

Reply to Reviewer #3

This reply is formatted as follows:

Reviewer's comments

Authors' reply

Changes to Text

This study describes aerosol chemical properties measured from both droplet residues and interstitial aerosol particles. The principal aims of this work are to study the cloud processing, including the enrichment of aerosol particles within clouds from the uptake of different gas-phase species. This paper also addresses the role of different chemical species in the activation of cloud droplets. The study is very thorough with an impressive instrumental setup and a large number of statistically relevant cloud events. The paper, figures, and text are well prepared. However, I have some major concerns regarding the experimental approaches used to derive the conclusions made in this manuscript.

General comments:

This experiment, the HCCT was intended to understand how aerosols are activated into clouds as well as the impact of different cloud processing on cloud properties. As outlined in Tilgner et al., (2014), this study was designed in such a way as to have three well equipped stations before, in, and after the formation of an orographic cloud. I would assume that combining measurements from these three stations would have made this study much more robust, rather than only comparing in and out of cloud residues on the cloud top.

It is correct that three field sites were operational during HCCT, one upwind, one downwind, and one summit site. In the ACP special issue (http://www.atmos-chem-phys.net/special_issue287.html) already 11 papers are published dealing with various aspects of the study from all three stations. A paper focusing on comparison between upwind and downwind site, especially with respect to aerosol composition, is currently under preparation. The purpose of the study presented here is to compare cloud residual composition with simultaneously measured interstitial particle composition, which can be done only at the summit site. Additionally, we chose to include out-of-cloud data measured at the same site, in order to minimize uncertainties arising from instrumental differences that we would have to face when comparing the data from the upwind and downwind station to the summit site data.

1) One of my major critics is the lack of a clear discussion on the aerosol (CDR and interstitial) physical properties (size and number concentration). These factors play an essential role in the activation of cloud droplets and should not be separated from aerosol chemical properties. Aerosol size distributions should have been taken into account to provide a measure of aerosol activation diameter. It would have been interesting to investigate how this parameter (aerosol activation diameter) varied as a function of chemical composition. It would have been equally interesting to study the sampling efficiency of the CVI inlet through comparison of the total number of CDR particles (CPC/SMPS) with the total number of cloud droplets measured with the FSSP.

The focus of the present paper is not the activation of aerosol particle to cloud droplets. We focus on uptake of gaseous compounds (nitrate, ammonium and organics) by cloud droplets. We fully agree that activation diameter as a function of chemical composition is a very interesting topic and can be achieved by using the available SMPS data, but this is outside the scope of this paper. The size-resolved AMS data can not be used for such an analysis due to the low duty cycle of the size-resolved measurement mode of the AMS (see below). Size-

segregated cloud condensation nuclei (CCN) measurements from upwind and downwind station have been published by Henning et al. (2014), and particle hygroscopicity and CCN activity at the upwind site have been compared to their chemical composition by Wu et al. (2013).

The CVI sampling efficiency has been studied exactly as suggested by the reviewer, by comparing the number of residual particles counted behind the CVI (using a CPC) and the number of cloud droplets measured outside (using the FSSP).

This is already described in section 2.4 of our manuscript, but will add the FSSP and CPC for clarity:

"The enrichment factor of the CVI is given by the ratio of the air flow in the CVI wind-tunnel to the sample flow inside the CVI inlet. Since both quantities are measured, the enrichment factor can be calculated. The sampling efficiency of the CVI is determined by comparing the number of residual particles counted **by a CPC** behind the CVI and the number of cloud droplets measured outside **by the FSSP** and by comparing the LWC measured in the CVI sampling line and the LWC measured outside. Both the enrichment factor and sampling efficiency were provided as a function of time and have been applied to the data presented here."

See also reply to reviewer #1 on the question to the sampling efficiency.

a. In section 2.3, the authors state that there are SMPS measurements available, however unless I am mistaken I do not find any other reference to these measurements, either in the manuscript or in the supplementary material.

SMPS measurements have been conducted during HCCT by TROPOS, but these data are not subject of the present manuscript. We removed the SMPS from that sentence in section 2.3:

Particle size distributions of the interstitial aerosol particles and the cloud residuals were measured using optical particle counters (OPC, model 1.109 and 1.108, Grimm Aerosol Technik, Germany).

b. Figure S6 shows OPC size distributions measured behind the CVI and Interstitial inlet. The GRIMM instrument normally provides particle size distribution measurements from 300 nm up to > 10 microns. At 300 nm, all particles are expected to act as CCN. Therefore, these measurements are not useful to observe activation parameters of aerosol particles. I did not find any reference to this figure in the main manuscript.

We added the OPC size distribution for completeness to the supplement. We agree that the OPC data can't be used to observe activation parameters, but, as said before, this is not the topic of the present manuscript.

