Response to Referees

We thank the referees for their interest in our manuscript and their 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 $\kappa_{\mathrm{H\text{-}TDMA}}$ 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 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.

Anonymous Referee #2
Overview
The authors have provided a detailed and extensive account of laboratory measured hygroscopic properties and CCN activity of mixtures of ammonium sulphate and a limonene organosulfate they synthesised. Such aerosol models serve as suitable approximations for atmospherically relevant particulate matter. A single laboratory apparatus has been set up so that H-TDMA and CCNc measurements can be made in parallel the same aerosol source, thus minimising source dependent compositional discrepancies in the case of two separate units. The analysis was carried out using both H-TDMA and CCNc instruments so as to scrutinize the properties of interest in both sub- and super-saturated regimes.

In addition, they have provided modelled values of kappa for various formulations of bulk-surface partitioning and surface tension effects of the surface active organosulfate as well as kappa values derived from the ZSR mixing rule. It is clearly illustrated that the non-linear compositional dependency of kappa could not be described by the models indicating that while bulk-surface partitioning effects aerosol activation it is not driving the hygroscopicity. The validity of the ZSR additive mixing rule was scrutinized well and found to only be applicable for mixtures close to pure AS or LS-250.

The reviewer notes that there is a lack of motivation provided for the broader atmospheric scientific community, in particular why should global climate modellers take note, in the context of droplet activation and the indirect effect? The end of the introduction should clearly summarise the aims of the study, but it is also of great importance that the motivation for trying to achieve these goals is highlighted. κ is a particularly useful quantity for modellers, on all scales, as it facilitates a reduction in parameter complexity when describing aerosol chemistry. Placing a greater emphasis on the results obtained concerning κ in the context of climate modelling and implications for cloud-aerosol interactions will increase the impact of the paper.

The authors want to caution against any tendency to use single, lumped κ-values for all organic aerosol compounds in climate models. The results obtained in this study shows that κ varies greatly with organic/inorganic mixing ratio and over the broad humidity regime. Although useful, a single κ-value is a too simple representation of the hygroscopic properties of organic aerosols and may lead to misrepresentations of aerosol-cloud interactions in climate models.
From the broad experience of the authors, chemical composition of aerosols varies greatly with geographical location, hence so should κ.
The authors thank the referee for suggesting to place a greater emphasis on κ in regard to climate modelling, which has been done in section 4 (see answer to general comment 7) and for drawing our attention towards including aims and motivation for the study in the introduction. The different sections of the introduction have been interchanged (see manuscript) and below the changes concerning aim and motivation are highlighted:

Page 17321 line 7-28: Despite the apparent atmospheric abundance and widespread relevance of organosulfates, their cloud forming properties have not yet been investigated; this gap has motivated the present study, where an atmospherically relevant organosulfate is characterized in terms of surface activity and hygroscopic properties.
Here, an organosulfate derived from limonene, with a molecular weight of 250 Da (L-OS 250) was synthesized. The hygroscopic properties of L-OS 250, ammonium sulfate (AS) and mixtures hereof were studied in the laboratory employing a unique custom-build setup, allowing parallel

measurements at sub-and supersaturated conditions. Furthermore the surface tension of aqueous solutions of L-OS 250 and L-OS 250 in mixture with AS were measured. κ was derived from the measurements at sub- and supersaturated conditions as well as modelled based on the volume additive Zdanovskii-Stokes-Robinson (ZSR) mixing rule (Petters and Kreidenweis, 2007) and three different partitioning representations, which can be used to represent cloud activation in global climate models. The specific aims of the study are to investigate how κ is influence by humidity, particle size and L-OS 250/AS mixing ratio as well as to scrutinize whether the model representations can reproduce the experimental κ-values for the system. The ability of the models to reproduce hygroscopicity measurements on process level is very important for their applicability in global climate models. Finally the study aims towards evaluating the cloud forming properties of organosulfates.

