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A. Roth, J. Schneider, T. Klimach, S. Mertes, D. van Pinxteren, H. Herrmann, and S. Borrmann, Aerosol properties, source identification, and cloud processing in orographic clouds measured by single particle mass spectrometry on a Central European mountain site during HCCT-2010, Atmos. Chem. Phys. Discuss., 15, 24419–24472, 2015

Reply to reviewer #2

This study presents the measurements from a field campaign where several on-line instruments were operating side by side. The focus of this paper is to characterize the chemical composition of aerosol particles measured by a single particle laser ablation instrument and determine how different aerosol species are activated into cloud droplets. Cloud droplet residues were analyzed using a counter flow virtual impactor (CVI). Aerosol chemical composition and size distribution are provided by a single particle laser ablation instrument (ALABAMA). This instrument is capable of generating both positive and negative spectra from individual particles and therefore has the unique feature of providing information of aerosol mixing state. Single particle spectra measured by the ALABAMA were classified using fuzzy clustering. This paper is well written and organized and I recommend it for publication. However, some additional information or discussion should be included.

We thank the reviewer for this positive rating of our manuscript.
In the following we answer the specific questions:

Was any attempt made to quantify the measurements from the ALABAMA using co-located instrumentation? How did the size distribution measured by ALABAMA compare with that of the OPC?

The ALABAMA size distribution is not representative for the ambient size distribution. The detection has its maximum between 550 and 600 nm, the ablation efficiency between 350 and 600 nm. The size distribution shown in Figure 3 can't be compared to the OPC size distribution. Thus, we report only the relative abundance of particles. The total number of particles detected by ALABAMA per time correlates rather well with the total number concentration measured by the OPC ($r = 0.72$), such that we can assume a representative sampling over the whole campaign time. But since the laser ablation method is not quantitative by nature of the ablation and ionization process (as we stated in section 2.1) we did not make any attempt to quantify the ALABAMA data.

CVI inlets can often lead to enrichment of aerosol particles. Has this CVI been validated to through comparisons with a whole air inlet (clouds particles +interstitial particles)/interstitial inlet set up? This information is not included in Mertes et al., 2005. More information on the flows and counter flows (and enrichment factors) of the CVI could be included in the discussion.

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. Typical values are around 7 (ranging between 4.6 and 11.3). The sampling efficiency of the CVI is determined by comparing the number of residuals counted behind the CVI and the number of cloud droplets measured outside 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 all quantitative instrumentation that was used in HCCT (for example the AMS, Schneider et al., manuscript in preparation).

For the ALABAMA analysis, however, this enrichment and sampling efficiency correction is not necessary, because we restrict the data evaluation and presentation to the relative abundance of particles.

Section 2.2: Can the authors provide more information on the types of clouds that were studied, and how the out of cloud periods were chosen? How are these out of cloud periods thought to be representative of aerosol particles activated into clouds, e.g include information on air mass trajectories and on wind direction?

Detailed information on the cloud type and meteorological conditions of each FCE is given in the supplement to Tilgner et al (2014). We added brief information on the cloud conditions to Table 1 and included a reference in section 2.2:

"Detailed information on cloud type and meteorological conditions of the individual FCEs is given in the supplement to Tilgner et al. (2014)."

The out-of-cloud periods were treated in different ways: For Figure 6 all available data from in-cloud and out-of-cloud were analyzed. This is described in section 3.2.

For the analysis presented in section 3.4, we selected air masses with comparable origins based on HYSPLIT back trajectories for in-cloud and out-of-cloud conditions. As an additional criterion it was required that the local wind direction at the Schmücke was constant. This is described in section 3.4 and Table 5.

The authors mention that after cloud processing, aerosol particles contain higher amounts of nitrate and sulphate. They mention that the increases in nitrate and sulphate particles will increase particle hygroscopicity and their ability to act as CCN. It is true that higher fractions of inorganic ions will increase the hygroscopicity of the aerosol particle, however given the size of the particles studied (> 200 nm) it is likely that they will be good CCN independent of their aerosol composition.

We agree, but there is no reason why the same cloud processing should not take place in all cloud droplets, and thereby also in cloud droplets that were activated by smaller particles that are just at the edge of the activation diameter. We added a statement to clarify this at the end of section 3.4:

"This process will occur in all cloud droplets formed from all CCN sizes and therefore influence also the CCN properties of aerosol particles smaller than analyzed here. For small particles that are in the size range of the activation diameter for a specific supersaturation the chemical composition plays an important role for the activation."

