Responses to Anonymous Referee #2

The authors appreciate the valuable comments of reviewer #2, which in combination with the critique by reviewer #1, has greatly improved the quality of our manuscript. As with the first reviewer, we provide a point-by-point response (normal font) to the reviewer's comments (italic font) with indicated additions or alterations to the manuscript indicated in bold font, where page numbers and sections correspond to the revised discussion manuscript unless otherwise noted.

Reviewer comment 1: *Page 6784: "When including MNC solubility limitations, i.e. applying the experimentally derived κ of pure MNC in the volume mixing rule, the predicted κ of the mixture is significantly less at 0.204 (open blue circles in Fig. 4). However, when excluding the effects of solubility, predicted κ=0.300 (closed blue circles in Fig. 4), is in excellent agreement with the measured κ." I found this sentence misleading. It sounds like the solubility limitation should be excluded to get correct result and when solubility limitation is included, the result is wrong. Maybe this should be reworded to make it clear, that the problem is the volume mixing rule used, and the best result is always achieved when solubility limitations and dissolved fraction of different compounds are correctly calculated.*

Response to reviewer comment 1: The reviewer makes a great point, and we agree that our statements regarding whether to include or exclude solubility limitations are perhaps misrepresented. We note that the statement referred directly to the results given in the figure (Fig. 4 of the original discussion manuscript). It is still true that we 'excluded' and 'included' solubility limitations in the volume mixing rule to assess which calculation leads to better agreement with the observations. Indeed, the best results are always achieved when solubility and dissolved fraction are correctly applied and known. We have altered the language in the text as suggested by the reviewer. Furthermore, and noting the reviewer's comment 2, below, we have updated Fig. 4 to include the predicted κ based on Köhler theory that accounts for the dissolution of compounds in growing droplets [*Petters and Kreidenweis*, 2008]. Figure 4 now more appropriately shows predicted κ based on the volume mixing rule applying the single-component experimentally-derived κ (κ=limit; colored symbols), κ calculated from Köhler theory (κ=KT; gray-scale symbols), and predicted κ assuming no solubility limitations, i.e. $C=\infty$, shown as horizontal lines. Note that the horizontal lines, which represent predicted κ in the absence of solubility limitations, expand the range of κ derived from $D_{p,c}$ measurements at each S.

Manuscript alterations resulting from reviewer comment 1: See "Manuscript alterations resulting from reviewer comment 2, below.

