Response to Referee #1

We thank referee #1 for taking an interest in our manuscript and for providing helpful comments, which has improved the manuscript. The manuscript has been revised accordingly and each comment is answered point-by point below.

Referee comments are copied in regular black font and our responses are given in regular blue font. Revisions to the manuscript are given in **bold blue font**.

Anonymous Referee #1

Overview

This contribution presents laboratory studies of particle hygroscopic growth and cloud drop formation of limonene generated organosulfates mixed with ammonium sulphate. Even though real atmospheric aerosols in general are composed of more complex mixtures, single compounds and simple mixtures of atmospherically relevant compounds still has to be studied in order to identify and test theoretical expressions and to evaluate relevant mechanisms. Hygroscopicity and cloud drop formation of many such simplified systems remain to be studied and organosulfates are key components in some of these.

The experimental work is carefully done and in general well described (see minor comments below). The analysis is also scientifically sound and the conclusions are well supported in the work but I recommend the authors to carefully address the comments about particle composition below.

In many studies the theory used to account for surface tension is far too simplified and results in an overestimation of the role of surfactants in cloud drop formation. In this paper, several models are compared to illustrate this and it thus makes a significant contribution to the awareness of this effect.

I thus recommend publication after minor changes.

General comments:

My main concern with the presentation relates to two effects that are discussed at several points in the paper: 1) kappa values varying with particle size for subsaturation and 2) kappa values being higher than theoretically expected, especially for particles with 20-80% ammonium sulphate showing kappa values that are similar to those for pure ammonium sulphate. Both these effects depend on the assumption that the particle composition is as expected. This is mentioned in the text, but in the later discussion, the conclusion and the abstract, the possibility of deviations from the expected composition is not fully taken into account. A deviation could be due to several effects, for example surface to bulk or micelle partitioning in the atomizer or in the droplets formed or evaporation during drying (are vapour pressures for the organosulfates known?). I recommend that either the composition should be verified or the possibility of composition deviation should be accounted for in the conclusions and abstract.

At present time it is not possible to verify the composition of the particles, as the original samples are no longer available and since it is not trivial to synthesize more L-OS 250.

The suggested deviations in the particle composition compared to the solute composition poses a very interesting question, which has been asked before but never been investigated. A future study investigating this, employing AMS measurements to verify the composition, would be highly valuable and worthwhile, both in the present and more general context. In these experiments magnetic stirring was used at all times and no sign of micelle formation was observed in the solutions. If bulk-to-surface partitioning or micelle formation did occur, the authors are furthermore convinced that this would produce particle with higher

amount of L-OS 250 and not lower, as this compound is present in the bulk as well as partitions at the surface of the formed droplets.
The vapour pressures of organosulfates are not yet known. However, previous studies (Surratt et al., 2010; Schindelka et al., 2013)) of organosulfate-formation, suggests that organosulfates are formed in the water film and a recent study by Kristensen et al. (2015), shows that organosulfates are not present in the gas phase but plenty in the particle phase, also OS 250 (here summed OS 250 from limonene and α-/β-pinene), based on this we don't think that evaporation of L-OS 250 during drying is likely.

Regarding the referees concern about deviations in the particle composition we have mentioned the possibility of partitioning in the bulk text, but as mentioned above we do not believe that this could cause increased particle concentration of AS, hence the observed non-linear composition dependency is not a result of composition deviations and is therefore not mentioned in the conclusion or abstract. Furthermore other studies for example the one by Hämeri et al. (2002) have also found non-linear composition dependency for mixed organic/inorganic particles, which are not significantly surface active and therefore should not be subjected to the mentioned effect.

Section 3.2: … It should be mentioned that the particle composition is assumed to reflect the composition of the aqueous solutions in these experiments. It has previously been suggested that deviations in the particle composition can occur through processes such as surface-to-bulk partitioning or micelle partitioning in the atomizer or the formed droplets. However it is our firm believe that such processes would increase the amount of L-OS 250 in the particles, not decrease it, hence these processes cannot explain the observed non-linear composition dependency towards the hygroscopic properties of AS.

Regarding the "k-values varying with particle size" in the subsaturated range, the possibility of artefacts, deviation in chemical composition and the uncertainty regarding if this trend is statistically significant have already been mentioned in the bulk text as well as the conclusion:

P 17335 l 12-16: The error bars, here representing ± two standard deviations, on individual κ-values for a given composition show some overlap for the high AS fraction composition, whereas no overlap is observed for pure L-OS 250 and L-OS 250 with 10 % w/w AS, suggesting that this trend may be statistically significant for at least the latter two.

