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Interactive comment on "On-line single particle analysis of ice particle residuals from mountain-top mixed-phase clouds using laboratory derived particle type assignment" *by* S. Schmidt et al.

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Reply to editor's comment (follow-up comment by Reviewer #1)

Initial comment from the reviewer:

3- In Section 2.3 when discussing the lab spectra it is stated "only those mass spectra that represented the majority of the different fragmentation patterns were considered". What % defines majority? Moreover, this % should be used to define a correction factor (with corresponding uncertainty propagated into the result). If only 60% of particles were measured for salt but 90% for soot, then the reported IPR numbers should be

scaled up by 1/0.6 and 1/0.9 respectively.

Response by the authors:

Correction of the reported IPR numbers can't be done in this way. First, we might end up with more particles that were actually measured. Second, it is only possible to assign marker ions of atmospheric particles to those reference spectra containing these marker ions. Speculating about spectra not containing the markers would only increase the uncertainty.

"follow-up comment" from the reviewer:

I'm not quite convinced by the arguments in this response. It would be appropriate to end up with more particles than were measured, if a correction for missed particles was applied. There are 2 ways the ALABAMA may miss particles. The obvious way is if the instrument only obtains a signal for, say, 10% of all particles (90% "missed"). Then a correction factor 1/0.1 should be applied. The second way is if the instrument obtains a full mass spectra (with marker ions) for 10 of 100 biomass burning particles and only a partial mass spectra (eg no signals except potassium) for 30 of 100 biomass burning particles. We can suppose that their remaining 60 are missed particles. In the second case, the correct number to be reported for the biomass burning class is 10*1/0.1. There is ambiguity about what to do with the 30 partial mass spectra: they could be put into a category "other" but careful thought would be needed before reporting total estimates for number concentration.

It is essential to include such a correction factor if the goal is to compare the abundances of different particle types. If a correction factor is not applied, it must be proven that the conclusions are unchanged by its omission – it is only valid to omit the correction if it would be similar for all particle types, in analogy to weighting or not weighting a linear regression.

Therefore I still think that the manuscript should include a report (discussion/table/graph) of the fraction of laboratory samples which included the marker ions and which did not. If this fraction was very different between classes, the comparative statistics in the abstract (13% dust, 3% aged particles in IPR) would be incorrect. There is another subtlety which I would like to state but do not expect the authors to address. A biomass burning particle missing certain markers may possibly be classified as aged, which would mean a second-order correction of overlapping particle classes could be made (this is just an example, and not based on the authors' marker ions). Without this correction, particle type numbers could indeed be overestimated, but I imagine this would be pushing the data analysis past what is reasonable.

Reply by Johannes Schneider (on behalf of all co-authors):

We considered the follow-up comment very carefully, but we still think that such a correction is not possible. We list our arguments here:

1) "missed particles": It would be necessary to determine a size-resolved detection efficiency for all reference particles. We did not size-select the test particles, but parallel measurements with an optical particle sizer are available. However, some uncertainty would result from this, because of the necessary conversion of the different equivalent diameters.

2) Assuming such size-dependent correction factors are available, a major obstacle is that parameters inferred from pure, laboratory-generated particles or directly from the source sampled particles can not be transferred to aged, processed particles found in the ambient atmosphere. The shape of freshly emitted soot or combustion particles will change through atmospheric processing from very non-spherical to more spherical, thereby improving the focusing properties of the particles in the aerodynamic lens. Thus, the detection efficiency will improve by processing. Also, non-spherical dust particles can be coated by secondary organic or inorganic material, leading to a more spherical shape. Matrix effects, altering the ionizations process of internally mixed

particles compared to the pure laboratory particles are also possible.

3) Particles that are ionized but do not show the marker peak spectra: Here the same argument as above holds: We would apply correction factors inferred for pure laboratory particles to aged and processed atmospheric particles.

4) Particles that are ionized but that do not show the marker peaks would in the current analysis either assigned erroneously to another particle type or to the group "others". Since it is not known where these falsely assigned particle end up, we can't correct for this error, too. Please note also that the cluster "others" is by far not large enough to account for all possible particle not showing the marker peaks. Additionally, although we investigated a large number of reference particles, there will by a large number of possible atmospheric particle types that we did not investigate and which may be included in the "others" group. Thus, subtracting particle from the "others" cluster is not a valid option.

Summarizing, we think that trying to correct for all these effects would lead to unacceptably high uncertainties and should not be done, neither for ALABAMA not for any other single particle mass spectrometer, and has to our knowledge not been done by other groups.

In contrast, we prefer to understand the relative abundances and absolute numbers of particles as "number of particles identified by the ALABAMA" and not as "number of particles in the ambient atmosphere". We will clarify this in the text and in the figure captions. We will also add a discussion of the points above to the manuscript.

Nevertheless, comparison between the relative abundances of particle types in out-of-cloud aerosol and ice residuals (which is the focus if this manuscript) is possible, because, to the best of our knowledge, the above effects affect both particle populations in the same way.

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