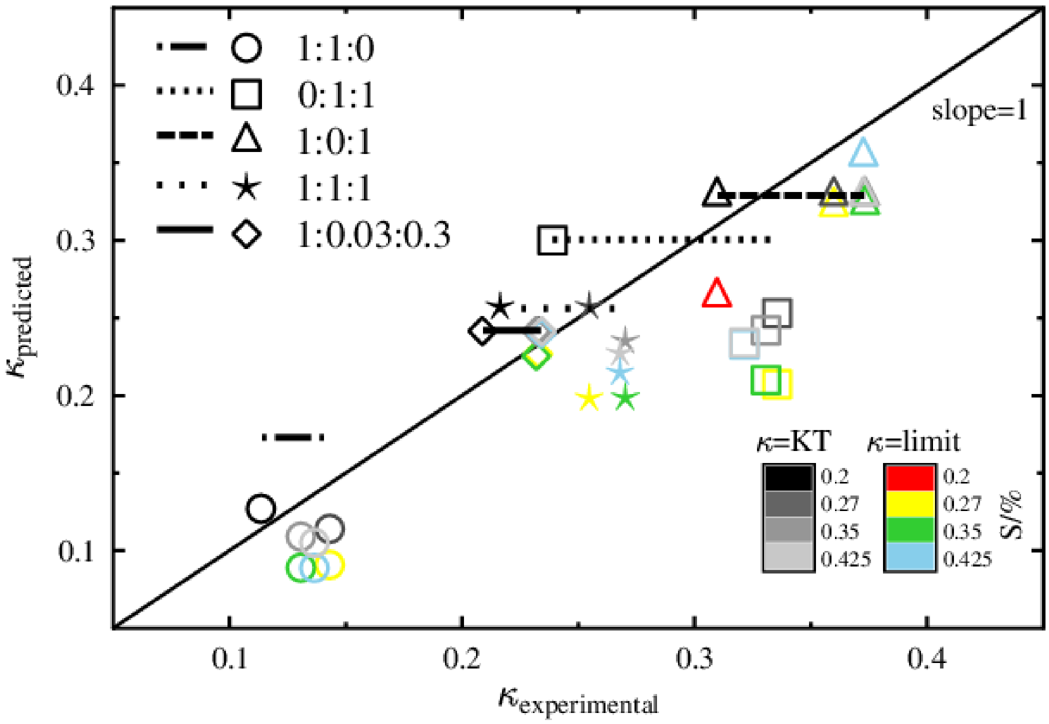

Figure 4. Predicted κ as a function of experimentally-derived κ at different supersaturation (*S*) for the binary and ternary particle mixtures of LEV, MNC, and KS. κ is predicted applying the volume mixing rule and based on single-component experimentally-derived κ including solubility limitations (κ=limit; color scale), κ calculated from Köhler theory (κ=KT; gray scale), and κ assuming no solubility limitations (horizontal lines). Note that the horizontal lines span the range of experimentally-derived κ. The black diagonal line represents a slope of 1 in the derived vs. predicted κ. The LEV:MNC:KS mass ratios are indicated in the legend for 1:1:0 (circle), 0:1:1 (square), 1:0:1 (triangle), 1:1:1 (star), and 1:0.03:0.3 (diamond).

Reviewer comment 2: *Page 6784: How close match the LEV:MNC mixtures do you get if you correctly calculate the solubility effect through Köhler-theory instead of assuming complete solubility?*

Response to reviewer comment 2: See previous comment and new Fig. 4, which also shows predicted κ calculated from Köhler theory. For the LEV:MNC mixtures, assuming complete solubility of MNC overpredicts the experimentally-derived κ. After applying Köhler theory, predicted κ is in much better agreement with experimentally-derived κ. However, it is important to note that for the other mixtures, κ calculated from Köhler theory is not always in best agreement with experimentally-derived κ, possible due to the enhancement in MNC water-solubility in the presence of hygroscopic KS that is not accounted for in the calculation. In addition, we have a limited understanding of MNC's actual water-solubility, which is based on a prediction using the Environmental Protection Agency's Estimation Program Interface (EPI) suite, i.e. a higher water-solubility would shift predicted κ to higher values for all particle mixtures containing MNC.

Manuscript alterations resulting from reviewer comment 2: Table 1 has been updated to include the estimated water-solubility of MNC based on calculations from the Environmental Protection Agency's Estimation Program Interface (EPI) suite, included now in the references. Figure 4 has been updated to include predicted κ applying Köhler theory, shown as grayscale symbols (see revised Fig. 4, above).

Section 3.1, page 13, lines 11-26: **"The water solubility of MNC is approximated as *C*=0.003, which is categorized as sparingly water soluble (Petters and Kreidenweis, 2008). To verify whether MNC behaves as if it is infinitely soluble in a solution with KS, Fig. 3 shows derived Köhler curves of pure MNC and mixtures containing variable KS volume fractions, and the MNC dissolved fraction, χ_{MNC}. In Fig. 3, the critical supersaturation, i.e. the maximum in the Köhler curve, decreases with increasing KS volume fraction. At a KS volume fraction of ~36% (MNC volume fraction of ~64%) indicated by the orange curves in Fig. 3, the maximum in the Köhler curve corresponds to $\chi_{MNC}\approx1$, implying that CCN activation is not limited by MNC solubility. This MNC volume fraction corresponds to the 1:1 by mass MNC:KS particles, which suggests that for this particular mixture, MNC behaves as if there are no solubility limitations during CCN activation (i.e. infinitely soluble, equivalent to *C*=∞) and κ of MNC can be predicted using Eq. (6). This result is consistent with the 1:1:1 by mass LEV:MNC:KS particles. In the presence of LEV, alone, MNC remains slightly insoluble during CCN activation."**

