

## Review 1

### Specific Comments:

1) The major limitation with the current study is the extremely low transmission factor of the CCN residuals (only 3%! ). Consequently, large CCN concentrations ( $\sim 9000 \text{ cm}^{-3}$ ) are required to obtain merely qualitative composition results. The organic and inorganic mass loadings for ambient aerosol shown in Figure 6-II have extremely low signal-to-noise, which makes drawing any compositional conclusions difficult. It may be unreasonable to expect this technique to perform well in very clean, pristine environments, but certainly it should work with total CCN concentrations as low as  $500\text{-}1000 \text{ cm}^{-3}$ . I think this is achievable and suggest the following (and highlight some potential problems with each suggestion that should be discussed in the manuscript):

A) The manuscript references a DMT Model 200 instrument, so I'm assuming that this is a dual-column design. If possible, I would suggest using both columns in the dual-column CCNC (operating at the same supersaturation) to feed the inlet to the pumped-CVI, thereby reducing the particle-free supplemental flow needed. This will introduce some supersaturation uncertainty because of slight differences between the two columns, but I would expect these differences to be minor for a well-calibrated system.

B) Increase the total CCN flow rate to, e.g., 1 lpm. This will reduce the outlet droplet size because the particle residence time will decrease from  $\sim 25$  seconds to  $\sim 12$  seconds. Depending on how much this decreases the droplet size, the minimum supersaturation required to produce droplets large enough to penetrate the pumped-CVI may increase. While a supersaturation of, say, 0.6% or greater may be unrealistic for many weakly forced clouds, the technique would still be useful in assessing aerosol mixing state and the composition of water-soluble species in the aerosols feeding these clouds.

C) Decrease the CCNC Sheath:Aerosol flow ratio. Currently, the manuscript uses a Sheath:Aerosol flow ratio of 10:1, but this could be decreased to 5:1 or even lower with modest broadening of the CCN-supersaturation transfer function. I would think that the beneficial gain in counting statistics would more than outweigh the increased supersaturation uncertainty.

D) Modify the pumped-CVI design to achieve the same droplet size cutoff but with lower flow rates. I suspect that this would require a large amount of work reengineering the design and constructing a new pumped-CVI, which would be unreasonable to request of the authors for this manuscript. However, I would like to see some discussion in the manuscript on the feasibility of this approach in improving instrument performance, which could then motivate future work/studies with this technique.

E) Decrease the pumped-CVI sample flow to the CPC/PALMS/AMS, if possible, to increase the enhancement factor. Adopting suggestions A-C: Operating both columns at 1 lpm (CCNC Sheath:Aerosol = 4:1) and combining their flows yields a CCNC output flow of 2 lpm. Only 8 lpm of supplemental flow is then required.

Let  $T = (Q_{\text{aerosol}}/Q_{\text{CCNC}}) \cdot (Q_{\text{CCNC}}/Q_{\text{PCVI}}) \cdot \eta \cdot R_e$   
where

$Q_{\text{aerosol}}$  is the CCNC sample aerosol flow (0.4 lpm from combined columns)  
 $Q_{\text{CCNC}}$  is the CCNC flow (2 lpm from combined columns)  
 $Q_{\text{PCVI}}$  is the pumped-CVI inlet flow (10 lpm)  
 $\eta$  is the pumped-CVI efficiency (0.75)  
 $R_e$  is the pumped-CVI enhancement ratio (10)  
 So  $T = 0.3$ , which is a ten-fold improvement over the previous transmission factor of 0.03.

Author's response

The authors wish to thank both reviewers for their extensive comments and thorough analysis which we believe makes this a much stronger paper. In particular we highly appreciate the prior comments/suggestions by Reviewer 1 on means to improve this technique. Our general response to these points is that we have now included these possible means of improvement in a new section of the text (Future Studies and Technical Improvements). We feel it is important to point out that the overlying concept of this paper is the use of readily available techniques to determine the composition of the aerosol which forms CCN; that is to say the technique we present uses largely commercial equipment without major modification. The aforementioned suggestions will almost doubtless improve performance but at the expense of equipment 'stability' (i.e., the instruments would no longer be used in their typical performance envelope). We believe this is an important limitation of these changes. Our decision is therefore to present the data for the 'unaltered' equipment. At the suggestion of the reviewer, we have added a section discussing possible modifications/improvements to the experimental apparatus to the paper.

Furthermore, the authors would like to point out that the particle count of the inset OPC attached to the DMT CCNC 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 CCN concentration by a factor of  $\sim 0.09$  (1:11). For example, the OPC readout of  $5000 \text{ cm}^{-3}$  corresponds to an estimate of  $\sim 455 \text{ cm}^{-3}$  residual particles passing through the OPC. Thus, particle numbers are explicitly reduced by the flow dilution inside the CCNC while the perceived dilution by the PCVI makeup flow is largely offset because the PCVI acts as a particle concentrator (Kulkarni et al., 2011).

We did undertake experiments per the reviewers suggestions but attempts to utilize both columns were unsuccessful. A significant reduction in the total transmittance factor ( $\frac{CCN_{CPC}}{CCN_{OPC}} \sim 0.006$ ) was measured for the experiment using both columns in the dual-column CCNC (operating at 0.75% S). The issues involved in utilizing two columns are collecting the droplets and focusing them to the center of the apparatus (i.e., achieving isokinetic mixing of the CCNC output flow and the supplemental flow) without loss on the tubing and CVI walls and these led to the lower transmittance. We note that future work on achieving better detection limit using our CCNC-CVI system will include altering the total dilution factor, which is the ratio of CCN incoming flow of 0.045 lpm to the PCVI output flow of 1 lpm (i.e., essentially, reducing output flow will enhance transmittance efficiency) as pointed out by reviewer in (1E), rather than altering CCNC sample-sheath flow rate (1C) or modifying physical configuration of PCVI (1D). These points are now addressed in section 4 "Future studies".

