acp-2016-365

Schmidt et al., On-line single particle analysis of ice particle residuals from mountain-top mixed-phase clouds using laboratory derived particle type assignment

Reply to Reviewer #2

Reviewer comments and questions are printed in this font type.

> Our replies are printed like this.
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> Changes to the manuscript text are printed in blue.

The manuscript by Schmidt et al. presents ambient and laboratory single particle mass spectrometer data to identify chemical components in aerosols and ice residuals on Jungfraujoch and to draw conclusions on the ice nucleation ability of different aerosol particle components. Given the importance of ice nucleation processes for precipitation and the climate, and the many uncertainties related to these processes, such studies are needed. The combination of laboratory experiments and ambient measurements makes this study especially useful for the single particle mass spectrometer community. I therefore recommend publication of this well-written manuscript in ACP after the following comments have been addressed:

> We thank the reviewer for the positive rating of our manuscript

General comments

The limitations and uncertainties of single particle mass spectrometry and the respective data should be addressed in more detail.

There are several aspects:

- More care should be given as how one describes the quantities. It should be made clear, e. g. in the introduction, that “a larger relative amount” cannot be interpreted as “more aerosol mass”, but can only refer to “a larger number of particles” assigned to a certain category.

> Agreed. This is a very important point for laser ablation single mass spectrometry. We replaced "relative amount" by "number fraction" in the abstract, in section 3.2.2 and 3.2.4, and in the summary.

- The presentation of marker mass fragments and reference spectra from different particle types is highly desirable for the single particle mass spectrometer community. For the spectra to be useful for other groups/instrument types however, information on uncertainties needs to be given. One of the issues of laser ablation single particle mass spectrometers is the (weak) repeatability of spectra/measurements; depending on particle size, chemical composition/morphology, and on the placement of the particle in the laser beam, the amount of ablated/ionized material can vary significantly. According to p. 4, l. 36, you were not size-selecting particles for your laboratory tests, which might have led to larger spectrum-to-spectrum differences. Showing e. g. standard deviations of the averaged spectra would give an idea on the uncertainty and variability of the marker spectra.

We have now added the reference mass spectra to the supplement. We show the most frequent spectra types (clusters) for each substance. This illustrates the variability of the mass spectra that are obtained from one particle type.

We consider standard deviations of the averaged mass spectra not as an ideal estimate of the uncertainty, because the abundance of a marker peak is the main criterion, not its height in the mass spectrum.

- Related to the above – how were the marker peaks identified? Given the overlap of marker peaks between different particle types, it seems to me that presenting the data as marker spectra would almost make more sense. How important are the individual markers for identification as opposed to the whole spectrum? In Table 3 you give the ratio of the number of spectra containing marker peaks (all marker peaks? just some?) to all spectra of a particular particle type. A better way to present uncertainties would be the standard deviation of the avergaed spectra (see above). The ratios in Table 3 are fairly low, I thus expect a relatively high scatter of spectra per particle type.

As already mentioned above, we included the reference spectra in the supplement. The scatter of spectra per particle type is illustrated by showing the main spectra types (clusters).

Regarding the overlap of marker peaks: It is the combination of the characteristic marker peaks that is used to assign a mass spectrum to a certain particle type. In cases where there is a complete overlap of all marker peaks between reference spectra, we can't distinguish these substances. As said above, the standard deviation of the averaged mass spectra are not the best estimate of uncertainty, because the abundance of the peak is more important that its height.

- More information should be given on the choice of clustering algorithm and the uncertainties of its outcome. There are a lot of references given to Roth (2014, 2016), but the main points should be conveyed to the reader in the manuscript (also in Table 1). A general result I infer from the ambient measurements is that secondary (here in the sense of formed from a chemical reaction/in combustion) components (both organic and inorganic) or particles containing a lot of secondary (organic) components (e. g. biomass burning) are less effective ice nuclei than primary organic particles such as e. g. biological particles. In this simple categorization, however, it is hard to place the engine exhaust particles. It would be helpful if the engine exhaust and PAH particle types were discussed in the manuscript (which is not the case now).

We have included a general explanation of the clustering and of the chosen algorithm to section 2.2 (as requested also by Reviewer #1). We also added a discussion on PAH and engine exhaust particles.

