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Discussions

Interactive comment on "On-line determination of the chemical composition of single activated cloud condensation nuclei – a first investigation of single urban CCN and CCN obtained from sea
water samples" *by* Carmen Dameto de España et al.

Anonymous Referee #1

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The authors' comments to the individual points raised by the reviewer are given below in italics and in blue

General comments:

The manuscript intended to introduce a novel method to characterize the individual activated CCN chemically. Based on a Cloud Condensation Nuclei-Versatile Aerosol Concentration Enrichment System (or CCN-VACES), particles can be firstly activated, followed by the detection. A Laser Ablation Aerosol Particle Time of Flight mass spectrometer (LAAPTOF) was deployed downstream to obtain the chemical composition of individual CCN particles.

The experiment design and data analysis presented are quite well. However, the way that the authors presented their results might require improvement. The discussion on the results is full of details (several mass spectra of the detected particles) rather than presenting new knowledge out of such information. The authors need to provide an in-depth scientific interpretation and discussion on what is unique with this newly developed technique. Another major concern is that the major conclusions might not be supportive in the current version. More comparisons between individual activated CCN and individual droplet residues should be done to validate their results on the measurements of individual activated CCN. Barely with the mass spectral data, it is hard to confirm that the detection particles are in the form of droplets. Is it possible that the detected particles are already dried?

The main question raised by the reviewer is: what is new? The answer to this question is: with this setup, we show that individual CCN can be analysed rather than aerosol particles in general. In short, the CCN-VACES activates CCN at a specific (selected) supersaturation, *separates them from non-activated particles and enriches them in concentration in the virtual impactor. These activated CCN are transferred as droplets into the LAAPTOF and analysed there. Single particle mass spectrometry cannot determine whether a particle is a CCN, and with the link to the CCN-VACES, "true" CCN can be analysed. To our knowledge, this has not been done before for previously non activated CCN.*

A point already made here: the LAAPTOF measures what is transferred to it, so the question of comparing spectra of droplets and droplet residues is not pertinent in our study – even if the droplets had dried to some extent by the time they passed the sizing laser triggering the ablation laser (in our case the lower size limit was set to 300 nm), the particles/droplets that are ablated to obtain spectra are particles/droplets that had been actually activated CCN, but not true cloud droplet residues.

We do see the point of this reviewer, however, will remove details and will shorten and re-focus the MS to clarify this main point.

Overall, the topic of this manuscript is relevant to the journal and has importance scientifically. Prior to publication, the authors should also address the specific comments below.

Specific comments:

1. Introduction: the introduction of the CCN should be more specific for SSA particles. The authors just put some basic knowledge together, which is not explicitly in line with the major conclusion of this study. Some sentences, such as "Ambient aerosols originate from multiple different sources. Chemical reactions of natural and/or anthropogenic precursor gases lead to particle nucleation events.", and "Water soluble organic carbon (WSOC) has been shown to influence particle activation (e.g. McFiggans et al., 2006, Jacobson et al., 2000).", and "Cziczo et al. (2003) and Cziczo et al. (2006) coupled a continuous flow ice nuclei counter (Rogers et al., 2001) to a single particle mass spectrometer (PALMS; Murphy et al, 1998) to focus on chemical characterization of IN, and single particle analyses of ice particle residuals where conducted by Schmidt et al (2017) at Jungfraujoch." are not necessary or duplicate.

   The introduction will be considerably shortened and focused on the main topic of the paper. SSA and the literature studies of cloud droplet residues (see reviewer comment #3) will be given more attention. **done**

C2

2. Introduction: the authors mentioned that there are challenges to measure the chemical compositions of a single ambient particle. This might be not accurate. The development of SPMS could be dated back to decades, and there are many results in this topic, as also listed in the manuscript. Besides, Aerodyne aerosol mass spectrometer (AMS) could not address this issue.

   We do not deal with aerosol particles in general (and we definitely do not say that the Aerodyne instrument can measure single particles), but with a <u>specific subset of the aerosol, i.e. CCN, which are defined as those particles, which can be activated and grow to (large) droplets under specific supersaturated conditions</u>. The problem is not how to analyse single particles (this can be done by a number of already existing instruments), but to extract the CCN out of the total set of particles and analyse only these CCN. This point will be clarified in the revised MS

3. Introduction: while there is no study to-date focusing on the chemical composition of single activated CCN, there are probably many results on the chemical composition of cloud or ice particle residues. Rather than listing the references, I suggest that the results related to chemistry compositions of SSA should be included to make the introduction more readable.