Based on our efforts to address the collective comments of the reviewer, we have updated our methodology section as well as equation 1 (now equation 3) to clarify the origin of multiple factors (e.g., dilution factors, etc.):

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:

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

where  $CCN_{OPC}$  is the CCN concentration measured by the CCNC OPC ( $cm^{-3}$ ),  $\delta_{CCNC}$  is the sample flow dilution factor inside the CCNC ( $0.09 \cong \frac{0.045 \text{ lpm}}{0.45 \text{ lpm} + 0.045 \text{ lpm}}$ ) which accounts for the ratio of the sample to sheath flow,  $\delta_{PCVI}$  is the sample flow dilution factor prior to entering PCVI ( $0.05 = \frac{0.5 \text{ lpm}}{9.5 \text{ lpm} + 0.5 \text{ lpm}}$ ) which accounts for the ratio of the sample to supplemental flow,  $\varepsilon_{PCVI}$  is the PCVI enhancement factor ( $10 = \frac{10 \text{ lpm}}{1 \text{ lpm}}$ ) which accounts for the ratio of sample to input flow, and  $\tau$  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  $\tau$ . Particle numbers are explicitly reduced by the flow dilution inside the CCNC while the perceived dilution by the PCVI makeup flow is largely offset because the PCVI acts as a particle concentrator (Kulkarni et al., 2011).”

P 695 line 20

The following sentence is now added after “... using an integrated optical particle counter (OPC) in the CCNC.”

“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  $5000 \text{ cm}^{-3}$  corresponds to an estimate of  $\sim 455 \text{ cm}^{-3}$  particles passing through the CCNC.”

2) The purported goal of this study is to validate the CCN-PCVI-AMS/PALMS technique using laboratory studies (p. 695, lines 2-4), and this is accomplished using an external mixture of ammonium sulfate and PSL aerosols. Sulfate peaks are used to show that the ammonium sulfate aerosols are CCN-active, while the missing (organic?) peak at  $m/z$  104 is used to show that PSL aerosols are not CCN-active. Probably due to the low transmission efficiencies discussed previously in this review, only qualitative composition information is presented (i.e., sulfate is present, PSL is not). While this nicely shows that the pumped-CVI is able to separate the CCNC droplets from the interstitial aerosols, I would like to see a more thorough validation that shows quantitative

compositions of the CCN droplet residuals. Quantitative compositions are important and will really unlock the potential of this technique in elucidating water-soluble aerosol composition and mixing state.

Additionally, while some organics are not CCN-active, many are, and I would like to see the authors use a soluble organic compound as well to validate the technique.

A low-molar-mass dicarboxylic acid (C2-C6) or similar compound would seem to be preferable given that the hygroscopicities of these compounds have been previously published. In addition to the experiments currently presented in the manuscript, I suggest the following to validate the technique:

A) CCN concentrations should not be greater than  $\sim 500\text{--}1000\text{ cm}^{-3}$ , which is more reasonable for many ambient environments. Furthermore, Latham and Nenes (2011) have shown that high CCN loadings in the CCNC can deplete enough water vapor to affect the instrument supersaturation and outlet droplet sizes. They find this effect starts to become important around  $1000\text{--}2000\text{ CCN cm}^{-3}$  and exceeds experimental uncertainty above  $5000\text{ CCN cm}^{-3}$ . Keeping CCN concentrations below  $2000\text{ cm}^{-3}$  (and preferably below  $1000\text{ cm}^{-3}$ ) avoids this issue.

Author's response

The review makes a good point in indicating that the condensational depletion of water vapor upon the growing CCN alters stability of supersaturation in the DMT-CCNC, e.g. accounting for  $\sim 10\%$  at  $5000\text{ CCN cm}^{-3}$  (Latham and Nenes, 2011). Although the depression in supersaturation and droplet size is simply correctable for larger CCN concentrations (Latham and Nenes, 2011), the goal of the experiment was to demonstrate the ability of the CCNC/CVI setup to separate particles based on their CCN activity. Therefore, in the tradeoff between achieving adequate signal-to-noise ratio (S/N) for our validation experiments and precisely quantifying the saturation field inside the CCNC, we chose to favor higher S/N.

To address the reviewers concerns, we now state that we did not account the effect of condensational depletion. We have added the following sentence in p 699 line 13:

“We note that the effect of condensational depletion of water vapor due to the high number of CCNC may reduce the effective saturation in the CCNC column; however, it should not affect the compositional analysis of the droplet residual (Latham and Nenes, 2011).”

B) Provide quantitative sulfate and organic mass loadings for an internally-mixed, equimass mixture of ammonium sulfate and a soluble organic. Does the AMS mass fraction of the droplet residuals agree with the mass fractions of each component in the atomizer solution?

The purpose of this manuscript was to demonstrate that commercial instrumentation can be used to separate and chemically analyze activated from unactivated droplets. There is extensive data in the literature validating the performance of the AMS in quantitatively determining the mass fraction of mixed organic/inorganic components. Addition of the CCNC/CVI would simply lower the total aerosol signal by a dilution factor ( $\sim 0.071$  in signal counts,  $\sim 0.034$  in

concentration). What is more important is assessing whether the mass spectrometers can verify the success of the CCNC/CVI technique to separate active and inactive droplets. We believe our current data indeed demonstrate this. To address the reviewers concerns have improved our discussion of the quantitation of the droplet residuals in our manuscript. The measured mass of the sulfate recovered from the activated CCN droplets (i.e., in Figure 5, panel IIIA) agrees well with the theoretically calculated mass concentration after accounting for the dilution factors and the PCVI transmission factor. The PSL particles are not expected to activate (i.e., theoretical signal is below detection limit) and the AMS signal characteristic of the PSL particles is indeed below the detection limit. It is impossible to prove the non-existence of signal; one can only claim that the signal was below detection limit. Therefore, we feel the data presented address the reviewers concerns.