Changes to the text describing the clustering (Section 2.2):

Basically, a clustering algorithm tries to find the optimum number of clusters (i.e. groups of mass spectra) that represent the particle population by their average mass spectrum. By nature of the aerosol particle diversity and the non-uniform ionization in laser ablation ionization, it can't be expected that all particles contained in a cluster equal the average cluster spectrum (Hinz et al., 1999). Rather, each spectrum is assigned to that cluster where the distance metric (in our case one minus Pearson's correlation coefficient r) of the single particle spectrum and the averaged cluster spectrum reaches a minimum. The fuzzy c-means algorithm differs from the k-means in that way that it accounts for the possibility that one particle may belong to two (or more) clusters by using membership coefficients, whereas the k-means assigns each spectrum strictly to that cluster where correlation with the averaged spectrum is highest.

Here we applied the fuzzy c-means algorithm because sensitivity tests conducted in the framework of a PhD thesis (Roth, 2014) with laboratory-generated particle of known composition and number have shown that the fuzzy c-means better separates the particle types and suffers less from false assignments. Also, various parameters that influence the clustering result where tested by Roth (2014), resulting in a "best choice" that was applied here as well: All mass spectra were normalized to reduce the influence of total signal intensity, and all m/z peaks were taken to the power of 0.5 to reduce the influence of the non-uniform laser ablation ionization, thereby increasing the influence of smaller peaks and decreasing that of larger signals. The "fuzzifier", a weighting exponent used for the calculation of the membership coefficients (Bezdek, 1982; Roth et al., 2016) was set to 1.2. A high number of start clusters was chosen to assure that also rare spectra types are considered in the data evaluation (for instance for the out-of-cloud data set from the JFJ campaign 2013 a number of 200 cluster was chosen; for a known particle composition as sampled during the laboratory studies a number of 10 to 50 cluster was chosen depending on the number of spectra). The start clusters were chosen randomly from the total particle population, under the condition that the correlation coefficient (r) between two randomly picked start spectra is less than 0.7. The procedure leading from the clustering algorithm to a certain number of particle types, as illustrated in Fig. 1, was as follows: After mass calibration, the spectra were clustered using the fuzzy c-means algorithm, yielding a certain number of clusters. The resulting cluster number can be lower than the chosen number of start clusters. If this is the case, the number of start clusters was sufficiently high not to suppress rare spectra types. Each cluster includes a certain number (≥ 1) of mass spectra based on the calculated membership and distance. From all mass spectra in a cluster an average spectrum is calculated which is used for the identification of the particle type represented by each cluster. All mass spectra which did not fulfill the distance criterion ($1 - r \leq 0.3$) compared to any of the clusters were sorted in the cluster "others". The averaged spectra of each cluster were manually examined with respect to the presence of the marker peaks derived from the reference mass spectra (Section 3.1) and assigned to a certain particle type. The "others" cluster was processed again using the fuzzy c-means algorithm, but with reduced constraints and again the resulting clusters were manually examined and, if possible, assigned to particle types. At the end all clusters of the same particle type were merged, whereas clusters that could not be assigned to a certain particle type were added to the cluster "others".

Changes to text with respect to PAH and engine exhaust particles (section 3.2.1):

The particle types that were assigned to the type "engine exhaust" also show C_n-fragmentation ($C_1^+ - C_5^+$, m/z 12 … 60) but can be distinguished by the peak at m/z 40 (Ca^+) which was observed in the reference mass spectra but also previously by other researchers (Vogt et al., 2003).

PAH containing particle were identified through the corresponding reference spectra and marker peaks from the laboratory studies, namely 50/51 ($C_4H_2/_3^+$), 63 ($C_5H_3^+$), 77 ($C_6H_5^+$), and 91 ($C_7H_7^+$). Even though cigarette particles (before inhalation) contain these markers as well, our reference spectra indicate that these two particle types can be distinguished because cigarette smoke additionally contains a C_n pattern (m/z 12 – 36).

I am confused about the similarity of sea salt and cooking emissions fragmentation pattern. How were the sea salt particles produced, what kind of cooking emissionswere investigated? The variety in cooking activities is incredibly large (food cooked?what method? fuel used? etc.), and without further information a “cooking spectrum”is not very meaningful.

