if the authors have used only one method, the reasons why selecting that method would be interesting to know more about."

Our answer:

We state in that very paragraph in line 27, that we ran diameter scans in this study. The reason for running diameter scan was that this method allows faster scanning than changing the supersaturation with this type of a CCNc, and therefore time resolution of the single scans is higher. However, a change in the CCNc software allows also for fast supersaturation change by changing the flow through the CCNc (so-called SFCA, Moore and Nenes, AST, 2009). But this method was not yet available to us for the HCCT campaign.

However, as we confused the reader, we straightened the paragraph and left out the possibility of saturations scans as we didn't apply those.

Moore, R. H. and Nenes, A., Scanning Flow CCN Analysis - A Method for Fast Measurements of CCN Spectra, Aerosol Science and Technology, 43, 1192-1207, doi 10.1080/02786820903289780, 2009.

Changed manuscript text:

The CCNc was used to measure diameter scans for which the saturation is fixed and the dry particle diameter is varied. In this study we ran diameter scans for four fixed supersaturations (0.07, 0.1, 0.2, 0.4 %). The critical particle diameter D_c , the diameter at which 50% of the particles are activated at a particular supersaturation, is derived from such a diameter scan.

"Section 2.3, second paragraph (page 1626, lines 17-28 + page 1627, lines 1-2): Maybe you could mention that the correction method makes use of the particle number size distributions. It's indirectly mentioned, but could be more direct mentioned as an introduction."

Changed manuscript text:

The **performed multiple-charge correction is based on the measured number size distribution** and is described in detail in Deng et al. (2011): in brief, starting at larger sizes the number of possible multiply-charged particles at one size is calculated based on the charge equilibrium (Wiedensohler, 1988) and subtracted from the particle number at the corresponding smaller sizes. This is done for the whole N and $NCCN$ distribution from large to small particles.

"Section 3.2: I cannot follow all details in the statistical analysis, but I suppose it would be possible to reproduce the analysis following the described method."

Our answer:

We have clarified our explanations concerning the statistical analysis. Please see here also our answer to reviewer 1.

Changed manuscript text:

second paragraph in section 3.1

In Fig. 3a and b the results are illustrated. The error bars were calculated by assuming a maximum absolute error in SS of $\pm 0.02\%$ for $SS = 0.2\%$ and assuming a 10% relative uncertainty for $SS > 0.2\%$ (Gysel and Stratmann, 2013), and applying Eq. (2) to calculate kappa. Due to the ~~asymmetric~~ **nonlinear** relation between SS and kappa ~~also~~ the error bars are asymmetric and give the maximum uncertainty in kappa. The increase in kappa after the cloud passage in the FCE is obvious, whereas in the NCE the data fall together on the 1 : 1 line. However, the observed effect is within the measurement uncertainty – especially for the lower supersaturations. Therefore, we tested the statistical significance of the change in critical diameters (and thus kappa values) between the stations during FCE and NCE, and re-estimated the uncertainty of kappa by modeling the instrumental error in supersaturation **by a Gaussian distribution**.

third paragraph in section 3.2

Next, we estimated the uncertainty distribution of κ with Monte Carlo simulations. **We have previously observed that** the instrumental supersaturation error of the CCNc is Gaussian, with standard deviations of 0.00714 for 0.07 %, 0.1 % and 0.2 % supersaturations and 0.01429 for 0.4 % supersaturation. **These standard deviations are obtained from repeated calibration results showing that with 95 % confidence level the absolute uncertainty for supersaturations ≤ 0.2 % is ± 0.014 % and for SS = 0.4 % the uncertainty is 0.027 %. The 95 % confidence level corresponds to 1.96σ , from which we can derive the aforementioned standard deviations.** However, due to the nonlinear relationship between κ and the critical diameter, the uncertainty distribution of κ is non-Gaussian. The distribution of κ is simulated for each data point separately by drawing 100 000 random samples from a Gaussian supersaturation distribution ($\mu = 0.07$, $\sigma = 0.00714$) and using Eq. (2). An example of a simulated κ distribution is presented in Fig. 5, showing the 2.5, 25, 50, 75, 97.5 and 100th percentiles. All the analyses were done using R statistical software (R version 2.15.3, 2013).

By applying this statistical approach to the data, it is possible to present more **realistic error bars. Using maximum absolute error is a bad way of representing a Gaussian distribution, and since we know that the error in SS is Gaussian, the original error bars are a crude approximation. By assuming a Gaussian distributed SS error we are able to calculate the uncertainty distribution of kappa (by Monte Carlo sampling), and from this distribution it is easy to calculate percentiles with which to represent error bars at desired confidence level. Percentiles, e.g. 95 % confidence intervals are a more correct way to represent the uncertainty in kappa than the maximum absolute error.** Figure 6a gives single κ values at the upwind station compared to the κ at the downwind station during FCE. The error bars presented in the figure are the **95 % confidence intervals** calculated from Monte Carlo simulations as explained above. All κ values derived for the downwind station are higher than those at the upwind station. The same analysis was again done for the NCE periods (Fig. 6b).

"Section 3.3: Arguments are missing for the interpretations and conclusions. How is sulfur isotope analysis used to draw the conclusion on page 1630, lines 22-26? I suppose it's explained in Harris et al. 2014, but maybe a short description could be included here or in the last paragraph of section 2.1."

Our answer:

We improved the explanation on the stable isotope method in the experimental section and the argumentation in section 3.3.

Changed manuscript text:
experimental section:

Combined scanning electron microscopy (SEM) and NanoSIMS measurements were used to determine **the isotopic composition of particulate sulfur samples ($\delta^{34}\text{S}$ fractionation factors) of the samples. Stable sulfur isotopes fractionate during reactions, so the isotopic composition of a product is not equal to the isotopic composition of the reactant. Using previous measurements of sulfur isotope fractionation factors characteristic for different oxidation pathways (e.g. oxidation by OH, H₂O₂ or transition metal ion catalysis, Harris et al., 2012, Harris et al. 2013), the isotopic analyses made during HCCT-2010 allow**

dominant sulfate production pathways to be determined and resolved for different particle types, as described in Harris et al. (2014).

Section 3.3:

This estimate is supported by measurement results from other groups during HCCT-2010, who focused on the chemical and isotopic signature of the particle population; **for example, sulfur isotope analysis of the particulate material was used to investigate the in-cloud production of sulfate.** Combined gas phase and single particle measurements allowed the dominating sulfate production sources to be identified (Harris et al., 2014). Direct sulfate uptake, through dissolution of H₂SO₄ gas and scavenging of ultrafine particulate, was found to be the most important source for in-cloud addition of sulfate to mixed particles (the most common particle type at HCCT-2010), while in-cloud aqueous oxidation of SO₂ primarily catalyzed by transition metal ions (Harris et al., 2013b) was most important for coarse mineral dust. **The isotopic analyses showed that the sulfate content of particles increased following cloud processing at HCCT-2010 by >10-40% depending on particle type (cf. table 5 in (Harris et al., 2014)).**

"Technical corrections

Section 3, first sentence (page 1627, lines 4-5): Something is wrong in this sentence. Either the grammar is not correct, or maybe just a word is missing."

We added the missing word.

"Ideally, a fixed time difference of 20 min would **be** applied to compare upwind and downwind measurements, i.e. the measurement from the upwind station would be paired with a measurement from the downwind station, which was taken 20 min later."