In addition, we have performed additional experiments demonstrating the ability of the technique to separate inorganic from soluble organic droplets in response to the concerns of this reviewer and Reviewer 2. Note, that our new experiments utilize external mixtures of the particles. In this case, the concentration of the analyte in the atomizer solution is not a good metric for predicting the mass loading of a narrow particle size cut generated from the solutions. Instead, what is instructive is to quantitatively compare the composition of the particles entering the CCNC to the composition of droplets passed by the CCNC/PCVI.

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 reveal 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.”

C) Use single-particle PALMS spectra to classify particles in an externally-mixed aerosol population containing ammonium sulfate particles and soluble organic particles. Is the external mixture detectable by the PALMS downstream of the CCNC-PCVI?

Author's response

The answer to the question in the second sentence is yes. While PALMS was not used during the initial calibration/proof-of-concept studies, it is able to determine particle composition on the single particle level. The text has been expanded in both the methods and results section to clarify this. Specifically:

P697 line 22 now reads:

“Single particle mass spectrometers such as PALMS are not inherently quantitative due to the different ionization efficiencies of common atmospheric aerosol components. The physical state of the aerosol components also affects the mass spectrum. One example is that different processes are involved in ionizing the same weight percent of an inorganic salt in solution in an aqueous aerosol versus in a crystalline form bound within a mineral dust particle. Collectively, these different ionization thresholds and processes are termed ‘matrix effects’ and limit the use of single particle instruments for quantitation. Trends in ion current (i.e., detector signal) can be used as an indication of relative abundance and particle fractions on the order of 1% are detectable (Cziczo, 2010 and references therein).”

and

p701 line 23 we now added:

“The normalized signal presented in Figure 8 is a count of detected ions and this is dependent on the specific particle matrix. As described in the instrumental section, PALMS provides universal detection of atmospheric particle components at a qualitative level. Trends of composition are given for the ambient and CCNC/PCVI periods.”

P700 line10 we added:

“The average mass spectra of ammonium sulfate and PSL measured by the PALMS are shown in Supplemental Figure 1.”

3) The experimental setup in Figure 1 and associated discussion in the text nicely shows the overall experimental setup; however, more detail should be included that shows: A) The details of the CCNC and PCVI connection. Since the DMT Model 200 is referenced, it sounds like only one of two columns is currently being used. Where is the connection to PCVI made? After traversing the column, the aerosol flow passes through the OPC and is then sent to a chiller and pump. Presumably, the connection is made after the OPC and prior to the chiller and pump, and investigators wishing to adopt this technique would need to make this minor modification to the CCNC. Also,

what is the length of the transfer tube from the CCNC OPC to the PCVI? Are there any special concerns with regard to wall losses, accumulation of water on tube walls, and droplet coalescence? A more detailed schematic of the CCNC (similar to Moore et al., 2010) and the PCVI (similar to that of Slowik et al., 2011) showing these connections seems warranted. Additional details of the inner workings of the atomizers, DMAs, CPC, AMS, and PALMS are probably unnecessary as presumably they are unmodified. B) The locations of pumps, blowers, gas cylinders, valves, critical orifices, filters, etc. It's unclear how the flow is driven through the CCNC since, presumably, the internal pump has been bypassed.

Author's response

Reviewer makes a good point. P 696 line 11-17 "A particle-free humidified... prior to the PCVI" now reads:

"Connection from the CCNC to the PCVI is made directly after the CCNC-OPC. The internal chiller and pump of the CCNC are bypassed to direct droplets to the PCVI. A 9.5 lpm particle-free humidified "supplemental flow" was added to the ~0.5 lpm CCNC flow in order to produce the required PCVI input flow, while preventing droplet evaporation. The supplemental flow was humidified by passing it through Nafion tubing (Perma Pure, Toms River, NJ, PD Series) immersed in ultrapure water (18.2 MΩ cm). Droplets formed in the CCNC were passed through a 0.34 m length of stainless tubing with a 4 mm inner diameter tube in the centerline of a 15 mm tube containing the supplemental flow. The tubing diameters were chosen to achieve isokinetic mixing of the CCNC output flow and the supplemental flow (i.e., the activated droplets are focused to the centerline of the tubing under laminar flow conditions)."