The following text has replaced the last paragraph of section 3.1, and begins on page 13, lines 27-29, and page 14, lines 1-21: **"Figure 4 shows the predicted κ plotted against experimentally-derived κ for all of the particle mixtures and *S* applied in this study. κ was predicted applying the volume mixing rule under three different scenarios, (1) calculated from experimentally-derived single-component κ (κ=limit; color scale symbols), (2) calculated from Köhler theory (κ=KT; gray scale symbols), and (3) assuming no solubility limitations (i.e. *C*=∞; horizontal lines). For all particle mixtures containing equal by mass MNC (i.e. 1:1:0, 0:1:1, and 1:1:1), applying the experimentally-derived single-component κ underpredicts the experimentally-derived κ of the mixtures. As discussed previously, this underprediction is due to the enhancement in MNC water solubility when in the presence of water soluble LEV and KS, which is not accounted for when applying the experimentally-derived single-component κ. Applying Köhler theory results in better agreement with the experimentally-derived κ, particularly for the 1:1:0 particle mixture. Predicted κ assuming no solubility limitations results in an over-prediction for the 1:1:0 particle mixture, but is in best agreement with the experimentally-derived κ for all other mixtures. The ability to predict experimentally-derived κ of the mixtures applying Köhler theory depends on the solubility and volume fractions of the different particle components, which have not all been measured. The solubility of MNC was estimated from the US Environmental Protection Agency's Estimation Program Interface (EPI) suite (EPI, 2015). Applying this estimated solubility results in an underprediction in the 0:1:1 and 1:1:1 κ, but is in best agreement for the 1:1:0 particle mixture. These results support that the volume mixing rule is most accurate when accounting for the changes to water solubility when the components are mixed. In the presence of LEV, MNC remains slightly insoluble.**

However, in the presence of KS, MNC behaves as if there are no solubility limitations during CCN activation."

Reviewer comment 3: *Page 6782 and Table 2: It would be interesting to see if there is size dependence in the measured kappa values for KS similar to ammonium sulphate. The reported uncertainty is quite high. Is this due to increasing kappa (increasing Van't Hoff factor) with increasing particle size? If it is, then this information should be used when hygroscopicity of particles is calculated.*

Response to reviewer comment 3: We thank the reviewer for bringing this to our attention. We did find that in general the derived κ values for KS increases with increasing particle diameter, similar to ammonium sulfate, likely due to an increasing Van't Hoff factor. In response to this and reviewer #1's suggestions, we have now included the dependence of the derived κ on the measured critical particle diameter and OH exposure. Furthermore, we have updated the prediction lines (i.e. κ vs. OH exposure) to account for the effects of the change in particle size in the revised Figs. 6, 7, and 8. This resulted in a complete update of all of the OH exposure plots and table 2. Please see table 2 below, which shows now these numbers in more detail.

Manuscript alterations resulting from reviewer comment 3: Figures 6, 7, and 8 have been reformatted to include the size dependence due to changing supersaturation. The values reported in table 2 are now shown for each supersaturation. The following text in regards to the increasing van't Hoff factor of potassium sulfate with increasing supersaturation was added to the third paragraph in section 3.1, page 12, lines 4-5: **"…, but exhibits a marginal increase as a function of *S*, possible due to an increasing van't Hoff factor at higher *S*, similar to ammonium sulfate."**