For the mineral particles (Section 3.2.4) why do the authors think that there is such a difference in activated aerosol composition? All particles of the sampled size should, according to theory, be activated into clouds. Chemistry of aerosol particles is not thought to play a role in the activation efficiency of aerosol particles with diameters > 200 nm (Duseck et al., 2006)

This effect may be due to metal-catalyzed sulfate formation in the cloud droplets. In the reply to reviewer #1, we argued as follows:

"The presence of metals in cloud droplets has important implications for the oxidation of sulphur containing species in the aqueous phase. Catalytic oxidation of SO_2 to sulphate by transition metals as Fe and Mn (Calvert et al., 1985), but also Ti (Harris et al., 2013) and V (Ault et al., 2010) is a process that has long been recognized (Calvert et al., 1985; Bradbury et al., 1999), but data obtained during HCCT2010 have shown that this process is of higher importance than previously thought (Harris et al., 2013). In marine environments, dimethyl sulphide can be catalytically oxidized by vanadium to methanesulphonic acid (Gaston et al., 2010). Enrichment of these transition metals in cloud droplets may be explained by cloud processing: Transition metal-catalysed sulphate production in the cloud droplets leads to a higher sulphate content of the metal-containing aerosol particles remaining after cloud evaporation and thereby to a better activation of these particles in the next cloud formation process."

Minor comments:
Page 24420, Line 14 suggestion: “having a diurnal variation”

changed

Page 24421, Line 1: On one hand, the presence…

changed

Line 28: What is meant by individual cloud?

We deleted "during individual clouds" because it was not necessary. The sentence now reads: "This technique has been coupled with on-line aerosol mass spectrometry before, such that the composition of cloud droplets can be measured with high time resolution."

Page 24422, Line 20: The second part of this sentence needs to be rephrased.

We changed the sentence to: "SO_2 oxidation in these clouds was inhibited by a lack of H_2O_2 and by the low pH-values, such that the observed sulphate in the cloud water derived most likely from pre-existing aerosol."

Section 2: Experiments and data evaluation: Although mentioned later on in the manuscript, it would be useful to have information where the site is located with respect to the nearest city, Suhl in the methods section.

We have included a map with the surrounding cities and a table with the population of these cities in the supplementary material and added a sentence to the introduction:
"A map of the surroundings of the measurement site along with a table giving the population number of the cities within a radius of approximately 50 km around the site can be found in the supplementary material (Figure S1 and Table S1)."

Page 24423, Line 24: I assume that the interstitial aerosol was not detected because of their small size. Can the authors include this information? Were any size distribution measurements made between the interstitial inlet and the CVI to calculate aerosol activation profiles?

Yes, with the ALABAMA it was not possible to detect interstitial aerosol. Size distribution measurements using SMPS have been made by TROPOS and will be published in a separate paper.
We clarified the reasons for not measuring interstitial in section 2.1:
"We did not attempt to detect interstitial aerosol because the ALABAMA size range (starting at 150 nm, see below) does not permit detection of small, unactivated particles."

Page 24424, Line 20: The authors mention that the HR-ToF-AMS and the MAAP were operating continuously alongside the ALABAMA. Were the fractions of soot measured by the ALABAMA comparable with the fractions of BC measured by the combined HR-ToF-AMS+MAAP.

The ALABAMA measures a number fraction of soot-containing particles in a size range between 150 and 900 nm. All particle types contained also secondary inorganic material like sulfate and nitrate (as stated in section 2.4.4). Thus the mass fraction of soot may be much smaller than the number fraction of soot-containing particles.
Additionally, the size ranges are different: The MAAP has no size selective inlet, the AMS inlet transmits between 60 and 700 nm. Thus, the number fraction measured by the ALABAMA can hardly be compared to the mass fraction of soot inferred from AMS/MAAP measurements. For completeness, we give here the mass fractions obtained from AMS/MAAP (resp. PSAP) measurements:

	ALABAMA number fraction	AMS/MAAP/PSAP mass fraction
Out-of-cloud	13.6%	7.1%
Cloud rediduals	27.0%	1.3%

Page 24425, Line 11: It would be useful to provide a summary of the criteria described by Tilgner.

We added a brief explained how the full cloud events were inferred to section 2.2:

During the campaign a measurement period was considered as a “full cloud event” (FCE) if the following criteria were fulfilled: liquid water content (LWC) of the summit site cloud above 0.1 gm^{-3}, wind direction from the southwest (200–250° sector), wind speed at the Schmücke site between 2 ms^{-1} and 12 ms^{-1}, no fog at the two valley sites, no precipitation at any site, and air temperature above 0°C. In the course of the data analysis, only those FCEs were chosen that fulfilled connected flow conditions which were inferred using cross-correlations and coefficient of divergence (COD) for O_3, particle number concentration in the Aitken mode (49 nm) and in the accumulation mode (217 nm). For details see Tilgner et al. (2014). Overall, 14 FCEs were identified and evaluated (Table 1).

Line 16: What is the number of spectra required for statistical evaluations?

Assuming Poisson statistics for the occurrence of a particle of a certain particle type, we required to have at least 100 particles per event. This information is also given in the caption of Figure 9 where the FCEs are individually analyzed.

Page 24426, Line 20: The abstract states that more than 170,000 bipolar mass spectra were obtained while sampling out of cloud aerosol and more than 14,000 bipolar mass spectra were measured from cloud residues.

