Review 2

General Comments

(1) - p 692 line 16: The two last sentences of the abstract are actually not clearly discussed in the body of the manuscript. Only one field sample using the PALMS shows an increase for the size of the activated particles compared to the ambient measurements. Influence of the particle size on activation has to be developed.

(2) - p 692 line 18: Could the authors explain the term "not irrelevant" regarding their measurements?

Author's response for (1) and (2)

We have updated the abstract to reflect the reviewers concerns.

The abstract now reads:

"Results from ambient measurements using this technique and AMS analysis were inconclusive, showing little chemical differentiation between ambient aerosol and activated droplet residuals, largely due to low signal levels. When employing as single particle mass spectrometer for compositional analysis, however, we observed enhancement of sulfate in droplet residuals."

(3) - p 694 line 5, 17 and 19: Authors referred to "recent studies", "other field studies" or "studies", please, provide some references.

Author's response

The reviewer makes a good point. We have reviewed some literature and have added references and discussion where appropriate. Specific updates are found below.

P 694 line 5 – 7: More recent research, … in CCN variability "(Nenes et al., 2002; Petters and Kreidenweis, 2007; Rose et al., 2010)".

Citations given in reference section.

P 694 line 17 – 19 → now p694 line 25: Several field studies have been conducted with simultaneous, parallel measurements of chemical composition and CCN activity "(Shantz et al., 2008 and 2010; Chang et al., 2010)";…

Chang, R.Y.W., Slowik, J.G., Shantz, N.C., Vlasenko, A., Liggio, J., Sjostedt, S.J., Leaitch, W.R., and Abbatt, J.P.D.: The hygroscopicity parameter (kappa) of ambient organic aerosol at a field site subject to biogenic and anthropogenic influences: Relationship to degree of aerosol oxidation. Atmospheric Chemistry and Physics, 10(11), 5047-5064, 2010.

Shantz, N.C., Leaitch, W.R., Phinney, L., Mozurkewich, M., and Toom-Sauntry, D.: The effect of organic compounds on the growth rate of cloud droplets in marine and forest settings. Atmospheric Chemistry and Physics, 8(19), 5869-5887, 2008.

Shantz, N.C., Chang, R.Y.W., Slowik, J.G., Vlasenko, A., Abbatt, J.P.D., and Leaitch, W.R.: Slower CCN growth kinetics of anthropogenic aerosol compared to biogenic aerosol observed at a rural site. Atmospheric Chemistry and Physics, 10(1), 299-312, 2010.

P 694 line 19 – 21: Alternatively, studies where… in a laboratory setting "(King et al., 2009; Shilling et al., 2007; Asa-Awuku et al., 2009)".

King, S.M., Rosenoern, T., Shilling, J.E., Chen, Q., and Martin, S.T.: Increased cloud activation potential of secondary organic aerosol for atmospheric mass loadings. Atmospheric Chemistry and Physics, 9, 2959-2971, 2009.

Shilling, J.E., King, S.M., Mochida, M., Worsnop, D.R., and Martin, S.T.: Mass spectral evidence that small changes in composition caused by oxidative aging processes alter aerosol CCN properties. Journal of Physical Chemistry A, 111, 3358-3368, 2007.

Asa-Awuku, A., Engelhart, G. J., Lee, B. H., Pandis, S. N., and Nenes, A.: Relating CCN activity, volatility, and droplet growth kinetics of beta-caryophyllene secondary organic aerosol. Atmospheric Chemistry and Physics, 9, 795–812, 2009.

(4) - p 695 section 2 "Methodology": The description of the experimental setup and its validation does not meet its requirements. It is too condensed and difficult to follow. The readability of the section would be highly improved by dividing it in several subsections (for example a general description of the different instrumentations, an exhaustive presentation of the coupling CCNc-PCVI-AMS/PALMS and a more detailed description of the different experiments conducted during the validation).

Author's response

We have improved our discussion of the experimental setup at the reviewer's suggestion. We have modified our discussion of the experimental setup to include many more details (see response to Reviewer #1). The Methodology section is now sub-divided into three different sub-sections (i.e., 2.1. Instruments, 2.2. Experimental Setup, and 2.3. Validation of Instrument Performance). We also subdivided the third section (i.e., 3.1. Laboratory Studies and 3.2. Atmospheric Measurements).

In addition, Figure 1 has been updated to remind readers that the particle count of this inset OPC is corrected for the dilution factor by the ratio of the CCNC sample flow (0.045 lpm) to sheath flow (0.45 lpm), accounting for a reduction of residual particle to initial droplet concentration by a factor of ~0.09 (1:11; Figure 1). For example, the OPC readout of 5000 cm^{-3} corresponds to an estimate of ~455 cm^{-3} residual particles passing through the CCNC.