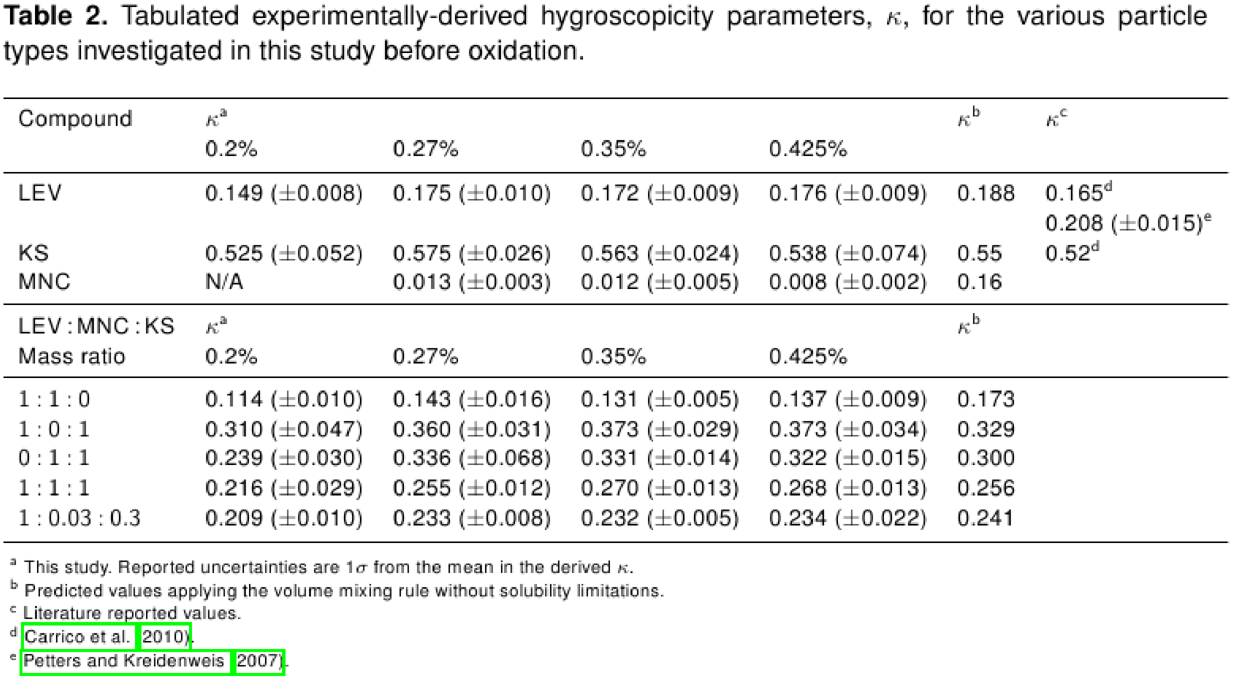

Table 2. Tabulated experimentally-derived hygroscopicity parameters, κ, for the various particle types investigated in this study before oxidation.

Compound	κ^a 0.2%	0.27%	0.35%	0.425%	κ^b	κ^c
LEV	0.149 (±0.008)	0.175 (±0.010)	0.172 (±0.009)	0.176 (±0.009)	0.188	0.165[d] 0.208 (±0.015)[e]
KS	0.525 (±0.052)	0.575 (±0.026)	0.563 (±0.024)	0.538 (±0.074)	0.55	0.52[d]
MNC	N/A	0.013 (±0.003)	0.012 (±0.005)	0.008 (±0.002)	0.16	
LEV : MNC : KS Mass ratio	**κ^a 0.2%**	**0.27%**	**0.35%**	**0.425%**	**κ^b**	
1 : 1 : 0	0.114 (±0.010)	0.143 (±0.016)	0.131 (±0.005)	0.137 (±0.009)	0.173	
1 : 0 : 1	0.310 (±0.047)	0.360 (±0.031)	0.373 (±0.029)	0.373 (±0.034)	0.329	
0 : 1 : 1	0.239 (±0.030)	0.336 (±0.068)	0.331 (±0.014)	0.322 (±0.015)	0.300	
1 : 1 : 1	0.216 (±0.029)	0.255 (±0.012)	0.270 (±0.013)	0.268 (±0.013)	0.256	
1 : 0.03 : 0.3	0.209 (±0.010)	0.233 (±0.008)	0.232 (±0.005)	0.234 (±0.022)	0.241	

[a] This study. Reported uncertainties are 1σ from the mean in the derived κ.

[b] Predicted values applying the volume mixing rule without solubility limitations.

[c] Literature reported values.

[d] Carrico et al. 2010).

[e] Petters and Kreidenweis 2007).

Reviewer comment 4: *It is already shown in 3.3 that with binary mixtures there is no change in the measured hygroscopicity after oxidation, so what is the motivation to present results with ternary mixtures?*

Response to reviewer comment 4: While the reviewer is correct that there is no change in κ as a function of OH exposure for the binary particle mixtures, which may imply there is no effect on the ternary particles, we felt it was still important to include the results for the ternary mixed particles for the following reasons. (1) It allows us to assess whether the particle's matrix could have an effect on its CCN activity as a function of OH exposure, not accessed with the binary mixtures. (2) It is a useful dataset for comparison with field-collected particles because it better represents a complex particle system, similar to particles observed in the 'real' environment.