2) The papers main results are based on the comparison of interstitial aerosol particles and cloud droplet residues. These two "types" of aerosol particles are found in largely different size categories, with interstitial aerosol particles generally having diameters < 90 nm and CDR particles having diameters > 90 nm. It has been reported in a large number of studies that the contribution of organic aerosol particles increases as particles size decreases. Equally inorganic nitrates are often measured in larger particle diameters. Can the authors show that the increased organic compounds measured in the interstitial aerosol during cloud events are significant to the cloud event itself and that the concentrations (in the same size class) are different in the NCE?

The finding that organics are large in the interstitial is likely just due to the effect that the reviewer describes: Organics have larger mass fraction in smaller particles which are less effectively activated as CCN. It has been reported that "Size matters more than chemistry for

cloud-nucleating ability of aerosol particles" (Dusek et al., 2006). However, the lower hygroscopicity of organic compounds may play an additional role and lead to less activation of particles in the size range around and slightly above 90 nm when they have a higher organic content. But generally one would not expect that the interstitial aerosol composition is much different from the composition of the out-of-cloud aerosol in the size range below the activation diameter of the cloud.

It would be very valuable to perform a size-resolved analysis of the particles. However, the mass concentrations below approximately 100 nm are so low that the "PToF-mode" of the AMS (that allows for size-resolved analysis) is not able to provide data above the noise level. It has to be mentioned here that the duty cycle of the PToF-mode is by a factor of 50 lower than the normal "MS mode".

a. Page 7, Line 35: The authors state that the mass concentration of the interstitial aerosol is lower than that of the CDR. This would be expected since CDR particles are larger in diameter (hence more mass) than the interstitial aerosol.

Yes, this is to be expected, but it is necessary to mention it here, because for black carbon it is not the case, which surprised us because impactor data at the upwind site showed a large BC fraction in a size range above 400 nm (aerodynamic). But apparently these large BC particles were not activated (here composition appears to matter more than size!) and therefore show up in the interstitial aerosol. Unfortunately, no size-resolved BC data are available from the summit site.

b. Figure 4. It would be useful to see the significance of the difference between the interstitial and CDR composition, through comparison of the similar size fractions (< 90 nm (INT) and > 90 nm (CDR)) during NCE.

As explained above, it is not possible to evaluate the size resolved data for diameters smaller than around 100 nm.

3) Another concern is that the transmission efficiency of the aerodynamic lens used for Aerodyne products sample aerosol particles with "good" efficiency between ~90 nm and ~300 nm (Liu et al., 2007), however below (and above) these limits the transmission efficiency of the instrument decreases rapidly. One needs to take this transmission efficiency into account and also the implications that this may have on the quality of the AMS data at these lower diameters. Baseline errors will likely have an impact at these diameters so it is necessary to take precautions to ensure that measured aerosol compositions and concentrations at these small diameters are real and not just arbitrary noise.

Peter S. K. Liu, Rensheng Deng, Kenneth A. Smith, Leah R. Williams, John T. Jayne, Manjula R. Canagaratna, Kori Moore, Timothy B. Onasch, Douglas R. Worsnop, and Terry Deshler Transmission Efficiency of an Aerodynamic Focusing Lens System: Comparison of Model Calculations and Laboratory Measurements for the Aerodyne Aerosol Mass Spectrometer *Aerosol Science And Technology* Vol. 41 , Iss. 8, 2007

We fully agree. This is one of the reasons why a size-resolved analysis of the AMS data is not possible for small diameters. Therefore we can only report size-integrated data from the "MS mode". However, the observed differences between interstitial, cloud residual, and out-of-cloud particle composition can not be explained by the lens transmission limitations, thus the findings and conclusions of our paper are not affected.

4) A large part of this manuscript is focused on the enrichment of nitrate in aerosol particles after cloud processing. However, these conclusions were made through comparing CDR with NCE before, and in some cases, after the cloud event. If cloud processing was indeed used

to result in the enrichment of nitrate in particles, would one not expect to observe higher nitrate in aerosol particles once the cloud event has passed?

We do not expect that this is the case, because the effect is most likely reversible. We detailed our arguments in two sections of the manuscript: In section 3.2.1 we argued:

"...while in ambient air, dependent of the gas-phase concentrations of HNO_3 and NH_3 , the situation will be different and a larger part of the nitrate and ammonium may be released back into the gas phase. If the air after the cloud returns to the same temperature and relative humidity conditions as before the cloud, is it to expect that the overall equilibrium between particle phase NH_4NO_3 and gas phase NH_3 and HNO_3 will be equal 30 to that before the cloud, as long as no chemical processing of nitrate and ammonium occurs in the cloud phase."

In the summary we repeated this argument:

"In general, cloud processing will tend to evenly distribute nitrate and ammonium over the processed aerosol particles: At the same temperature and relative humidity after the cloud passage as before, it is to be assumed that the same equilibrium between particle-phase ammonium nitrate and gas phase nitric acid and ammonia as before the cloud is established. Thus, the absolute amount of particle phase ammonium nitrate should be the same after the cloud as before the cloud."