The reviewer particularly notices, and commends, the attention given to errors and uncertainty throughout the paper.

The reviewer recommends the manuscript for publication subject to some minor revisions and consideration of some more general comments detailed below.

General comments:

1) The study employs various bulk-partitioning and surface tension considerations and the reviewer feels that this paper requires further referencing and attention to be given to the subject. While the a full account of the theoretical background is not necessary, the reviewer believes the paper will benefit an appendix or supplementary material section that outlines the assumptions, limitations, thermodynamic principles and corresponding key mathematical relationships (Gibbs adsorption isotherm) that underpin modelling such phenomena. In addition, there is extensive literature that has led to the development of such sophisticated bulk-surface partitioning models - see Sorjamaa et al. (2004) 1 and Topping et al. (2010, 2012)2,3 – which remains uncited in the introduction, bulk text or conclusion here. In particular, Petters and Kreidenweis (2013) 4 carried out a surfactant study using a kappa parameterisation.

The authors have added a section in supplementary where the different assumptions regarding bulk-to-surface-partitioning in the model are outlined. The text is not included here as it is comprehensive, but we believe that the section will satisfy the requests.

We are well aware of the models presented by Sorjamaa et al. (2004) and Topping et al. (2010, 2012). Calculations of the bulk-to-surface partitioning with these models have not been included in the current study, as the model used here, presented by Prisle et al. (2010), follows the considerations of Sorjamaa et al. (2004) which is clearly stated in Prisle et al. (2010) and have been shown to obtain very similar results as the model presented by Topping et al. (2010) (e.g. Prisle et al., 2012).
A reference to the Sorjamaa et al. (2004) and Topping et al. (2010) models have been included in the manuscript (see answer to general comment 6 and supplementary).

2) Some more discussion is required regarding how reflective the composition of the aerosols in this study are of real atmospheric aerosols. In particular, can the author say that the results found here, for laboratory-generated aerosols, are also true for much more complex aerosols mixtures that are present in the atmosphere?

Atmospheric aerosols are very complex, often composed of thousands of different organic compounds; hence the laboratory studies presented here are probably not fully representative for complex atmospheric aerosols. It was the intension to investigate how a main compound class (organosulfates) in organic aerosols behaves by themselves and in simple mixtures. This kind of study is very important as it reveals something about the interactions of complex organic compounds with common inorganic compounds as well as how the mixing ratio of organics to inorganics affect κ.

We thank the referee for the suggestion and have included a comment regarding this in section 4:

Page 17342 line 21: Atmospheric aerosols are very complex, often consisting of many thousands organic compounds (Hamilton et al., 2004; Hallquist et al., 2009), thus the two-component particles studied here are properly not fully representative for atmospheric aerosols. However investigation of simplified systems can reveal the important interactions between complex organic compounds and common inorganics, which may influence cloud activation as well as expose how κ is influenced by the mixing ratio of organics to inorganics.

3) While the paper is indeed readable, the English could be better. Please read through the manuscript again with this in mind and adjust the grammar accordingly so as to improve the readability of the paper.

Changes have been introduced to language and gramma which we hope have improved the readability of the manuscript.

4) A more detailed explanation of exactly how the κ values are derived from the H-TDMA and CCNc measurements is required.

An explanation of how H-TDMA-derived κ was obtained has been included and the explanation of how CCN-derived κ is iterated has been rephrased:

Page 17327 line 9: From the H-TDMA measurements κ can be calculated by inserting the experimental HGFs into equation 5 and then isolate κ by re-arrange the equation.

Page 17327 line 19: When the experimental critical particle diameter is inserted into equation 6 as D_{dry}, κ can be iterated by varying the droplet diameter, D_{wet}, and κ itself until the minimum difference between the theoretical supersaturation, $S(D_{wet})$, and the experimental supersaturation is obtained. Reported CCN κ-values are thus the κ-values resulting in minimum difference between theoretical and experimental supersaturation (Petters and Kreidenweis, 2007; Rose et al., 2010).