P17336 L.4-6: It should be mentioned, that the observed dependence on size could potentially be an indirect effect of a changing chemical composition or from an artefact in our experiments.

P.17344 l.19-21: However, whether κH-TDMA is truly size dependent, or the size dependency is a result of an experimental artefact, cannot be concluded from these experiments alone.

The authors have now mentioned this in the abstract as well.

P.17318 l. 10-12 The κ-values derived from measurements with H-TDMA decreased with increasing particle dry size for all chemical compositions investigated, indicating that $\kappa_{H\text{-}TDMA}$ depends on particle size and/or surface effects**, however it is not clear if this trend is statistically significant.**

As a possible reason for the size dependence of the hygroscopic growth, kinetic effects are discussed. I thus strongly recommend that details concerning the residence times in the DMAs and in the sampling lines before and after the humidifier are given.

Kinetic effects are mentioned as one possibility for the difference in H-TDMA-derived and CCN-derived κ-values, not to account for the size dependence observed from the H-TDMA measurements.
The referee makes a good point though, and the residence times for the humidifying units of the H-TDMA and the CCNC (from top of the column to detector) have been assessed and included in the bulk text.

Page 17339 line 24: …secondly the difference in instrumental design of the H-TDMA and CCNC, such as the residence time in the **humidifying unit** of the instruments relative to the aerosol equilibration time at sub- and supersaturated conditions. **In the setup used here residence times in the humidifying units were assessed to be 1s in the H-TDMA and 10 s in the CCNC.**

Minor comments to the authors:
p. 17320 l. 17 the expression "activation diameter" can refer to either the droplet diameter corresponding to the maximum supersaturation in the Köhler curve, or to the minimum dry diameter for particles that can activate at a given supersaturation. Please clarify here and in the rest of the manuscript.

The authors have not been alert to the fact that both the expression "activation diameter" and "critical particle diameter" have been used in the manuscript. All mentioning of activation diameter has been changed to critical particle diameter and the definition of critical particle diameter is now given on p. 17320. L. 17:

p. 17320 l. 17: i.e. the critical particle diameter defined as the dry particle diameter, where 50% of the particles can activate at a given supersaturation.

p. 17321 l. 14 The set-up used in this paper is referred to as "unique". In what way is it unique? Is it really the first time that hygroscopic growth and critical supersaturations are measured on the same aerosol?

We only found two studies (Carrico et al., 2008; Herich et al., 2009) employing parallel measurements at sub- and supersaturated conditions, where slightly different experiment setups were used; hence we think the setup is a unique custom-build system.
If the referee is familiar with other studies employing such a setup we would be happy to know of them. We have changed unique to "**unique custom-build**" to clarify.

p. 17323 l. 22 "unique", see above.

The word "unique" has been changed to "**unique custom-build**".

p. 17326 l. 2-5 From looking at the data, I guess that the procedure is to set one supersaturation and then scan over particle sizes to find the size for which 50% of the particles activate. This is not clearly described and I recommend changes to avoid miss-understandings and confusion.

Yes this is the procedure used, and p. 17326 l. 2-8 has now been changed for clarification:

p. 17326 l. 2-5: CCN activation spectra were measured at thirteen different SSs, ranging from 0.099 to 0.922 % (corresponding to 100.099 to 100.922 % RH), **by defining one supersaturation at the time and then scanning over the particle sizes.** The fraction of activated particles to total particles was thus obtained as a function of the particle dry size from the activation spectra. Activation spectra were corrected for multiply charged particles simultaneously selected in DMA3 and subsequently fitted using a sigmoidal function as done by Paramonov et al. (2013). From the fitted sigmoidal curve, the critical particle diameter (d50) was then determined.

p. 17326 l. 23-26 This could be explained in a more correct and pedagogical way. The kappa parameter is not primary size dependent, but composition dependent.

We agree that the sentence could be misunderstood it has been changed to clarify that κ is primarily composition dependent.

p. 17326 l. 23-26: According to κ–Köhler theory, the κ parameter relates the dry diameter of particles of a specific chemical composition to the water uptake at a given RH or SS (Petters and Kreidenweis, 2007). **Hence, κ primarily expresses the influence of chemical composition on water uptake.**

p. 17328 l. 23-25 Check the language.