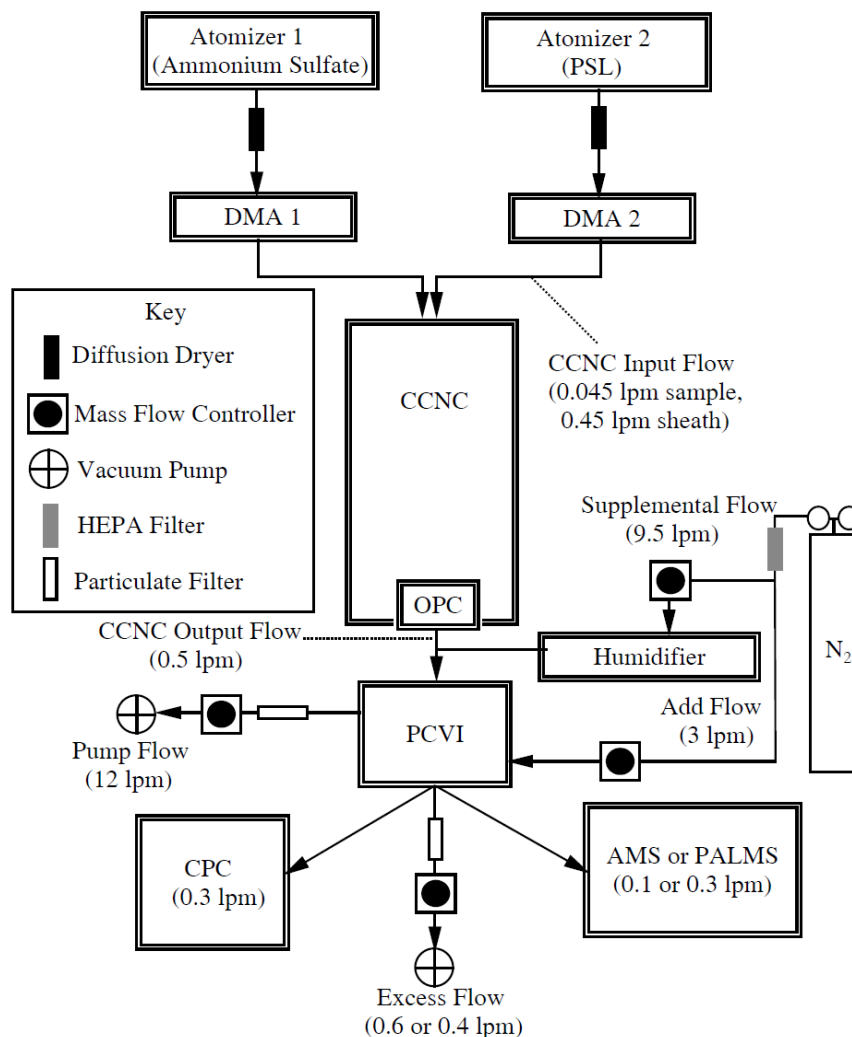
Regarding the concerns of particle loss in the system, we use lumped transmittance parameter ( $0.034 \cong \frac{CCN_{CPC}}{CCN_{OPC}}$ ), which is in a good agreement with our measurement without any additional particle loss. Thus we believe further quantification of particle loss in line/connections is unnecessary.

P699 line10 now reads:

"During the period of time given in Figure 4b the average CCN concentration measured by the CCNC was 9365/ cm<sup>3</sup>. After the PCVI, we measure particle concentrations of 331 /cm<sup>3</sup>, which compares well with expected number of particles (319 /cm<sup>3</sup>) calculated as described above. Thus, the data indicate that ~100% activation was achieved and that droplets were collected and transferred to the PCVI with no measurable loss or coagulation."

Figure 1 is updated based on the reviewer's suggestions. Further details of flow path and detailed description of the PCVI beyond materials provided in our manuscript are available in elsewhere (Boulter et al., 2006; Kulkarni et al., 2011) as mentioned in section 2.1.





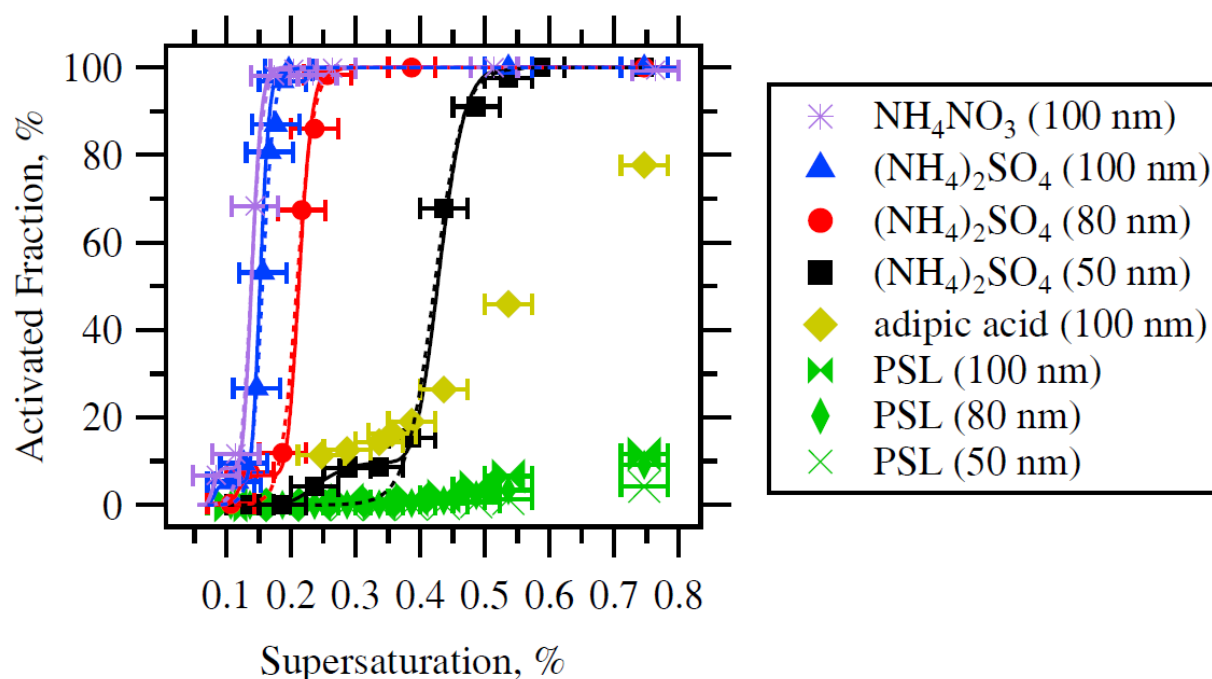
**Figure 1 :** Schematic of the experimental setup. The diffusion dryer ensured a relative humidity below 5% upon entry to the DMA.