5) In figure 5 there are two fewer data points for the pure L-OS 250 curve when compared with mixtures and pure AS. This is again evident in figures 7 and 9. Please add to the main text why this is the case.

Yes, we had problems with measuring the dry diameters for two of the SS when measuring on the pure L-OS 250 particles, resulting in negative (or NaN-value) dry diameters, which is why these are missing.

P.17334 l.2: Unfortunately measurements at SSc 0.099 and 0.442% resulted in negative values of the dry diameters for the pure L-OS 250 particles; hence these data points are absent.

6) It is not transparent how κ values are modelled in 3.4.4, please detail further in the text how this is done. Adding additional equations if necessary. In particular, it is not immediately clear to me how one models the κ from modelled HGF/SSc. As I understand it, one must know HGF/SSc to back out κ (from equations 5/6) or vice versa. In the case of the supersaturated regime, please add equation for SSc (i.e. Köhler curve maximum) in terms of κ. Perhaps you mean to say experimentally derived HGF/SSc values are used to model κ? This is unclear to me, please clarify and add to text.

Thank you for bringing this to our attention, we have clarified the modelling section 2.4, where the main corrections have been applied to P. 17328 l.23-25. Please see manuscript for other corrections to this section.

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). The bulk-to-surface partitioning model is a development of the model from Sorjamaa et al. (2004) and returns results similar to the model presented by Topping (2010) (e.g. Prisle et al., 2012).

The Köhler equation (8) is analogous with Equation 5 and 6, but without the κ approach used to calculate water activity:

$$S(D_{wet}) = x_W \cdot \gamma_W \cdot exp\left(\frac{4\sigma MW_W}{RT\rho_W D_{wet}}\right) \qquad (8)$$

Where x_w is the water mole fraction and γ_w is the activity coefficient of water, which is here set to unity. The dry particle size and composition and the droplet size are the input parameters, which means that HGF must be known; hence the equilibrium RH can be calculated. HGF is varied until equilibrium RH is equal to the experimental RH (80, 85, 90 or 93%). Similarly, when the dry size and composition are the input parameters, critical supersaturation can be solved numerically by varying droplet size. In both cases, droplet composition is always known and it can be used to calculate droplet solution surface tension (Equation 1). In addition, surface tension can be fixed to that of pure water or the effects of surfactant bulk-to-surface partitioning on water mole fraction and the concentrations used to calculate surface tension can be accounted for.
The model thus returns HGF-values and SSc under different assumptions, which are used to calculate κ from Equation 5 and 6 respectively.

7) In section 4 it should be highlighted that the CCNc measurements are of greater importance for cloud formation owing to supersaturation in clouds. In addition, some discussion is required here for the implications of your results for global climate models. Specifically, please add Prisle et al. 2012 5 reference to this section whilst noting that σb is a particularly erroneous representation for global simulations of droplet activation and link to your results presented in figure 9. Please also comment explicitly on whether you expect there to be significant sensitivity of droplet concentrations if organosulfates are included as a separate compound in global climate models or can they be aggregated with general organics? Relate also to organic and organosulfate κ values.

This is a very good point. CCNC measurements are directly relevant to cloud droplet activation, however in many studies H-TDMAs are employed to measure the hygroscopic properties at subsaturated conditions and then κ-theory is used to extrapolate these properties to supersaturated conditions. Subsaturated measurements are not necessarily representative to predict CCN activation as our results clearly show. A comment has been added in section 4, emphasising that the CCNC measurements are of greater importance to cloud formation.

Page 17343 line 10: The discrepancy between $\kappa_{H\text{-}TDMA}$ and κ_{CCN} for L-OS 250 shows that extrapolation of κ from the subsaturated to the supersaturated range is connected with significant uncertainties. In regard to the cloud forming potential of L-OS 250 it should therefore be emphasised that the CCNC measurements are of greater importance as clouds are supersaturated with water.