Manuscript alterations resulting from reviewer comment 4: No alterations to the main text of the original discussion manuscript were made in response to reviewer comment 4.

Reviewer comment 5: *Section 3.5: I agree with Referee #1 here. Particles of different sizes have different mass fractions of coating material. Better analysis of different particle sizes and corresponding hygroscopicities could be conducted. It should be quite straightforward task to estimate coating thickness for different sized particles and use Köhler theory to estimate the solubility limitations. At the moment this is only speculated. Also there could be more discussion why observed 10 nm coating is not slowing down water uptake and decrease CCN activity.*

Response to reviewer comment 5: Figure 8 in the discussion manuscript (see new Fig. 9 below) and section 3.5 have been updated to include the effects of particle size and thus coating-thickness (or organic volume fraction) on derived κ for both OH unexposed particles (see new Fig. 9 panel A and B) and OH exposed particles (see new Fig. 9 panel C). We find that a 10 nm coating does not completely prevent water uptake by the KS core, such that the coated particles behave similarly as MNC. Our speculation is that at sufficiently high RH (i.e. >100%), the particle-phase diffusivity increases significantly and water molecules can readily reach the KS core [*Koop et al.*, 2011].

Manuscript alterations resulting from reviewer comment 5: Figure 9 has been updated to include how volume fraction and predicted κ, excluding or including solubility limitations, depend on the particle diameter. In panel C of new Fig. 9, predicted κ accounting for the enhancement in MNC κ due to OH exposure now includes the effects of varying supersaturation.

Section 3.5, page 21, lines 25-28, and page 22, lines 1-5 describes new Fig. 9, panels A and B: **"The 25th, 50th, and 75th percentiles of the number-weighted particle size distribution grew in size by ~20 nm as indicated by the red, black, and blue circles in Fig. 9A, respectively. For the 50th percentile, this corresponds to an enhancement in the MNC $V_{f,org}$ from 0% at time=0 min to ~70% shortly after, close to the $V_{f,org}$ of the atomized MNC:KS binary component particles of 64%. The similar $V_{f,org}$ between the atomized and coated MNC/KS particles enables a direct intercomparison of their hygroscopicity, since relatively larger MNC $V_{f,org}$ would bias towards lower κ and vice versa, as indicated in the colored dashed and dotted lines in Fig. 9B."**

Section 3.5, page 22, lines 16-18: **“The change in $V_{f,org}$ with time is indicated by the red, black, and blue circles according to the 25th, 50th, and 75th percentiles of the particle population, respectively.”**

Section 3.5, page 22, lines 21-27: **“To determine if the solubility of MNC impacts the MNC-coated KS particles similarly to the atomized mixture, κ is predicted using the volume mixing rule and applying the experimentally-derived pure MNC κ corresponding to a specific *S* (i.e. including solubility limitations), as indicated by the dotted lines in Fig. 9B, and compared to predicted κ applying a pure MNC κ of 0.16 (i.e. pure MNC κ in the absence of solubility limitations calculated from Eq. 6), as indicated by the dashed lines in Fig. 9B.”**

The following text regarding MNC coating and κ has now been included at the end of the second-to-last paragraph in section 3.5, page 23, lines 16-19: **“One possible explanation for the higher than expected κ when KS is coated with MNC is that the particle-phase diffusivity is sufficiently high to allow water molecules to penetrate the KS core [Koop et al., 2011].”**