5) A constant correction efficiency (CE) of 0.5 was applied to all data. However, there are several periods (shown in Figure 2 a)) where the contribution of nitrate aerosol particles was greater than 25% to the total aerosol mass. In general, within the aerosol mass spectrometry community, it is recommended to apply a composition dependent CE as outlined in the manuscript Middlebrook et al., (2012). Middlebrook, A.N R. Bahreini, J. L. Jimenez, and M. R. Canagaratna (2012) *Aerosol Sci. Tech.*, 46:258– 271.

We have chosen to apply a constant collection efficiency of 0.5 for simplicity. We are of course familiar with the Middlebrook parameterization. But it must be said that the parameterizations by Middlebrook et al. are based on data sets with a combined uncertainty (2σ) of 45 %. There are a few time periods in our data set where the composition dependent CE calculated using the Middlebrook formula is significantly higher than 0.5, but it did not change a lot in the overall correlation between the mass inferred from SMPS and the sum of AMS and MAAP when it was tested.

Furthermore, many parameters used in our analysis are not affected by the CE value: Mass fraction (Fig 4), f_{44} , f_{43} (Fig 8, 9, 10), $\text{NO}^+/\text{NO}_2^+$ (Fig 11).

6) Cloud events listed in table 1 varied from 3 hrs up to 12 hrs. Air mass trajectories were used to verify that there was no change in air mass properties, however could there be more robust criteria used to classify these cloud events. Could the authors incorporate the FSSP cloud droplet distribution and LWC measurements to evaluate whether the cloud properties changed outside a certain limit. For example Fig. 12 shows the cloud droplet diameters and concentrations changing during the cloud event, this was accompanied also by a change in the LWC. How can the authors ensure that these changes in cloud properties were not accompanied by slight air mass changes, or entrainment of new aerosol types. This might influence the comparison with NCE. a. Likewise, how long a time period should be compared from the NCE data? It might not be judicious to include data from 24 hours prior to the measurements.

Cloud events were selected and defined based on robust criteria, as described in Tilgner et al. (2014). Coefficient of divergence (COD) analyses were performed using continuous measurements of ozone and particle concentration (49 nm diameter size bin). We do not want

to modify these cloud event times, in order to maintain comparability among the HCCT cloud studies.

For non-cloud events it was necessary to find times without clouds as close as possible to the respective cloud event. Only in the case of FCE11.2, the corresponding non-cloud event (NCE 0.8) was more than 24 hours apart from the cloud event itself.

Minor comments: The only mention of orographic clouds is in the title of this manuscript. Although, full details of the experimental design is included in Tilgner et al., some discussion of the importance and how these cloud events were verified as orographic should be included.

See also reply to reviewer #2:

A description of the cloud types is given in detail in other publications in the special issue on the HCCT campaign, e.g., Tilgner et al. (2014) or Roth et al. (2016). Therefore, we added only a brief description of the cloud to section 3.1.:

The whole time series of the cloud droplet number distribution measured by the FSSP is given in Figure S4. The 14 FCE are also indicated by the grey bars. These FCE were chosen based on certain criteria as detailed in Tilgner et al. (2014), focusing on connected flow conditions between the upwind, the summit and the downwind station. These conditions went along with stable south-west flow conditions, thus the clouds were mainly of orographic nature, however in certain cases the meteorological analysis revealed that the clouds were not purely orographic (FCE1.1, FCE2.1, FCE26.1). For details see Table 5 in Tilgner et al. (2014) and Table 1 in Roth et al. (2016).

Page 4, section "Analysis instruments" How was the aerosol dried prior to sampling in the interstitial aerosol?

The interstitial aerosol (and therefore also the out-of-cloud aerosol) was dried using a Nafion dryer. Humidity measured in the sampling line was below 35%. This was added so section 2.2 (Aerosol and cloud sampling at the summit site):

The air sampled by the interstitial inlet was dried using a Nafion dryer. Measured relative humidity in the sampling line behind the dryer was below 35%.

Page 13, Line 33: The authors mention that biogenic emissions could be a source of the higher OA measured at higher temperatures. Is there any evidence of biogenic emissions during these periods? Gas-phase measurements, lower than average BC concentrations, etc.

No, there is no evidence for biogenic emissions, only indications: The field site is surrounded by forest, and in the upwind direction there are no large cities. In the supplement to Roth et al. (2016) (<http://www.atmos-chem-phys.net/16/505/2016/acp-16-505-2016-supplement.pdf>) there is a map and a list of cities within a 50 km radius around the field site. Thus, the assumption of biogenic emissions is plausible but can't be proven.

Page 16, Line 29: What is the significance of these correlations? 99%, 95% and how is the 'significance' determined?

Significance was determined using both t-test and F-test (using Wavemetric's IGOR function "statslinearregression") with 95% confidence interval. All correlations but Graph 6 (NO₃ vs LWC in 2nd half of cloud) are significant.

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