We thank the referee for drawing our attention towards discussing the results in regard to global climate models; we believe that this will increase the impact of the paper.
At this point it is not possible for the authors to evaluate on how the sensitivity of droplet activation is influenced by including organosulfates as separate compounds in climate models. This study reveals how organosulfates behave on their own and in mixture with inorganics, but it is not necessarily representative for complex organic mixtures. A brief discussion of this has been included in section 4 as well:

Section 4: The results presented in section 3.4.4 are important for global climate models, as the partitioning representations, σ_w, σ_b and σ_p, tested here, may be used in such models. From figure 9 it is clear that σ_b in particular fails to represent the experimental data at supersaturated conditions. When the partitioning representation σ_b is implemented in global simulations of droplet activation, the predicted cloud droplet number is much larger, than when σ_w or σ_p is used (Prisle et al., 2012), hence σ_b predicts a greater indirect aerosol effect than the two other representations. Our results imply that σ_b should not be used in global simulations to represent cloud droplet activation as it cannot reproduce experimental data on process level. Introducing σ_b in climate models would thus result in even larger uncertainties on the future climate.

Concerning global climate models it is of high interest to consider whether organosulfates can be merged with other organics and represented by one common κ-value. The κ-values found here are within the range of other organics (approximately 0.01 to 0.3 for CCNC measurements), including carboxylic acids, sugars and HULIS (Petters and Kreidenweis, 2007; Chan et al., 2008; Jing et al., 2015). Hence considering κ alone, it would seem that organosulfates can be merged with other organics, however this study reveals how organosulfates behave on their own and in mixture with inorganics, but this is not necessarily representative for complex organic mixtures. For example a recent study by Jing et al. (2015) shows that κ of organic mixtures can be much higher compared to what was expected by considering κ of the individual compounds, hence we do not think that all organics can be represented in climate models by one common κ-value based on the mean of individual κ-values.

Minor revisions:

Section 2.2: Are surface tensions taken after reaching steady state, equilibrium values? See and reference Nozière et al. (2014) 6.

Surface tension was measured after 2 min. in these experiments, where steady-state was reached. After approximately 1 min. the surface tension-values did not change beyond 2% over the next 28 min. which is the uncertainty to be expected from the instrument. This has been clarified in the text:

Page 17323 line 8: According to Noziere et al. (2014) surface tension of a pendant drop is reduced over time until the minimum equilibrium surface tension is ultimately reached, hence surface tension was measured for a L-OS 250 and a L-OS 250 with 80% AS solution (C(L-OS 250) = 0.005M) over a 30 min. time period. The surface tension was found to be stable after approximately 1 min., and the following measurements were thus initiated after 2 min.

Section 2.2: Equation 1 is missing dσ/dminorganic term from cited paper. Please find alternative reference for equation or explain why this term vanishes here. Also, it's not necessary to explain 'ln' to the reader, "Ln is the natural logarithm (to the base of e)", and state that molar concentration is the bulk quantity.

The term dσ/dm_inorganic is omitted here because the slope is very small and can therefore be ignored. The sentence regarding ln has been deleted.

Page 17320 line 17: Please define activation diameter. In different literature this can refer to the wet diameter that corresponds to the maximum of a given Köhler curve or to the dry diameter of the smallest aerosol size that can be classified as a CCN for a given supersaturation. It should be the latter.

The authors have not been alert to the fact that both the expression "activation diameter" and "critical 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.

Page 17324 line 15: "Dry gas (N2) was applied after atomization to dilute the particle concentration." – The casual reader, not familiar with this kind of experiment, may not know why this is required, please explain.

Compressed air was applied (not N2, sorry for the mistake) of technical reasons to prevent coagulation due to high particle concentration and efficient humidification. This has been clarified in the manuscript.