4) While Figure 2 succeeds in showing that ammonium sulfate aerosols are CCN-active and PSL aerosols are not, I find the comparison between measured and modeled curves to be confusing. This is because the model is not described in the text (other than to say that  $\kappa_{AS} = 0.61$ ) and because the shapes of the measured and modeled curves look dissimilar. Presumably the shape of the modeled curves comes from the DMA transfer function, which creates the doubly-charged hump and the slope of the curve, but this should be explained more clearly. Also, the fraction of doubly charged particles should not be invariant with size. The authors may also wish to dispense with having the separate modeled curve and just correct the data for the multiply-charged particles, fit the curve with a sigmoidal function, and compare the inflection point to that expected from Kohler theory. Finally, it would be good to have the range of supersaturations in Figure 2 correspond to the range of supersaturations in Figures 3-4 (i.e., up to 0.75%) to show that PSL do not act as CCN even at the largest supersaturations.



Author's response

The review is correct in pointing out the effect of the doubly charged particles on the CCN activation curves. At the reviewers suggestion, we have simply fit the single charged portions of the activation curves separately, as was suggested by (Rose et al., 2008). Further, we suspect  $>5000 \text{ cm}^{-3}$  of CCN concentration used in our calibration caused a loss in sharpness in efficiency curve [fortunately minimum impact on computation of critical supersaturation ( $\Delta S$  during the calibration remains within  $\pm 0.04\%$ ) and our study goal; please refer to the specific comment 2(A)]. We have re-conducted the calibration measurement with a diluter in line and updated Figure 2 (shown below). Our diluter contained two split lines, namely aerosol feeding line made of 1/4 inch (inner diameter) stainless steel tubing coupled with a Swagelok® needle bulb to adjust the apparent aerosol concentration and a bypass venting line through a HEPA filter. Through diluter, the total CN concentration was diluted to  $<5000 \text{ cm}^{-3}$  to prevent the condensational depletion of water vapor upon the growing CCN in CCN column uncertainty (Latham and Nenes, 2011). We note that  $5000 \text{ cm}^{-3}$  corresponds to 10% change in supersaturation, which is within instrumental uncertainty (Rose et al., 2008).



**Figure 2 :** Fraction of aerosols active as CCN as a function of supersaturation. The size and composition of the aerosol is differentiated by the shapes given in the legend. Dashed lines represent sigmoid fits to the single charged portions of the activation curves following Rose et al. (2008). Solid lines represent activation model of single and doubly charged components. The x-axis error bar represents  $\Delta S$  of  $\pm 0.04\%$ .

Figure 2 caption now reads:

“Figure 2 : Fraction of aerosols active as CCN as a function of supersaturation. The size and composition of the aerosol is differentiated by the shapes given in the legend. Dashed lines represent sigmoid fits to the single charged portions of the activation curves following Rose et al. (2008). Solid lines represent activation model of single and doubly charged components. The x-axis error bar represents  $\Delta S$  of  $\pm 0.04\%$ .”

Other corrections to respond the reviewer’s comment and clarify our calibration method include:

P698 line 1-16 now reads:

“Calibrations were performed with monodisperse particle sizes ranging from 50 – 100nm. Activation curves were generated by scanning the CCNC supersaturation (0.07 to 0.75%) while comparing the number of activated droplets counted by the CCNC OPC to the total number of particles counted by a CPC (TSI 3775). By following Rose et al. (2008), the calibrated supersaturation was then calculated from the measured critical supersaturation ( $S_{crit}$ ; where 50% of the single charged particles are CCN active), the known particle diameter ( $D$ ), and the literature value of the ammonium sulfate hygroscopicity parameter ( $\kappa$  of 0.61; Petters and Kreidenweis, 2007). Specifically, to determine the calibrated saturation, the portion of the activation spectrum corresponding to the singly charged particles was fit with the formula:

$$\left(\frac{S_{crit}}{100} + 1\right) = \exp\left(\frac{4A^3}{27 \cdot \kappa \cdot D^3}\right)^{\frac{1}{2}} \quad [1]$$

with

$$A = \frac{4\sigma_w M_w}{RT \rho_w} \quad [2]$$

where  $\sigma_w$  is the surface tension of water ( $0.072 \text{ J m}^{-2}$ ),  $M_w$  and  $\rho_w$  the water molecular weight ( $0.018 \text{ kg mol}^{-1}$ ) and density of water ( $997 \text{ kg m}^{-3}$ ),  $R$  the universal gas constant ( $8.3 \text{ J K}^{-1} \text{ mol}^{-1}$ ), and  $T$  the air temperature ( $25^\circ \text{C}$  for laboratory measurements),  $\kappa$  the hygroscopicity of the aerosol particles (Petters and Kreidenweis, 2007), and  $S$  the measured supersaturation. Calibrations before, during, and after the experiments agreed in saturation to within  $\pm 0.04\%$  indicating that the CCNC was stable during the entire project and validating the performance of the CCNC.