> The similarity in the fragmentation pattern of sea salt and cooking emissions only holds for the cations. Unfortunately, only cations were available from the Jungfraujoch field data (as explained in section 2.4.1). The cation spectra (with m/z 23, 39, 46, 81, 83, 139) occur both in sea salt and in barbecue emissions, and we assume that they are from salt contained in the spicing of the meat and the cheese.
> In Table 2 (now Table 1) we noted that we sampled the particles directly from a barbecue (charcoal) in outside air. We used sausages, steaks and cheese. The marker peaks listed in Table 3 (now Table2) were found in all three spectra types. We will add this information to Section 2.3 and will refer to this particle type as "cooking/barbecue emissions" throughout the whole text in the revised version.
> The sea salt particles were produced atomizing a solution of commercially (Sigma Aldrich) available sea salt.

Soil dust and minerals are categorized as “natural” aerosol, in accordance with classifications in literature. However, soil dust aerosol concentrations can directly be influenced by anthropogenic activities (e. g. farming, mining, forestry).These are all important factors, especially when looking into/modelling anthropogenic influences on climate via aerosol-cloud interactions. I am fully aware that soil dust source apportionment lies outside the scope of this paper, but I suggest leaving out the word “natural” and potentially add a sentence on this issue.

> We agree with the reviewer and have left out the word "natural" when describing the dust particles. However, biological particles can be attributed to natural sources. We therefore refer to "primary and/or natural sources", and added a brief explanation of the different source types at the beginning of section 3.2.2:
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> In comparison to the out-of-cloud aerosol the IPR ensemble shows a higher number fraction of particles from primary and/or natural sources. We attribute biological and sea salt to primary natural sources, whereas soil dust and minerals emissions can directly be influenced by anthropogenic activities and can therefore not be regarded as purely natural. Biomass burning particles generated from forest fires are not primary particles, but can be related to natural sources as well.

Specific comments

P. 3 - 4, l. 37 – 2: Please give the reason for choosing the fuzzy c-means algorithm over the other two possibilities.

> As mentioned above, we included a general explanation of the clustering and of the chosen algorithm to section 2.2.:
>
> Basically, a clustering algorithm tries to find the optimum number of clusters (i.e. groups of mass spectra) that represent the particle population by their average mass spectrum. By nature of the aerosol particle diversity and the non-uniform ionization in laser ablation ionization, it

can't be expected that all particles contained in a cluster equal the average cluster spectrum (Hinz et al., 1999). Rather, each spectrum is assigned to that cluster where the distance metric (in our case one minus Pearson's correlation coefficient r) of the single particle spectrum and the averaged cluster spectrum reaches a minimum. The fuzzy c-means algorithm differs from the k-means in that way that it accounts for the possibility that one particle may belong to two (or more) clusters by using membership coefficients, whereas the k-means assigns each spectrum strictly to that cluster where correlation with the averaged spectrum is highest.

Here we applied the fuzzy c-means algorithm because sensitivity tests conducted in the framework of a PhD thesis (Roth, 2014) with laboratory-generated particle of known composition and number have shown that the fuzzy c-means better separates the particle types and suffers less from false assignments.

P. 5, l. . 3 – 9: See general comment on uncertainties and limitations of marker/spectra identification.

We added the description of the error estimation and included the error ranges in the tables and throughout the text.

Changes to text (section 2.2)

The uncertainties reported along with these numbers were estimated by manual inspection of a subset of the data, as described in Roth et al. (2016). The assignment of a certain cluster to a particle type is based on the presence of the reference marker peaks in the averaged cluster mass spectrum. Upon inspection of all mass spectra in one cluster it may occur that the marker peaks (or not all of the marker peaks) are not present in an individual mass spectrum. Such a mass spectrum has nevertheless been correctly (from a mathematical point of view) assigned to the cluster by the algorithm, because the overall correlation of the mass spectrum with the cluster average is sufficiently high ($r > 0.7$). This can especially occur in cases when many other peaks are similar, as is often observed for organic particles.

For the error estimation, such particle mass spectra were regarded as "uncertain assignments". The percentage of such uncertainly assigned mass spectra was regarded as the relative error. Of the out-of-cloud data set we inspected two clusters, one assigned to biological particles (338 particles) and one assigned to biomass burning aerosol (473 particles). It turned out that 52 of the 338 inspected "biological" mass spectra (15%), and 48 of the 473 inspected "biomass burning" mass spectra (10%) had to be considered as uncertain. Thus, we conservatively estimated the relative error to be about 15% and generalized this error for whole out-of-cloud data set.