Page 17324 line 15: Compressed air was applied after atomization to dilute the particle concentration in order to prevent coagulation.

Page 17324 line 28: "Number size distribution" should be "Number concentration size distribution".

Yes, this has been changed.

Page 17325 line 16: "Error bars presented in the following sections on reflect the variations between these measurements according to the observed relative standard deviations (±2 standard deviation)." Poor English – "Error bars presented in the following sections reflect the variation in measurements according to observed relative standard deviations (±2 standard deviation)."

Changed to suggestion.

Page 17325 line 24: Incorrect figure reference – please change to Fig. 2.

Changed to suggestion.

Page 17325 line 25: "Monodisperse", are these the same four sizes as used in H-TDMA? Unclear.

No, the size distribution resulting from DMA3 is not the same four sizes as in the H-TDMA measurements. Here we scanned over different particle sizes, meaning that we change the particle size distribution in small steps, for example from 30 nm to 37 nm with a few minutes interval until we have measured the CCN activity of a sufficient particle size range (typically 20-200 nm).

Page 17325 line 25: …the dried particles were transferred to DMA3 (see Figure 2)**, which scanned over the particle sizes. This means that the specific particle size selected in DMA3 was changed every second minute.**

Page 17326 line 1: 1 micrometre is not the only definition for cloud droplet classification. This can also be defined in terms of the dry activation diameter or the critical supersaturation; this is worth mentioning for the droplet activation community.

The referee makes an excellent point, however Page 17326 line 1, describes how the instrument defines a cloud droplet, and not how cloud droplet activation in general can be defined. The sentence was included to inform the aerosol community hereof.

Page 17326 line 3: There has been no mention of the supersaturation band calibration yet, that should come prior to this for clarity – it's not clear at this stage that these are the calibrated values.

This is a very good point. The sentences regarding calibration of the CCNC has been moved and are now given prior to the calibrated SS-values.

Page 17326 line 2: The nominal SS given by the CCNC was corrected to obtain the actual SS profile created in the instrument, based on measurements with AS following suggestions by Rose et al. (2008). Information regarding the calibration is given in Supplement. CCN activation spectra were measured at thirteen different SSs ranging from 0.099 to 0.922 % (calibrated values, corresponding to 100.099 to 100.922 % RH)…

Page 17326 line 18: Please define critical particle diameter.

See answer to minor comment Page 17320 line 17.

Page 17327 line 23: While I follow the logic of capturing surface tension effects in kappa, I'm not familiar with this method, nor will the average reader be, I feel this requires some elaboration, validation or a word of caution (if it can't be referenced from another study).

The sentence has been deleted.

Page 17328 line 6: Please state that pure component kappa values will be taken to be mean measured values.

Page 17328 line 6:… by applying the **mean measured** κ-values for pure AS and L-OS 250…

Page 17328 line 23: “Equilibrium growth by water uptake and cloud droplet activation of the studied particles from Köhler theory as described in Prisle et al. (2010b). “ change to “Equilibrium growth by water uptake and cloud droplet activation of the studied particles is calculated from Köhler theory as described in Prisle et al. (2010b).”

Changed to:

Page 17328 line 23: 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).

Page 17328 line 24: Remove “following”.

Done.

Page 17328 line 25: First instance of SSc abbreviation, please write in full. Abbreviation introduced on page 17334 line 1, only use abbreviation there.

Changed to suggestion.

Page 17329 line 7: It is not clear what the ‘b’ refers to in ‘σb’ making it easy for the reader to forget which partitioning scheme this is referring to. Please change or state what the ‘b’ stands for.

b refers to bulk solution properties, which has been clarified in the manuscript.

Page 17329 line 7: Second, reduction of droplet surface tension from L-OS 250 is considered, but the influence of bulk-to-surface partitioning is still ignored (σ_b), **thus bulk solution properties are assumed.**

Page 17329 line 10: remove parentheses and replace with “and thus kappa and droplet surface tension”.