Figure 2 shows the measured activation curves for the test particle species employed in CCNC/CVI validation experiments. Modeled CCN activation curves derived from the  $\kappa$ -Köhler model for ammonium sulfate (assuming  $\kappa$  of 0.61 at  $25^\circ \text{C}$ ) and ammonium nitrate (minimum 99.0%, Sigma-Aldrich;  $\kappa$  of 0.67 at  $25^\circ \text{C}$ ) are also plotted (Petters and Kreidenweis, 2007). Polystyrene latex (PSL) spheres (Duke Scientific, Palo Alto, CA) and adipic acid (99.6-101.0%, Riedel-de Haën) were specifically chosen for a surrogate of hydrophobic organics and secondary organic aerosol ( $\kappa$  of 0.096; Kreidenweis and Petters, 2007), respectively. We note that previous observations suggest that  $\kappa$ -Köhler theory is applicable to atmospheric aerosol that is characterized by  $0.1 < \kappa < 0.9$  (Petters and Kreidenweis, 2007). Since hygroscopicity parameters of adipic acid and PSL are  $< 0.1$  due to their solubility-limitation ( $V_{solute}/V_{water} < 0.1$ ),  $\kappa$ -Köhler model for these compounds are not shown in Figure 2 (Petters et al., 2009b). The activated fraction appearing as a plateau at lower supersaturations corresponded to larger, doubly charged particles with an equivalent mobility diameter as the single charged particles (e.g., selecting a

mobility diameter of 80 nm in the DMA results in transmission of particles with nominal geometric diameters of 80 nm and 117 nm). The size distributions of singly and doubly charged particles were measured by the SMPS. It should be noted that higher orders of multiply charged particles than +2 charges were neglected due to their small population in this study.”

Although this is not the main focus of this paper (therefore not included in text), we also point out that the modeled CCN activation curves derived from the  $\kappa$ -Köhler model for ammonium sulfate (assuming  $\kappa$  of 0.61 at 25 °C) and ammonium nitrate ( $\kappa$  of 0.67 at 25 °C) are also plotted as solid lines in Figure 2 (Petters and Kreidenweis, 2007). The activated fraction appearing as a plateau at lower supersaturations corresponded to doubly charged particles (Rose et al., 2008) (e.g., 117 nm mode of doubly charged component on an electric mobility equivalent to 80 nm particles of +1 charge selected by DMA in Figure 2). The size distributions of singly and doubly charged particles were measured by the SMPS. To accurately model an activation curve integrating singly and doubly charged component, critical diameter (where 50% of polydisperse aerosols are activated at given supersaturation),  $D_{crit(S)}$ , was first calculated. Then, activated CCN concentration at a given supersaturation ( $CCN_{model}$ : sum of particles in all bins) was consequently estimated by incrementally summing the CN number concentrations from the SMPS’s upper bin ( $j = 110^{th}$  bin) downward until the computed  $D_{crit(S)}$  was realized. For instance, the following cumulative criteria are used to fit activation model:

$$\sum_{i=D_{crit(S)}}^{j=110} CN_{i(S)} \cong \sum_{i=1}^{k=20} CCN_{i(S)}$$

$CCN_{model}/CN_{SMPS}$  (calculated for incremental step of  $S$  by 0.1) was then compared to the measured activated fractions.

P698 line 6 – we now added:

“Polystyrene latex (PSL) spheres (Duke Scientific, Palo Alto, CA) and adipic acid (99.6-101.0%, Riedel-de Haën) were specifically chosen for a surrogate of hydrophobic organics and secondary organic aerosol ( $\kappa$  of 0.096; Kreidenweis and Petters, 2007), respectively. We note that previous observations suggest that  $\kappa$ -Köhler theory is applicable to atmospheric aerosol that is characterized by  $0.1 < \kappa < 0.9$  (Petters and Kreidenweis, 2007). Since hygroscopicity parameters of adipic acid and PSL are  $< 0.1$  due to their solubility-limitation ( $V_{solute}/V_{water} < 0.1$ ),  $\kappa$ -Köhler model for these compounds are not shown in Figure 2 (Petters et al., 2009b).”

Also, please clarify in the text how the instrument superaturation was calibrated (e.g., using the thermal-resistance model of Lance et al., 2006, following one of the empirical methods detailed in Rose et al., 2008, or some other method).

Author’s response

P698 line 3 – we now added:

“Calibrations were performed with monodisperse particle sizes ranging from 50 – 100nm. Activation curves were generated by scanning the CCNC supersaturation (0.07 to 0.75%) while comparing the number of activated droplets counted by the CCNC OPC to the total number of particles counted by a CPC (TSI 3775). The calibrated supersaturation was then calculated from the measured critical supersaturation, the known particle diameter, and the literature value of the ammonium sulfate hygroscopicity parameter (0.61; Petters and Kreidenweis, 2007; Rose et al., 2008). Calibrations before, during, and after the experiments agreed in saturation to within  $\pm 0.04\%$  indicating that the CCNC was stable during the entire project.”

P695 line 10 error:

0.07-0.5%  $\rightarrow$  0.07-1%

5) While this is the first time that a pumped-CVI has been coupled to a commercial CCN instrument to study water-soluble component of aerosol, there is past work in this area that should be referenced in the introduction. Ji et al. (1998) developed a "CCN Remover" to study interstitial aerosols that did not act as CCN. In the design, aerosols are exposed to a specified supersaturation in a thermal diffusion chamber, and particles that form droplets gravitationally settle out of the fluid streamline and are deposited to the bottom wall, which enables subsequent characterization of the interstitial aerosol. Osborn et al. (2008) extended the design of Ji et al. by incorporating a second chamber with a slightly higher supersaturation where particles not removed in the first chamber could activate to form droplets and be separated to a different streamline. Called the "Differential Activation Separator", this design of Osborn et al. enables characterization of both the interstitial aerosol and the cloud droplet residuals, and seems very relevant for this work. Finally, the introduction should clearly differentiate this study from that of Slowik et al. (2011) beyond the mere substitution of the DMT CCNC for the thermalgradient diffusion chamber.

