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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 #1

Roth and co-authors describe a set of single particle mass spectrometer measurements of ambient aerosol performed at a mountain site in Germany 2010. Ambient "out of cloud" particles and cloud residuals were alternately analysed by bypassing or flowing air through a counterflow virtual impactor, respectively. All data were combined and classified using a series of approaches. Mass spectra were first clustered using c-means "fuzzy clustering" and the resulting clusters were merged with similar types using distance metrics to create a more manangeable set of final particle classes. Differences between out of cloud particles and cloud residuals were then assessed. Interstitial aerosol was not investigated. The main findings are that cloud processed particles at the site are enriched in sulfate, nitrate and aminium ions relative to out of cloud particles. Larger, possibly aged, soot particles were also found to represent a higher fraction of the in-cloud than out of cloud population, because of internal mixing with hygroscopic inorganics. The manuscript is well written and scientifically sound, with some nice tweaks on existing single particle mass spectral classification. I have some minor comments only.

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

The article would benefit from a map of the site and surrounding region/topography to complement the local wind data. The proximity to local carbonaceous aerosol emission sources could be included here. Also on this point, Figure 4 would be better represented in 2 panels. Readers will be more used to seeing a windrose like this applied to wind speed and direction frequency. It is easy to miss that the radial axis is actually the fraction of the mass spectral population detected. A standard windrose showing windspeed and direction would be more useful. A second panel could show the dependence of particle hits on wind direction. This could be normalised by frequency of wind from each sector if suitable.

We added a map of the area to the supplement (Fig S1) and also a table with the population of the cities in an area of approximately 50 km around the site (Table S1). We added a reference to that Figure in section 2.1:
"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)."

We replaced Figure 4 by three panels: One panel with a standard windrose showing windspeed and direction frequency and two panels showing the number of analyzed particles per wind direction, one of them normalized by the measuring time per wind direction.
In that context we also modified the description of Figure 4 in section 3.1.:

"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."

An expanded discussion of the merits of fuzzy clustering would be helpful. My understanding is that the advantage is that each spectrum can "belong" to several clusters to differing extents. However the classification approach here is exclusive, in that all spectra end up "belonging" to only one cluster or group. In this case, what is the advantage over traditional "hard" clustering techniques like neural network algorithms or k-means?

In our case, we did not make a full use of the advantages that fuzzy clustering can give. This would be a much more extended analysis. We chose the fuzzy means algorithm for two reasons:

1) In tests that we performed with known data sets, consisting of a certain number of real mass spectra from two particle types with the typical spectrum-to-spectrum variation, it had turned out that with the fuzzy approach yielded a better result than the k-means (Roth, 2014).
2) In our analysis, only those spectra were assigned to a cluster whose correlation between the mass spectrum and the cluster center (after the termination threshold was reached) was higher than 0.7. All other mass spectra (which had correlations smaller than 0.7 with all clusters) were sorted into the "others" cluster. This "others" cluster was then analyzed further by searching for certain marker peaks, as described in section 2.4.4. This would not have been possible with the k-means algorithm, because the k-means assigns all mass spectra to the "best" cluster, i.e. to that with the highest correlation, even if the absolute correlation coefficient is small.

We added this explanation to section 2.4.1:
"The main reason for choosing the fuzzy c-means algorithm was that in a test with two distinct particle types from laboratory data the fuzzy c-means yielded the best results (Roth, 2014). Furthermore, the fuzzy c-means accounts for mass spectra that don't fit to any cluster by creating one additional group of spectra ("others"). These mass spectra can then be treated separately by searching for certain marker peaks (see sections 2.4.3 and 2.4.4)."

In section 2.4.2 it is not clear how the authors determined a false positive or false negative assignment of a spectrum to an "incorrect" cluster. How is the incorrect assignment identified? Hasn't the particle already been objectively assigned mathematically to the most "correct" cluster using Pearson's r?

From the mathematical point of view, the algorithm assigns each mass spectrum to the "best" cluster, i.e. to that having the highest correlation to the mass spectrum in question. But manual inspection of the mass spectra sometimes suggested that certain spectra belonged to another particle type because of certain marker peaks. Although we compressed the peak height (by a power of 0.5) it cannot be ruled out that single large peaks (especially K^+ or Na^+) lead to a high correlation coefficient to a specific cluster, while smaller peaks, which can by much more characteristic for a certain particle type, are not sufficiently considered by the correlation.

After the positive and negative mass spectra were normalised separately, they were combined and normalised again. Why are they normalised again? Isn't this redundant? Or is it simply to express everything as a fraction of 1 rather than 2?

You are right, it is only done to express everything as a fraction of 1 for convenience.

In section 2.4.3, last line, what are the counting statistics that the authors refer to?

Counting statistics in this case refers to the counted number of particles of a certain type and the assumption that the occurrence of these particles can be described by Poisson statistics. Thus, the error bar for those particle types identified by the marker peak search is the square root of the counted number of particles. We added this information to section 2.4.3.

Section 3.2.4 contains only two sentences, but to me this is one of the most interesting findings in the article. The possibility of catalytic oxidation of SO2 (and other species like DMS) in by iron and vanadium has impacts for the atmospheric lifetime and climate impacts of thee particles. This is briefly referred towards the end of section 3.4 but the authors have good evidence here and should expand the discussion to consider their results in the context of other single particle studies that have focused on this topic, eg (Gaston et al., 2010; Ault et al., 2010).

Thank you for point this out. We added the following discussion on that issue to section 3.2:

"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."

Section 3.2.3 The difference in hygroscopic behaviour for smaller soot particles with little inorganic content and larger soot particles with higher inorganic content has been predicted in Western Europe using single particle mass spectrometry previously and found to agree well with HTDMA measurements (Healy et al., 2014).

We included a reference to the findings of Healy et al. (2014) in section 3.2.3:
"Similar findings have been reported for growth factors of coated black carbon particles measured in Paris using a hygroscopic tandem differential mobility analyser and a single particle mass spectrometer (Healy et al., 2014)."

Page 24420, line 2: replace "have been" with "were"

Changed

24421, line 20: replace "during" with "within"

We removed "during individual clouds" because it is not necessary here

24422, lines19-21: Rephrase, unclear

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."

24423, line 16: replace "in southwesterly direction" with "facing southwest"

Changed

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