This section has been changed according to General Comment 6, and this correction no longer applies.

Page 17329 line 15: Please add reference or justification for no dissociation of L-OS250 (or similar organic compound).

L-OS 250 has not been studied much prior to this work, so no investigation of its dissociation has been carried out. L-OS 250 is not a salt but a molecular species and since it is expected that L-OS 250 is a very weakly acid (due to the alcohol group) it is here assumed that L-OS 250 primarily is in its molecular form and not dissociated in solution. This has been formulated in the manuscript.

Page 17329 line 15: Since L-OS 250 is a molecular species and expected to be a very weak acid it is assumed that L-OS 250 does not dissociate in solution but primarily is present in its molecular form.

Page 17331 line 13: “mixing ratios from 1-0” suggests half AS and half LS-250 to pure AS. Please change.

Page 17331 line 13: L-OS 250/AS mixing ratios from **0 to 100% AS**

Page 17331 line 19: It seems these fitting parameters are used for all compositions, is that correct? This doesn't seem logical, can't these be re-evaluated for each w/w% composition? Please also add R 2 values for quantitative illustration of the ability (or inability) of equation 1 to capture the surface tension depression effect. Different fitting parameters and corresponding R2 values should be collected in a table.

Yes, it is correct that the fitting parameters are used for all compositions. This is because a continuous ternary fit is needed for the partitioning model. Anyone can calculate fit parameters for specific w/w% using Equations 2 and 3, as done here. The R2-value for the fit is 0.942, which has been included in figure 3.

Page 17332 line 16: As the lowest subsaturated RH value explored is approximately equal to the DRH we don't see the deliquescence action in the results here. If additional measurements were taken at 75% RH, for example, we would hope to see the deliquescence manifest itself in the HGF between that data point and one at 80% RH.

Yes, the authors have thought about this as well.

Page 17334 line 9: "The curves for all six compositions follow the Köhler slope of approximately −3/2 in log-log space" contradicts sentence starting line 12 "Pure AS and L-OS 250 with 80, 50 and 20 % w/w AS had a slope of −3/2, whereas the slope for pure L-OS 250 and L-OS 250 with 10 % w/w AS were slightly smaller (approximately −1.4)".

The authors intended to state that the curves for all compositions have slopes close to the Köhler slope of -3/2, where pure AS and L-OS 250 with 80, 50 and 20 % w/w AS had a slope of −3/2, while the slope for pure L-OS 250 and L-OS 250 with 10 % w/w AS were slightly smaller (approximately −1.4). this has been clarified in the text.

Page 17334 line 9-15: The curves for all six compositions **have slopes close to** the Köhler slope of approximately −3/2 in log-log space. According to equilibrium Köhler theory **a slope of -3/2** means that no explicit size-dependent effects are present in the obtained CCN spectra (Seinfeld and Pandis, 2006). Pure AS and L-OS 250 with 80, 50 and 20 % w/w AS had a slope of −3/2, **while** the slope for pure L-OS 250 and L-OS 250 with 10 % w/w AS were slightly smaller (approximately −1.4), consistent with the presence of a modest size- 15 dependent effect attributed to L-OS 250.

Page 17337 line 28: I don't see this trend. One might argue that a minimal trend might be present for pure L-OS 250; however, in the case of the 10% w/w AS mixture, the variability in κCCN between the first and last data points is too large to conclude that there is a trend. Please revise.

The page and line referred to by the referee, mentions the very real trend observed, where particle compositions with >/=20% AS have k-values converging towards those of pure AS. The rest of the line (and the following sentences) then concerns a weak increase in the CCN-derived κ-values of pure L-OS 250 and L-OS 250 with 10% AS with increasing supersaturation. The authors believe that the referee is concerned regarding the latter? however the authors have already mentioned that the trend might not be significant:

Page 17338 line 6: However, including the uncertainty on κCCN, the increasing trend for L-OS 250 and L-OS 250 with 10 % w/w AS is likely not significant."