(5) - p 699 line 22: the description of the validation procedure is the core of the presentation of a new setup. The authors solely used pure ammonium sulphate and a mixture of ammonium sulphate and PSL particles. More details are expected here, e.g. the range of the tested particle sizes and concentrations, the ratio between ammonium sulphate and PSL concentrations, the detection limit of the system, the temperature of the AMS vaporizer during the experiments (600_C or higher)? Did the authors test different mixtures of aerosol? As PSL is not relevant for the atmosphere, mixtures of different organic compounds with known hygroscopic properties should be expected and could, for example provide similar profiles to those presented in Figure 2.

Author's response

We have improved our description of the test mixtures used to validate the experiments. In addition, at the suggestion of both reviewers, we have performed an additional validation experiment in which we demonstrate separation of ammonium nitrate and adipic acid particles. The adipic acid particles have hygroscopic properties that are similar to laboratory-produced SOA. We feel this additional test should address the reviewer's concerns.

P 699 line 22-24 now reads:

"In the second validation experiment two particulate flows, one of ammonium sulfate "(0.00076 M)" and the other of PSLs "(100 nm diameter)", were produced by two identical atomizers. Two identical DMAs "selecting 100 nm diameter particles for ammonium sulfate and PSL" were used to produce monodisperse flows of the same rate that were combined."

P700 line 10, we added:

"To demonstrate our ability to separate more atmospherically relevant aerosol populations using this technique, we conducted a similar calibration experiment utilizing an external mixture of ammonium nitrate (0.0015 M) and adipic acid (0.00082 M). As before, an external mixture of monodisperse ammonium nitrate (100 nm mobility diameter) and adipic acid (100 nm mobility diameter) particles were generated, mixed, and passed into the CCNC/PCVI setup. Results for this experiment are shown in Figure 6. Period I shows AMS analysis of the particle mixture entering the CCNC. During Period II the combined particle flow was passed through the CCNC and PCVI when the saturation, 0.5%, was sufficient to activate droplets from both particle types (see Figure 2). However, as indicated by the AMS signal trace, only one population of droplets (ammonium nitrate) grow to sufficient size to pass through the PCVI. During Period III the saturation, 1%, was sufficient to activate droplets of both particle types to a size large enough to pass the PCVI and particles are detected in the sample flow (Panel III). Thus, we were able to separate more atmospherically relevant organic species from inorganic salts, enhancing the potential of this technique to revel CCN-active aerosol composition and mixing state."

P702 line20, we added:

“Finally, we successfully demonstrated that the CCNC/PCVI apparatus was able to separate an external mixture of ammonium nitrate particles and soluble organic (adipic acid) particles with similar CCN activity as SOA particles.”

(6) - p 700 section 3: A short presentation of the sampling place is needed here. Is it a rural, suburban, or urban station? The AMS sample presented was performed on 20.10.2010 and the PALMS one was performed on 9.11.2010; so did the system continuously worked during this period? It would be more informative to illustrate the field section by at least two different examples for each aerosol mass spectrometer. This would also be helpful for the discussion of the AMS sensitivity and the influence of the chemical composition on particle activation.

Author’s response

We have added details on the ambient sampling to address the reviewers concerns.

P 700 line 13

“… were conducted in Richland, WA to gain insight…” now reads:

“…the semi-urban town of Richland, WA (home to the Pacific Northwest National Laboratory) to gain insight…”

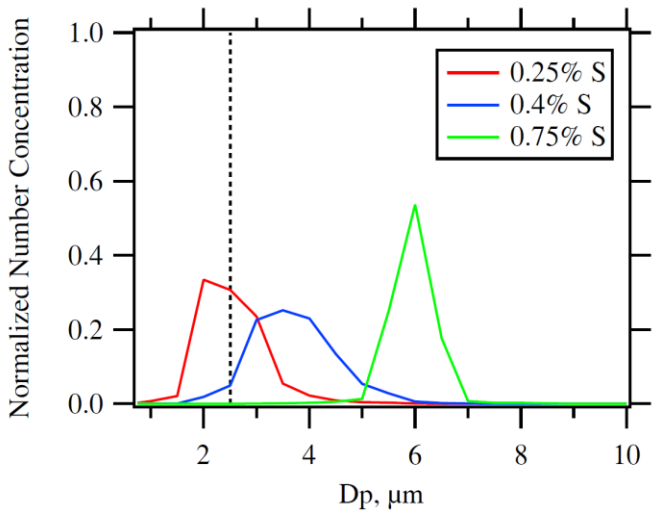
The system did not run continuously over this period. Instead, one day was dedicated to AMS experiments and another to PALMS experiments with the two mass spectrometers in different locations in the same building (i.e., the CCN/PCVI was moved between the two samples). Our intention for these experiments was to demonstrate the ability to perform studies with both mass spectrometers and we intend to use both simultaneously in the future. AMS sensitivity is discussed in p697 line 9, p 700 line 28- , p 701 line 5 – 7, and p703 line 7.

(7) - p 700 line 23: Could the authors explain the reason for a supersaturation of 0.4% (instead of 0.5%, as mentioned in the rest of the manuscript) during the AMS measurements? Why the authors did not present any results at a supersaturation of 0.75%?