Section 3.5, page 23, lines 23-29, and page 23, lines 21-29 describes the OH exposure hygroscopicity data presented in panel C of new Fig. 9: **“The κ values resulting from an OH exposure of $3.3\text{x}10^{11}$ molecule cm^{-3} are given by the filled circles, whereby the different colors represent the applied *S* during the experiment. Open circles correspond to κ in the absence of OH. At $V_{f,org}$=0%, κ is ~0.55 and independent of OH exposure. κ decreases when $V_{f,org}$≈70%, but undergoes a slight enhancement following OH exposure. The dotted lines indicate the modeled change in κ as a function of $V_{f,org}$ applying the volume mixing rule and applying the experimentally-derived κ for MNC and KS at a given *S* (i.e. including MNC solubility limitations). Similar to the atomized 1:1 MNC:KS binary-component particles, modeled κ as a function of $V_{f,org}$ underpredicts the experimentally-derived OH-unexposed κ, even after accounting for the enhancements in pure-component MNC κ due to the high OH exposure. This suggests that in the presence of KS at this $V_{f,org}$≈70%, MNC may not be limited by its solubility, similar to the atomized 1:1 mass ratio MNC:KS binary-component particles, and that OH exposure can have very little impact on the CCN activity of sparingly-soluble organics coated on water soluble compounds.”**

Section 3.5, page 24, lines 15-18: **“This suggests that the water solubility of the more soluble component of mixed-component aerosol particles can be more important for CCN activation than the actual mixing state of the particle.”**