The sentence has been changed.

p. 17328 l. 23-25: Equilibrium growth by water uptake and cloud droplet activation **was modelled for the studied particles using Köhler theory and the bulk-to-surface partitioning model presented by Prisle et al. (2010).**

p. 17330 l. 22-25 Check the language.

p. 17330 l. 22-25: The difference in surface tension of the individual organic solutions, when AS is added, can be explained by a difference in surface activity of the organics and a difference in interaction effects between AS and the organics.

p. 17331 l. 13 “mixing ratios from 1-0” means 50-100% AS. Is this correct or do you mean 0-100% AS?

Mixing rations from 1-0 refers to 100-0% L-OS 250 (or 0-100% AS, but we prefer the first, since L-OS 250 is the compound of interest). p. 17331 l. 13 has been changed to:

p. 17331 l. 13: L-OS 250/AS mixing ratios from 100 to 0% L-OS 250.

p. 17331 and figure 3. The deviation in the shape of the curve for surface tension as a function of concentration deviates from the theoretical expressions: according to experiments, most of the decrease takes place in the concentration interval 0.5 – 2,5 mmol/L. The deviation is discussed for the mixtures, but seems to be there also for the pure L-OS 250. Have you any idea why and if it has an effect on the surface to bulk partitioning?

Yes the deviation is also present for pure L-OS 250. Impurities can cause the observed behaviour, and it is known that L-OS-250 is not a single component (90% purity). For bulk-surface partitioning, it is expected that L-OS-250 is a single component, which is not completely true, but the impurities are very alike L-OS 250 and they will probably interact with AS and L-OS 250 in the same manner as L-OS 250 itself and should therefore not affect the surface-to-bulk partitioning modelling.
The deviation of the fits from the experimental data has been considered a bit further in the manuscript, also including pure L-OS 250.

p. 17331 l. 20: From Fig. 3 it is evident, that there is some L-OS 250 molarity regions with slightly different surface tension slopes, which cannot be captured by the simple surface tension fit. This is true for all solution compositions and is most likely caused by the impurities in L-OS 250. Furthermore the fit had difficulties capturing the composition-dependent surface tension variation….

p. 17332 l. 10 "There are no indications of deliquescense,. . ."Do you have the resolution in RH to observe a deliquescence? Also, for mixtures, no abrupt deliquescence step is expected, but rather a smooth increase in HGF values. Isn't this what is observed here?

No, we did not measure HGF-values at an RH below 80%. The sentence is included to establish that deliquescence activation at supersaturation is not likely for L-OS 250, since we see a smooth curve in the subsaturated range, this has been clarified:

p. 17332 l. 10: No deliquescence is observed for L-OS 250 in the monitored RH range but since the hygroscopic growth occurs smoothly, deliquescence activation at supersaturation, as previously observed for some insoluble or slightly soluble organics (Kreidenweis et al., 2006), is not expected.

p. 17332 l. 15-16 This could be interpreted as water solubility influencing the growth factors, while it only influences the deliquescence.

In order to avoid misunderstandings the sentence has now been changed to "**consistent with the well-documented hygroscopic properties and deliquescence RH (DRH) of AS of 79.9 (±0.5) % at 295 K (Seinfeld and Pandis, 2006).**"

p. 17332 l. 27-28 ". . .any reduction of droplet surface tension from L-OS 250 should increase particle hygroscopicity." The effect of surface tension on particle hygroscopic growth is, however, very limited. Compare with p. 17341 l. 21-24 and figure 9, where there is almost no difference in the models with different surface tension expressions. Consider rephrasing these lines and the end of the paragraph.

The two model presentations including surface tension uses the same surface tension input but one also includes consideration of bulk-to-surface partitioning, hence the results presented in figure 9 does not show that surface tension effects are limited, but rather that effects of bulk-to-surface partitioning is limited in the subsaturated range (but definitely not in the supersaturated range).

Some of the discussion in sections 3.2, 3.3, and 3.4 would be stronger if the results of the modelling (Figure 9) were also taken into account.

The authors have considered this, but we wish to keep the current structure of the manuscript, as it was chosen to compare κ-values from experiments and models instead of comparing measured and modelled HGF-values and CCN activities.

p. 17336 l. 5-14 Was the bimodal size distribution observed in DMA 2b? If so, that would, as you mention, imply external mixture and deviations in composition. From my point it is difficult to see if the size dependence in kappa for pure AS is significant, but if so, it is surprising that it has not been observed before. Could there be measurement artefacts causing the size dependence: for example the parameterization of the dry particle correction between the DMAs or evaporation between DMA1 and DMA2a? In the end, I am not convinced about the conclusion that particle composition issues are not involved.