Author’s response

We employed 0.4% for ambient measurement because this supersaturation achieves [1] >98% of incoming aerosol (Figure provided below) and [2] better transmission efficiency compared to higher supersaturations (i.e, as droplet size gets bigger, particle loss rate increases) (Boulter et al., 2006; Kulkarni et al., 2011).

We added “(>98% activation)” after “A supersaturation of 0.4% produced 2255 droplets cm^{-3}” to clarify why we used 0.4% S instead of 0.5% S.



(8) - p 700 line 25: The authors indicate an AMS detection limit during ambient measurements of 0.1, 0.03, 0.02 and 0.15 µg m-3 for organics, nitrate, sulphate and ammonium, respectively. As mentioned in the manuscript, the results presented in Fig. 6 II-b are very close to these values. In such conditions, it appears to be extremely difficult to integrate the PCVI dilution ratio and to deduce any influence on activation from this. This point should be discussed in more details.

We have acknowledged this point in the manuscript in detail. In addition, we have added a section of text providing recommendations to overcome these limitations related to the low S/N ratio for AMS sampling. We note that single particle techniques are not limited in the same way as the AMS.

Specific Comments

(1) - p 692 line 2: please add CCNC.

Corrected.

(2) - p 692 line 5: please add AMS and PALMS.

Corrected.

(3) - p 696 line 16: please put 18.2 M cm in brackets.

Corrected.

(4) - p 696 line 27: The authors report that the transmission efficiency of the AMS aerodynamic lenses was nearly 100% in the range 70-500 nm while in the conclusion (p702 line 24) they indicate a range of 70-1000nm.

The text on p 696 is rigorously correct; the AMS transmits particles in the range 70-500nm with nearly 100% efficiency but particles up to 2000nm are transmitted with lower efficiency.

Therefore, some but not all particles in the range 500- 2000nm are sampled. The AMS 50% cut size is roughly 1 um at the high end. By most definitions of cut size (e.g., EPA), therefore, the AMS is approximately a PM_1 instrument. The conclusion on page 702 was meant to paraphrase this information.

(5) - p 696 line 24: reference Jayne et al. 2000 is missing in the references section.

Corrected.

(6) - p 699 equation 1: Could the authors describe a bit more this equation and the origin of the different numbers?

Author's response
We have improved our description of the equation. Specific changes are below:

P 698 line 29 – P 699 line 11

"The number density of these particles… by a factor of ~1:29 (i.e., 0.034)" now reads:

"Assuming all the particles are fully activated into droplets larger than the PCVI cut-size the number density downstream of PCVI, CCN_{CPC} (cm^{-3}) can be estimated as:

$$CCN_{CPC} = CCN_{OPC} \cdot \delta_{CCNC} \cdot \delta_{PCVI} \cdot \varepsilon_{PCVI} \cdot \tau \qquad [3]$$

where CCN_{OPC} is the CCN concentration measured by the CCNC OPC (cm^{-3}), δ_{CCNC} is the sample flow dilution factor inside the CCNC ($0.09 \cong \frac{0.045\ lpm}{0.45\ lpm + 0.045\ lpm}$) which accounts for the ratio of the sample to sheath flow, δ_{PCVI} is the sample flow dilution factor prior to entering PCVI ($0.05 = \frac{0.5\ lpm}{9.5\ lpm + 0.5\ lpm}$) which accounts for the ratio of the sample to supplemental flow, ε_{PCVI} is the PCVI enhancement factor ($10 = \frac{10\ lpm}{1\ lpm}$) which accounts for the ratio of sample to input flow, and τ is the PCVI efficiency (0.75) which accounts for a 25% particle loss in the PCVI (Kulkarni et al., 2011). Equation 3 implies that the total transmittance factor ($0.034 \cong \frac{CCN_{CPC}}{CCN_{OPC}}$) for this DMT CCNC-PCVI experiment results from a combination of the dilution factor ($0.045 = \delta_{CCNC} \cdot \delta_{PCVI} \cdot \varepsilon_{PCVI}$), which is the ratio of CCN incoming flow of 0.045 lpm to the PCVI output flow of 1 lpm, and τ. Particle numbers are reduced by the flow dilution of the CCNC (δ_{CCNC}) while the PCVI dilution factor is largely offset (i.e., to 0.5) by its virtual impaction (i.e., particle concentrator) function (Kulkarni et al., 2011)."

P 695 line 20

The following sentence is now added after "… using an integrated optical particle counter (OPC)."

“We note that the particle count of the integrated OPC is automatically corrected for sheath flow dilution factor of 0.09 given above. For example, the OPC readout of 5000 cm^{-3} corresponds to an estimate of ~455 cm^{-3} particles passing through the CCNC.”

(7) - p 699 line 26: it is before the CCNC not before the PCVI.

Corrected.

(8) - p 700 line 19 and p 701 line 13: please, used the same time unit (Pacific Daily Time or Pacific Standard Time).

Corrected.