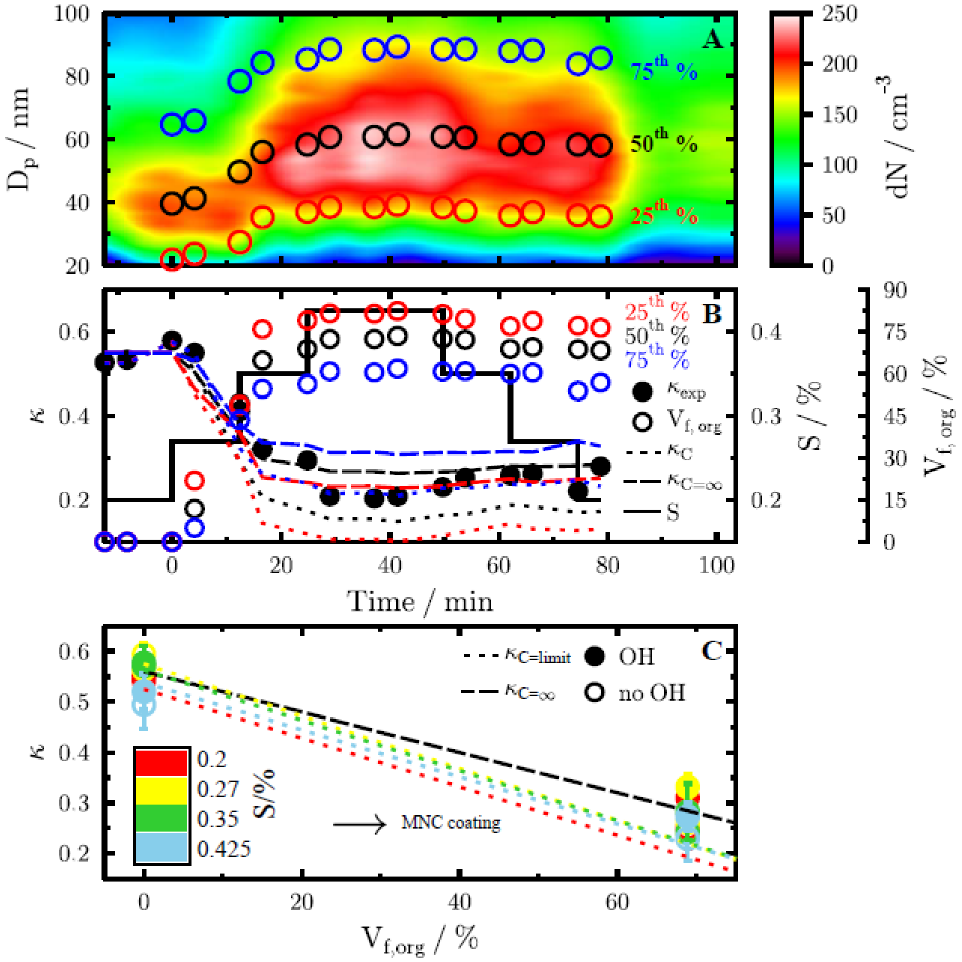

Figure 9. OH exposure effects on the CCN activity of MNC-coated KS particles. Panel A shows a color map of the number-weighted particle size distribution (dN) of KS and MNC-coated KS particles plotted as a function of MNC coating. The open circles in panel A refer to the measured percentiles of the total particle population (25th – red, 50th – black, 75th – blue). Panel B displays the change in particle hygroscopicity (filled circles) and MNC volume fraction ($V_{f,org}$, open circles) with time as a function of *S* given as black solid line. The dotted lines show the predicted κ using the volume mixing rule corresponding to the $V_{f,org}$ at a given time and based on the experimentally-derived κ for KS and MNC given in table 2 as a function of *S*. The dashed lines represent the predicted κ using the volume mixing rule corresponding to the $V_{f,org}$ at a given time and assuming the CCN activity of MNC is not limited by its solubility (i.e. MNC κ=0.16 calculated from Eq. 6). Panel C displays the change in κ for the MNC-coated KS particles as a function of $V_{f,org}$, OH exposure, and *S*. OH unexposed particles are plotted as open circles. Filled circles correspond to particles exposed to OH at 3.3×10^{11} molecule cm^{-3} s. The error bars represent 1σ from the mean in κ. The colored dotted lines show predicted κ as a function of $V_{f,org}$ at different *S* using the volume mixing rule assuming the CCN activity of MNC is limited by its solubility. The black dashed line shows the predicted κ using the volume mixing rule assuming the CCN activity of MNC is not limited by its solubility.

Reviewer comment 6: *Page 6796: "Chemical aging has no major impact on the CCN activity of mixed water-soluble and insoluble compounds beyond the point that the insoluble component becomes infinitely soluble. Below this point, chemical aging can influence the CCN activity of the insoluble component." This is quite strong statement and valid only for compounds studied here. Also, how insoluble compounds become infinitely soluble? Maybe weakly soluble compounds, or compounds with low solubility would describe these compounds better. Also state more clearly that these weakly soluble compounds become fully dissolved in dilute liquid aerosol before activation into cloud droplets."*

Response to reviewer comment 6: We feel, as the reviewer does, that the language in the manuscript should be updated to emphasize that it is only in this specific case (weakly soluble MNC mixed with sufficiently soluble LEV or KS) that the observed enhancement in the CCN activity of MNC following OH exposure does not translate when MNC is mixed with LEV or KS. This may be the case for other similarly mixed particle systems, but clearly more studies are needed to verify this. We have removed the term 'insoluble' from this discussion since it is contradictory than an insoluble material would become infinitely soluble. Based on the reviewer's recommendation, we have also made minor changes to the text to indicate more clearly that the weakly soluble compounds become fully dissolved in dilute liquid aerosol before activation into a cloud droplet and that it is this very point that chemical aging may play less of a role in the CCN activity of mixed aerosol particles than expected.

Manuscript alterations resulting from reviewer comment 6: The last two sentences of the conclusion section 4, page 26, lines 25-28: **"Chemical aging has no major impact on the CCN activity of the mixed water-soluble and sparingly-soluble BBA compounds studied here, beyond the point that the less water-soluble component becomes infinitely soluble. Below this point, chemical aging can influence the CCN activity of the mixed particle."**

Reviewer comment 7: *Figure 3: Please mention also the dry particle size used in the calculation.*

Response to reviewer comment 7: We have now included the dry particle size (110 nm) in the figure description of Fig. 3.

Reviewer comment 8: *Is the legend correct? Now the particles with the highest mass fraction of KS are not the most hygroscopic.*

Response to reviewer comment 8: The reviewer is correct, there is a typo in the figure. Referring to the original Fig. 4, the data points shown in purple should be switched with the data in gold. We have made a new Fig. 4 that includes this correction (see new Fig.4 in response to reviewer comment 2 above).

References

Koop, T., J. Bookhold, M. Shiraiwa, and U. Poschl (2011), Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere, *Phys Chem Chem Phys*, *13*(43), 19238-19255, doi:10.1039/C1cp22617g.

Petters, M. D., and S. M. Kreidenweis (2008), A single parameter representation of hygroscopic growth and cloud condensation nucleus activity - Part 2: Including solubility, *Atmos. Chem. Phys.*, *8*(20), 6273-6279, doi:10.5194/acp-8-6273-2008.