Author's response

We thank the reviewer for this useful reference and have added Slowik et al. (2011) and Osborn et al. (2008) in the introduction. We note that although relevant and now referenced Ji et al. (1998) and Osborn et al. (2008) did not present any chemical composition analysis of activated CCN in their work; therefore, we feel detailed discussion of DAS and CCN remover is not suitable and necessary in our current manuscript. We also thank the reviewer for the comment regarding the work of Slowik et al. which was submitted simultaneously with this manuscript. We regret that specific information was not available when our paper was submitted but we intentionally left a 'placeholder' that could be expanded once Slowik et al. was available and appreciate being able to do this per this point.

P 695 line 5: we added:

“To the best of our knowledge this is the first time a commercial CCNC has been coupled to a CVI and mass spectrometer to study CCN-active aerosol chemistry, and we are aware of only one other such instrumental combination using a custom built CCNC (Slowik et al., 2011).”

P694 line 25: we added:

“Thus, there is a surprisingly lack in direct measurement of CCNC formed droplet composition to date (Osborn et al., 2008; Slowik et al., 2011).”

#### Specific and Technical Comments (by line number):

p. 693, lines 8-10: The statement "The vapor pressure over a small droplet is always larger than that over a planar water surface due to its curvature..." is incorrect because of the solute effects discussed in the next sentence. This statement is true only for pure water droplets, which do not exist in the atmosphere.

Corrected.

In conjunction with next two suggestions, p 693 line 9- now reads:

“The vapor pressure of a solution droplet is enhanced by its curvature; this is known as the Kelvin effect (Thomson, 1871). Atmospherically occurring droplets are not pure water, however, and normally contain soluble material, which reduce the vapor pressure over the droplet according to Raoult’s law (Raoult, 1887). The combination of these two effects leads to Köhler theory which predicts the critical supersaturation which must be overcome in order for a particle to activate as a droplet. This critical supersaturation is therefore a function both of the particle size and composition (Köhler, 1936).”

p. 693, line 10: Replace "Nascent" with "Atmospherically occurring" or something similar

Corrected.

p. 693, line 16: Please cite the original paper instead: Kohler, 1936.

Corrected.

p. 693, lines 25-27: These techniques are not necessarily limited to laboratory studies. Also, in addition to Moore et al., 2010, I would suggest citing Petters et al., J. Geophys. Res., 2009, who used a coupled CCN-DMA and a stepping-DMA-voltage technique to study size-resolved CCN activation.

Corrected.

p. 694, lines 19-21: Please add example citations for the studies referred to

The reviewer makes a good point. We have reviewed some literatures and now added these on the following sections. In addition, we have updated our reference list to include the following additions, based on our efforts to address the collective comments of the reviewers.

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., Liggi, 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-Saunty, 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  $\alpha$ -caryophyllene secondary organic aerosol, *Atmospheric Chemistry and Physics*, 9, 795–812, 2009.

p. 694, line 26: Insert "commercially-available" before "CCNC". The fact that this study employs a widely-used, commercial-available CCNC makes it more relevant for many in the community and this should be emphasized.

Corrected.

p. 694, line 29: Suggest replacing "the aerosol particle which formed the droplets" with "the CCNC droplet residuals"

Corrected.

p. 695, line 1: Is the AMS a HR-ToF-AMS as stated later? The AMS acronyms seem somewhat inconsistent through the manuscript.

The instrument was an HR-ToF-AMS. For brevity, we refer to the instrument as the AMS after the initial specification of the instrument.

p. 695, lines 2-3: "Laboratory studies...to validate the technique" Good summary statement, but I'd like to see a more extensive validation as described under General Comments.

Discussed above.

p. 695, lines 7-8: No indication is given that this is a dual-column CCNC design except for the model number.

We now indicate in the text that this is a dual column model of the CCNC although only a single column was used. We note the model numbers are different between the two units.

p. 695, line 17: Assuming column dimensions given by Lance et al., 2006 ( $R_{\text{inner}} = 1.15 \text{ cm}$ ,  $L = 50 \text{ cm}$ ) and the reported flow rate of  $500 \text{ cm}^3 \text{ min}^{-1}$ , yields a column residence time of 25 seconds, not 10 seconds. I'm not familiar with the dimensions of the dual column design, but was under the impression that they are the same as the single-column design used by Lance et al.

We thank the reviewer for pointing out this error. It is indeed 25 s instead of 10 s.

p. 695, line 20: Note that the integrated OPC is in the CCNC

p 695 line 18- now reads:

Once activated, the number and size distribution of droplets (from 0.75 to 10  $\mu\text{m}$  diameter) is measured using an integrated optical particle counter (OPC) "in the CCNC".

p. 695, lines 21-22: What is the difference between the "CVI" and the "pumped CVI"?

PCVI utilizes a vacuum pump to produce a jet of air to replace the relative velocity traditionally generated by aircraft flight or wind tunnels in counterflow virtual impaction (Boulter et al., 2006). We believe this and the following point should mostly be left to previous references although minor text changes have been made.

p. 696, lines 5-6: How was the cut-size set? Is this cut-size adjustable within the current experimental setup? If so, how?