The numbers on Page 24426 are correct. We changed the numbers in the abstract to "more than 160 000" and "more then 13 000".

Page 24427, Line 3: Define MPIC and TROPOS.

Both acronyms occur only once in the manuscript, thus we decided not to use them anymore.

Page 24429, line 22: remove "actual"

done

Page 24430, Line 2: Reformulate sentence "Due to the fact that a reduced data set….."

We changed that sentence to: "This reduced test set contained no particles of the type "mineral dust" and "Ca"."

Page 24430, Line 27: "more from fuel combustion than.."

No, this sentence is correct, because without the references it reads:
"…while Vanadium (V^+, m/z 51) originates rather from fuel combustion and industrial sources like refineries than from mineral dust."

Figure 3: Relative high fractions of soot particle were observed by the ALABAMA. How do these compare to the fractions of soot observed by the MAAP + HR-ToF-AMS instrument? Was there any attempt to compare absolute numbers/volume measured by the MAAP/HR-ToF-AMS with that of ALABAMA.

See our reply to the same subject above.

Page 24432, Line 9: Laser ablation techniques have a tendency to be sensitive to matrix effects that favor certain species with low ionization efficiencies, e.g. K. Do the authors consider that matrix effects influence the measured composition of the aerosol particles?

This is certainly a general problem in the laser ablation technique and explains the high relative abundance of the type "org, K" and "K". Also, detection of metals like Fe, V, and Ni is likely to be favored by this technique. Thus, the number fraction observed by ALABAMA may not reflect in absolute terms the number fraction in ambient air. However, these effects are the same for all subsets of this study, such that the observed differences between the individual cloud events and between the cloud residuals and the out-of-cloud aerosol are meaningful.

Page 24432, Line 14: Aerosol particles with diameters between 200 nm and 450 nm are relatively large. Freshly emitted (anthropogenic particles) or freshly formed aerosol particles are principally measured at diameters < 100 nm.

We agree. These particles can't be "freshly" emitted. But since these particles are found in the smaller size classes of the ALABAMA we suggest "recently" emitted and rephrased this statement to: "This indicates that these particles were recently emitted and had only little time to grow by condensation or coagulation."

Page 24432, Line 15: "had no time to grow by condensation…"

See above

Page 24432, Line 26: east north-east direction

According to the suggestion of Reviewer #1 we modified Figure 4 and thus changed the paragraph describing Figure 4:
"Figure 4 shows the number of detected particles as a function of the local wind direction at the Schmücke. Panel a) gives the standard wind rose for the whole time period. The dominating wind direction was southwest, with about 50% probability for wind directions between 200 and 270°. This direction corresponds to the requirements for cloud events. The absolute number of detected particles is given in Panel b), showing that the majority of the detected particles were measured when the wind came from southwest. However, as shown in Panel c), per unit of time more particles were detected when the local wind direction was between 0 and 90°. In these directions lie several larger cities (Erfurt, Weimar, Jena, see Map in Figure S1) such that in general a higher pollution level may be expected."

Page 24434: The authors state that their measurements are different to those observed in other studies with other instruments (Aerodyne, AMS). The reason for this is explained as being a result of the short averaging time of the Aerodyne instrument compared with a single particle instrument.
Is there so much variation observed over the period of the cloud that would cause different averaging results? Are the size distributions measured by the two instruments in the two studies comparable? It would be better for the authors to focus on the comparison with Schneider et al., from the same study than from observations by Drewnick et al. (2005). In general how does the fraction of organic material observed by ALABAMA compare with that observed by the C-ToF-AMS instrument. How does the size distribution of aerosol particles measured by the ALABAMA compare with that measured by the C-ToF-AMS instrument?
How much was the scavenging efficiency of organic species dependent on their mixing state?

As explained earlier, the size distribution of the ALABAMA is not quantitative and can therefore not be compared with the size distribution measured by the AMS. Also a comparison of the organic mass fraction measured by the AMS with the number fraction of ALABAMA is problematic, because:

- We would compare number fraction and mass fraction
- The single particle types containing organic material ("org, K", "org", "amines", "diesel exhaust", "biomass burning") contain also other material (like nitrate and sulfate) that would not be accounted for. In the AMS data product, these mixed particles would be separated into organic and inorganic mass. On the other hand, the AMS would not detect refractory material in biomass burning aerosol.

Thus, we conclude that such a comparison would be misleading and would be subject of a much more detailed analysis, including a discussion of the measuring capabilities of both instruments. This would clearly be beyond the scope of this paper.

Page 24434, Line 10: “data”…… “single particle analysis”.

changed

Page 24435, Line 4: “…mass spectra show peaks”

changed

Page 24435, Line 9: the definition of TMA should be made earlier.

We defined TMA on its first occurrence.

Figure 8: The AMS biomass burning axis could be change to be in the same range as the EBC axis

That would lead to a too small signal in the graph. In contrast, we preferred to expand the axis (0 to 0.4 µg m^{-3}) such that the correlation of the AMS biomass burning signal and the EBC signal is better visible.

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