   Yes, there are several studies focusing on the chemical composition of cloud droplet or ice particles residues. We did not include these studies in our MS, as we focus on CCN. The scientific question behind our experimental setup is: which particles can be activated and what is their chemical composition. Cloud droplet residues may have undergone chemical reactions during their "life" as cloud droplets, while the CCN that can be studied with our setup are those particles that can form cloud droplets after activation.

   Further, an answer to why direct measurements of droplets are essential is also necessary.

   The focus was on activated CCN, which are of course droplets. Had these droplets been dried to their original size, they would have been too small to be analysed with the LAAPTOF, which was set intentionally to analyse only particles >300 nm to exclude unactivated (i.e. non-CCN) particles still present in the minor flow of the virtual impactor.

4. Introduction: as noted in Line 59, "The role of the contribution of organic material to SSA in remote regions", more results on the observed of the chemical composition of single SSA in the atmosphere or cloud should be included to make it more complete.

It will be added. Additionally, we will include already in the introduction that we do not analyse SSA, but nebulized (re-aerosolized) sea water samples.

5. Line 94 "…only a short time": please be specific.

The activated CCN enter the LAAPTOF definitely as droplets, as the water vapour content of the aerosol stream is definitely above the efflorescence humidities (typically around 40%).

6. Instrumentation: It is not clear enough in the text to show how to separate the particles and droplets. Even if the cut size of the virtual impactor is 1.5 micrometer, the number fraction of particles with sizes larger than this should be estimated and accounted for in such measurements. In addition, the sizes of the produced SSA should be given to evaluate the property of droplet separation.

For atmospheric particles, the number size distribution drops sharply towards the large size end. In our large data base on number size distributions measured in Vienna, concentrations of particles >1.5 µm are typically at least four orders of magnitude less than the concentrations of particles below this size.

To be precise: we do not measure SSA, but we nebulize (re-aerosolize) sea water samples in a Collison Atomizer, so we do not have real SSA. The droplets coming from the Collison atomizer are dried and then drawn into the CCN-VACES for activation. All droplets with sizes > 1.5µm resulting from the activation of these dry particles are then passed to the LAAPTOF

7. Again, how to test if the separated droplets are evaporated in the vacuum before being ionized?

Because of the construction of the LAAPTOF, such a test cannot be performed

8. Line 275: In the negative ion spectrum signs of O^- (m/z=16) and OH^- (m/z=17) correspond to water. References would be helpful here. Why were these peaks not shown in every droplet?

This interpretation is based on the paper by Neubauer et al. (1998), Neubauer et al. (1997) and Johnston (2000). In some of the individual spectra, the O^- and OH^- peaks are rather weak, which leads to their suppression in the central spectra obtained from the fuzzy clustering algorithm.

9. Figure 5-7: I do not understand why these peaks are present in the negative ions spectrum.

Does this refer to the O^- and OH^- peaks? The references for assigning O^- and OH^- to water are the studies by Johnston (2000), Neubauer et al. (1998) and Neubauer et al. (1997). In the Neubauer et al. (1997) study, the authors state that the presence of water is indicated by the presence of strong O^- and OH^- peaks.

10. Line 369: "The presence of Si^+ (m/z = 28) in the spectrum in Fig.12 might indicate a CCN not originating in the area of Vienna". Such a statement is not satisfying and does not help in the discussion.

The statement can be deleted. The main point here is that we saw fine Si-rich particles mainly in long-range transport air masses (Okada and Hitzenberger, 2001). **done**

11. Section 5.2.2: Is there only one type of SSA? This is apparently different from previous laboratory studies.

We analyse CCN originating from two different sea water samples – as stated above, we will state already in the introduction that we do not analyse real world SSA

12. Section 5.2.3: I would recommend the authors focus more on what is new about this mass spectra. Does it provide more information than those for droplet residues? Only with more validation, can the author state that such a technique would provide insights into the composition of individual activated CCN.

There is a difference between droplet residues and CCN before activation. Droplet residues have spent time in clouds and their chemical composition might have changed because of chemical reactions and / or coalescence with other cloud droplets. We look at the initial state of activated CCN. This point will be clarified in the revised MS – ***done***

C4