For the IPR data set, where the absolute numbers of particles are much lower, it was possible to do a more detailed inspection of the clusters: We inspected one cluster assigned to biological particles, where we found that 28 out of 76 were uncertain (37%), and one cluster of the "PAH/soot" particle type, where 9 out of 23 spectra were uncertain (40%). Those particle types containing only a small number of particles ("industrial metals", "Na + K", "aged material") were completely inspected manually, yielding uncertainties for the "industrial metals" of 14%, of the "Na + K" type of 0% (no uncertain particles), and of the "aged material" type of 44%. Thus, we estimated the relative error (from uncertain particle type assignment) of the IPR population to be 40% with the exception of the industrial metals (14%) and the "Na + K" type.

These error estimates are conservative upper limits for the error range, because the reference laboratory measurements have shown that, e.g., not all biological particles contain the characteristic marker peaks. It may therefore well be that mass spectra that are similar to the cluster average spectrum of a "biological particle" type are really biological particles, even if they do not contain the marker peaks. The uncertainty inferred from manual inspection was combined with the Poisson counting statistics error (by error propagation) for each particle type.

P. 5, l. 25 – 28: Was the inlet heated to 20_C to prevent condensation? Did you perform any assessment of the influence of the heating on the chemical composition (e. g. evaporation of semi-volatile material)? What was the residence time in the inlet? The evaporation of semi-volatile material could be especially important for SIA and SOA. Were parts of the ICE-CVI heated as well? Please add more information on sampling/inlet conditions.

Weingartner et al (1999) describe the inlet and give two reasons for heating the inlet:

"Therefore the main inlet at the Sphinx observatory was designed to sample the interstitial aerosol as well as the activated droplets. The inlet consists of a heated and insulated vertical stainless-steel tube (length: 200 cm; diameter: 6 cm) and a heated snow-hood. The temperature of the sampled air was measured 15 cm downstream of the inlet entrance and was electronically regulated to +20°C. As already mentioned, heating was necessary (1) to dry essentially all activated droplets as early as possible to reduce transmission losses and (2) to prevent riming of the inlet system during harsh conditions, especially in winter."

We can therefore refer to the Weingartner-Paper for details of the inlet and it is not necessary to repeat this information in our manuscript.

The Ice-CVI was not heated (see Mertes et al., 2007). We did not assess the influence of the heating of the total inlet on the chemical composition, and we can't think of a method that allows for doing this. But, if heating of the total led to a loss of SIA and SOA, it would result in an underestimation of particles of the type "aged material" in the out-of-cloud aerosol. This would not affect the finding that the number fraction of "aged material"-particles is much smaller in IPR than in out-of-cloud aerosol.

P. 5, l.34: What about the transmission of particles with diameters larger than 500 nm? A relatively large fraction of the particles measured at Jungfraujoch was larger than 500 nm, according to Figure 3.

The transmission decreased from 99% to 95 between 500 and 1000 nm, thus sampling line losses are not an issue for the interpretation of the ALABAMA data. We added this information to section 2.4.1:

For both sampling lines the transmission efficiency was about 99 % for particle sizes between 200 nm and 500 nm and decreased to 95 % for particle sizes up to 1000 nm. The upper 50 %-cut-off of the Ice-CVI was at about 4900 nm and for the total inlet about 3300 nm.

P. 7, l. 7 – 8: Many of the marker mass fragments of the biological particles (especially bacteria and pollen) have negative marker mass fragments. How were they identified in ambient air where you only had positive spectra?

In the positive spectra we used the peaks at m/z 47 (PO^+) and at m/z 58 ($C_3H_8N^+$) and 59 ($C_3H_9N^+$), the latter two indicating trimethylamine. We named this particle type "biological/amine".

P. 9, l. 31 – 38: See general comment above. A more thorough discussion on the properties and uncertainties of engine exhaust and PAH spectra in comparison with biomass burning spectra might shed some light on their differences in ice nucleation behavior.

We added a description on how PAH and engine exhaust were identified:

The particle types that were assigned to the type "engine exhaust" also show C_n-fragmentation ($C_1^+ – C_5^+$, m/z 12 … 60) but can be distinguished by the peak at m/z 40 (Ca^+) which was observed in the reference mass spectra but also previously by other researchers (Vogt et al., 2003).

PAH containing particle were identified through the corresponding reference spectra and marker peaks from the laboratory studies, namely 50/51 ($C_4H_{2/3}^+$), 63 ($C_5H_3^+$), 77 ($C_6H_5^+$), and 91 ($C_7H_7^+$). Even though cigarette particles (before inhalation) contain these markers as well, our reference spectra indicate that these two particle types can be distinguished because cigarette smoke additionally contains a C_n pattern (m/z 12 – 36).

