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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Influence of cloud processing on CCN activation behaviour in the Thuringian Forest, Germany during HCCT-2010" *by* S. Henning et al.

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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. We attached the changed manuscript text as pdf, where we highlighted the changes in the text in bold.

Answers to Anonymous Referee ♯2

"General comments The manuscript presents a novel method to study cloud process-

ing of aerosol parti-cles, 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 ques-tions 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

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"Section 2.1, page 1623, line 21: What is $\delta^{34}S$? 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. $\delta^{34}S$ is a measure for the isotopic composition of a sulfur sample, given as the permil deviation of the ratio of a heavy isotope (34S) to the most abundant isotope (32S) 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 34S/32S = 0.044163. (e.g. Harris et al., 2012)

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

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 (δ^{34}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, H_2O_2 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 Dc, 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.

Changed manuscript text, 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 $\leq$ 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 the 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 κ (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 κ than the maximum absolute error. Figure6a 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 (δ^{34}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, H_2O_2 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 H_2SO_4 gas and scavenging of ultrafine particulate, **as well as in-cloud aqueous SO_2 oxidation by H_2O_2, were found to be the most important sources** for in-cloud addition of sulfate to mixed particles (the most common particle type at HCCT-2010). While in-cloud aqueous oxidation of SO_2 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.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/14/C2854/2014/acpd-14-C2854-2014-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 1617, 2014.