Both traditional and PCVIs can adjust the cut-size primarily by variation of the counterflow and secondarily via the other instrumental flows and pressures. For this study the size cut-off of 2.5  $\mu\text{m}$  is set to achieve the best performance of our PCVI (i.e., transmission efficiency of 0.75 by empirically adjusting input/output/add/pump flow in our experimental configuration). Boulter et al. (2006) showed that this PCVI is capable of generating cutoffs from below submicrometer up to  $\sim 3 \mu\text{m}$  aerodynamic diameter by changing flows through the PCVI (Note: change of the flows inherently changes distance between two stagnation planes, which is relevant to the cut size). We used the same nozzle to collection orifice distance as reported in Boulter et al. (2006) and Kulkarni et al. (2011), but special flow settings to achieve best transmission efficiency at reasonable cut size. The flow settings were chosen based on our direct calibration of the PCVI (Kulkarni et al., 2011): input (10 lpm)/ output (1 lpm)/ add (3 lpm)/ pump (12 lpm). Please note that this and the previous comment led to changes at the given points in the text although a full PCVI description is left to the mentioned references (i.e., it is beyond the scope of this manuscript).

p. 696, line 6: Remove the word "thus"

Corrected.

p. 696, lines 9-13: Why are such large flow rates required? I suspect this is an "off-the-shelf" PCVI, but could it be reengineered to accommodate lower flow rates?

Discussed above (specific comment 1). If the reviewer's concern is the transmittance efficiency, it is not the amount of flow causing particle loss, it is the ratio of input flow to output flow, which is largely contributed by the CCNC.

p. 696, line 13: How was the CCNC modified to divert the flow? See general comment about clarity of experimental setup, instrument modifications.

Discussed above (specific comment 3A and 3B).

p. 696, line 20: This is the first instance of this acronym, so spell out high-resolution, time-of-flight aerosol mass spectrometer. Perhaps move this definition to p. 695, line 1.

P 694 line 28 now reads:

"We then evaporate the condensed-phase water in order to determine the size and composition of the CCNC droplet residuals using an Aerodyne Research (Billerica, MA) High Resolution Time of Flight Aerosol Mass Spectrometer (hereafter referred to as AMS for brevity)..."

p. 696, line 26: Is it an oven or a plate?

It is an oven with an inverted conical shape.

p. 697, line 3: Change "electron impact" to "electron impaction"

Electron impact is the correct terminology.

p. 697, line 5: Can high-resolution mass spectra still be obtained in "V" versus "W" mode?

The V mode provides resolutions of approximately 2000 while the W mode provides resolutions of approximately 5000. The resolution in the V mode is sufficient to separate ions of the C<sub>x</sub>H<sub>y</sub> family from those of the C<sub>x</sub>H<sub>y</sub>O<sub>x</sub> family. These details are available in the references cited and are extraneous to this manuscript.

p. 697, line 10-11: Please explain what is meant by treating the PSL as a nitrate equivalent mass?

The signal at m/z 104 is converted to a mass assuming an ionization efficiency equivalent to ammonium nitrate particles (i.e., 1.1). Because we only present a single fragment peak from the PSL particles (to improve quantification), it would be incorrect to label this as an absolute mass concentration and may lead to reader confusion. Nitrate equivalent mass is rigorously correct.

p. 697, line 16: The laser also ionizes the components?

Yes.

p. 697, line 19: Hyphenate "in-situ"

"in situ" is not normally hyphenated.

p. 697, line 21: Remove "respectively"

"respectively" denotes that each bound is dependant on a different process. It is used correctly in this context.

p. 697, lines 20-21: PSLs do not act as CCN, within uncertainty, based on Figure 2.

Mentioned in p 698 line 18-21.

p. 699, lines 1-5, Eqn. 1: First, I would suggest using T as a transmission factor (i.e. remove CCN). Second, please replace all numbers in this equation with variables, as T will change with different operating conditions. Ways to optimize T to achieve better performance should be explored more fully as discussed under General Comments.

Discussed above (specific comment 1).

p. 699, line 18: I'm not sure that I understand "sputtering". Do some droplets shatter into smaller droplets when they hit the counterflow? Are there ways to avoid this problem (i.e., different flow rates)? As you say, the AMS does not detect these small particles, so perhaps it is not really a problem.

We believe the sputtering results when humidified air condenses, collects, and finally drips in a low-flow eddy region in the pump-flow ports of the CVI. These large droplets likely shatter when they hit the counterflow because they have little initial velocity. The AMS did not detect any perturbation from the sputtering events, likely because the particles produced from them are too small to have aerosol core or enough soluble material to produce detectable aerosol in completing with evaporation.

p. 701-702, lines 28-4: What is the meaning of ion current used in the context of Figure 7? Does it give a feel for the total fraction of these species across the entire aerosol population or within individual particles?

Note this repeats some of previous comments/changes regarding the PALMS instrument method. As a single particle instrument PALMS should be able to differentiate single CCN residuals but at the expense of quantitation – is should be considered qualitative. Ion current is the specific form of detector signal for PALMS but this should not be confused with a quantity and it is therefore incorrect to consider this value as a quantify due to different ionization efficiencies among particle components. The text has been changed to clarify this as well as to note that a full descript of single particle ability and limitations is described elsewhere.

p. 703, lines 3-7: This is the major limitation of the technique, but one which I think could be overcome by adjusting the operating parameters to achieve a higher transmission factor or by increasing the sample averaging time to improve statistics. The goal should be not to merely "chemical differentiate" particles, but rather to quantify the chemical composition using the HR-ToF-AMS.

The goal of the current study was the development of the technique utilizing chemical properties to prove the separation of CCN active component from interstitial component. Please refer to the author response in specific comment 2(C).

Figure 7b: The PALMS data for periods I and III show greater ion current for nitrate and sulfate than for organics. Meanwhile the AMS data from the day before show low sulfate loadings with most of the aerosol mass as organics and nitrate. Are these inconsistent with each other?

The AMS and PALMS experiments were conducted on different days.  
AMS 10-20-10 (p 700 line 19)  
PALMS 11-09-10 (p 701 line 14)