P.10, l. 34 – p. 11, l. 3: Please elaborate further on the comparison and discrepancy of OPC and ALABAMA size distributions. The size distributions shown in Figure 3 are completely different and basically do not allow to draw any conclusions. Are there no artefacts of the Sky-OPC?

We chose to include the size distribution measured with the OPC because the size distribution measured with the ALABAMA is not representative as a total number size distribution. The black lines in a) and c) show the number of analyzed particles in each size bin. From this it can be seen that the ALABAMA detection efficiency decreases for particles smaller than 400 nm. However, the relative number fraction of particle types in each class is not affected by this, as long as there are sufficient particles per size bin. It is therefore possible to apply the relative composition as a function of size to the size distribution measured by the OPC which we regard here as a "realistic" distribution. There are certainly artefacts to an optical particle counter, but this discussion is beyond the scope of our paper.

A second reason why we chose to show the size distribution measured by the OPC is the marked difference between the IPR and the out-of-cloud aerosol particles: The slope of the distribution is much steeper for the out-of-cloud aerosol, showing that larger particles are relatively more abundant in IPR than in the out-of-cloud aerosol.

We restructured the paragraph describing the size distributions and added more explanation.

P.11, l. 22 – 34: Whereas the meteorological conditions were similar for the two periods, they do no coincide in termns of time of day, which however can have large influences on (anthropogenic) emission patterns (e. g. engine exhaust, cooking: : :). Please take this into account in your data interpretations.

It was not possible to find two events with similar meteorological conditions, air mass origin and time of day. We added the following text:

Further, it has to be noted that both sampling periods differ in their sampling length and their time of day: The IPR sampling period lasted almost from midnight to noon, while the corresponding out-of-cloud sampling period lasted only 72 minutes in the afternoon. This may lead to different aerosol particle population due to different emission patterns of anthropogenic particles like engine exhaust, cooking etc. However, it was not possible to find two sampling periods having the same time of day and similar meteorological conditions and air mass origins. Also, the IPR sampling period could not be shortened because a sufficient number of particle needs to be sampled for a meaningful analysis.

P. 12, l. 27: This "conclusion" is a rather minor finding of your study (or put in different words, a potential reason for differences in composition between activated and non-activated aerosol particles that can be ruled out). This sentence should not be at the end of the results section.

We deleted this sentence here because this conclusion (scavenging does not play role) has already been discussed in section 3.2.2

P. 13, l. 1 – 28: Again, in your summary, please a add a few sentences on uncertainties and the limitation of the method concerning single particle marker spectra identification and particle type detection/identification in ambient air.

We added the following text at the beginning of the summary:

Uncertainties of the method arise from the finding that not all particle mass spectra from one particle type display the characteristic marker peaks. This is a result of the non-uniform ionization process of laser ablation particle mass spectrometry. For some particle types (pollen, sea salt, cooking/barbecue emissions) the fraction of mass spectra showing characteristic marker peaks was high (60 – 84 %), whereas for mineral particles (desert dust, soil dust etc.) the percentage of reference mass spectra with specific markers peaks was markedly lower (20 – 37 %). The resulting particle assignment to particle types can't be corrected for this effect, but it is likely that this is the cause for the large fraction of "unknown" particles (17 – 19 %).

Technical comments

P. 1, l. 19 – 21: "As outcome: : :" – weird sentence structure, rephrase

We rephrased to: "The outcome of these laboratory studies was characteristic marker peaks for each investigated particle type. These marker peaks were applied to the field data."

P. 1, l. 32: "and" instead of "an"

This was meant to be "an". We added a comma behind "clouds", maybe this helps:

"Depending on their chemical and microphysical properties aerosol particles have a strong impact on the solar radiation budget, an influence on the life-time of clouds, and hence also on precipitation."

P. 4, l. 37: Phrase structure; should read "Coating experiments were also…"

Changed.

P.7, l. 4 – 5: Weird sentence structure

We do not see why this sentence is unclear.

P. 9, l. 5: Dot at the end of the sentence is missing.

Corrected.

P. 12, l. 15: Sentence structure: Should read "It has to be noted further..."

We deleted this paragraph with respect to a comment of reviewer #1.

P. 12, l. 27: conclusion

Corrected.

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