Yes the bimodal size distribution was observed in DMA 2b. As mentioned in the manuscript (see answer to general comment) the authors also point out that it is not certain that the size dependence is statistically significant or that artefacts/particle composition deviations are not involved.

p. 17337 l. 19-20: The high molar weight and low dissociation (to a large extent independent of molecular structure) of L-OS 250 implies low kappa value. Solubility only influences kappa values in a small range of solubility; it is very much an on-off effect.

p. 17337 l. 19-20 does not relate solubility or molecular weight of L-OS 250 to κ, but relates the chemical structure of L-OS250, which is semi-polar, to the obtained κ-values of L-OS 250, and simply states that the modest hygroscopicity implied by the obtained κ-values is expected since L-OS 250 is semi-polar.
We have tried to express this differently:

p. 17337 l. 19-20: …contains a hydrophobic ring structure and is thus expected to be semi-polar; hence it is not surprising that the hygroscopicity of L-OS 250 is weak to modest.

p. 17337 l. 20-22 What is the theoretical value of kappa for AS?

The theoretical value of k for AS depends on which assumptions are made in the calculations, for example regarding the dissociation of AS. This is why we have compared κ of AS with values obtained from other studies including theoretical calculations and not one theoretical value.

p. 17341 l. 15-18 This is an example of a conclusion that depends on the assumptions of particle composition.

As mention in the answer to the general comments, possible deviations of the particle composition are not likely to explain the observed non-linear composition dependency; hence this conclusion should be fine.

p. 17342 l. 15-16 Check the language.

The sentence has been changed:

p. 17342 l. 15-16: … as was found for other atmospheric surfactants (Prisle et al., 2008, 2010b). **However, partitioning does not seem to drive the variation in water uptake between the sub- or supersaturated regimes.**

p.17342 l. 27 Do you say that solubility influences kappa values for L-OS 250 at supersaturation? Is this consistent with -3/2 power dependence seen in figure 5.

Yes we point out that there are some solubility limitations of L-OS 250, even in the supersaturated range, which fits with the observed power dependence of approximately -1.4 for pure L-OS 250 and 90% L-OS 250/10% AS as given on p.17334 l. 13-15.
This has been clarified in the caption for figure 5 as well.

Figure 5: Critical supersaturation (SSc) as function of dry particle diameter for the six investigated particle compositions. **The curves follow the Köhler slope of approximately -3/2 for L-OS 250/AS compositions with ≥ 20% AS. The curves for pure L-OS 250 and L-OS 250 with 10% AS have a slope of approximately -1.4.** Error bars represent the uncertainty on the particle dry size (x-axis) and SSc (y-axis). Note that the data is plotted in log-log space.

p. 17343 l. 17-21 As the authors state, the additional hydroxyl groups may influence solubility, and may thus influence hygroscopicity at sub- or super-saturation. But an increased solubility, increasing the hygroscopic growth at subsaturation, may have no effect on the cloud droplet formation, since the concentration at activation is much lower than at subsaturation. Effects of solubility can thus not easily be extrapolated between sub- and super-saturation. It is therefore important to be specific when it comes to the humidity regime in which the changes are observed when it comes to solubility effects. Molar weight, in contrast, is expected to influence water up-take at sup- and super-saturations in similar ways. Please consider rephrasing.

We understand the referees concern regarding extrapolation of the hygroscopic growth and solubility at subsaturation into the supersaturation range, however we have been very careful not to make this extrapolation, as we first of all do not mention solubility in p. 17343 l. 17-21 and as we simply base our statement “These organosulfates with additional hydroxyl/carboxylic acid groups are likely to be more hygroscopic, and therefore more prone to activate into cloud droplets” on the study by Suda et al. (2014), where CCN activity was measured for organic compounds showing the CCN activity to increase with addition of hydroxyl/carboxylic acid groups.
We therefore believe that this section is phrased correctly.

p. 17345 l. 7-9 In my opinion, this conclusion depends on the composition assumption that has not been verified. Please consider rephrasing.

See answer to minor comment regarding p. 17341 l. 15-18.

Thank you very much for interesting reading and an important contribution to science!

We thank the referee for showing interest in our work and for this very kind comment. We are grateful for the comments and questions asked by the referee, which has helped improve the manuscript.

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