Page 17339 line 13: "An exception is found for pure AS at 90 % RH, and L-OS 250 with 20 to 80 % w/w AS at 93 % RH, where κH-TDMA were below κCCN for the three larger particle sizes." If possible, please add a hypothesis as to why this might be the case.

At writing point the authors have no hypothesis to why this is, however we thought the observation was worth mentioning.

Page 17339 line 24: It would be instructive to specify the residence time of the instrumentation to provide transparency regarding any kinetic effects that may be present.

Yes, the authors agree on the matter and residence times for the humidifier of the H-TDMA as well as the humidifying unit in 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 estimated to be 1s in the H-TDMA and 10 s in the CCNC.**

Page 17340 line 6: "extend" should be "extent".

Has been changed.

Page 17341 line 8: should read "upper left"

Has been changed.

Page 17341 line 27: "non-ideal droplet interaction effects", are these internal droplet mixture effects? This terminology is not familiar to the reviewer and is therefore most likely not familiar to the average reader, please revise or explain.

Yes "non-ideal droplet interaction effects" refers to internal droplet mixture effects. This has been changed in the manuscript.

Minor comments regarding figures:

Figure 1: Please add stoichiometric coefficients if possible.

In theory limonene oxide should react 1:1 with $NaHSO_4$, however in the synthesis excess $NaHSO_4$ is used and stoichiometric coefficients are therefore not included.

Figure 8: Please change x-axis tick resolution to match y-axis. Rephrase "as a function" neither derived value of kappa is a function of the other.

The tick resolution has been changed and "as a function of" has been rephrased to "**plotted against**"

Figure 9: Add modelled values to legend. Add space between "modelled" and "κ".

It has not been possible to add model-values to the legend, as the lines represent different assumptions in subfigures ZSR compare to the others as explained in the figure caption.
Space has been added between "modelled" and "κ" in the caption.

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5 :Prisle, N. L., Asmi, A., Topping, D., Partanen, A.-I., Romakkaniemi, S., Dal Maso, M., Kulmala, M., Laaksonen, A. , Lehtinen, K. E. J., McFiggans, G., and Kokkola, H.: Surfactant effects in global simulations of cloud droplet activation, Geophys. Res. Lett., 39, L05802, doi:10.1029/2011GL050467, 2012.

6 : Noziere, B., Baduel, C., and Jaffrezo, J. L.: The dynamic surface tension of atmospheric aerosol surfactants reveals new aspects of cloud activation, Nature Communications, 5, 3335– 3342, doi:10.1038/ncomms4335, 2014.

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Hygroscopic properties and cloud condensation nuclei activation of limonene-derived organosulfates and their mixtures with ammonium sulfate

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Abstract

~~Even though o~~Organosulfates have been observed as constituents of atmospheric aerosols in a wide range of environments; ~~spanning from the subtropics to the high Arctic, their~~ however, their hygroscopic properties ~~have not been investigated prior to this study~~remain uncharacterized. Here, limonene-derived organosulfates with a molecular weight of 250 Da (L-OS 250) were synthesized and used for simultaneous measurements with a Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA) and a Cloud Condensation Nuclei Counter (CCNC) to determine the hygroscopicity parameter, κ, for pure L-OS 250 and mixtures of L-OS 250 with ammonium sulfate (AS) over a wide range of humidity conditions. 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~~indicating size dependency and/or surface effects~~. For pure L-OS 250, κ was found to increase with increasing relative humidity, indicating dilution/solubility effects to be significant. Discrepancies in κ between the sub- and supersaturated measurements were observed for L-OS 250, whereas κ of AS and mixed L-OS 250/AS were similar. This discrepancy was primarily ascribed to limited dissolution of L-OS 250 at subsaturated conditions. In general, hygroscopic growth factor, critical ~~activation~~ particle diameter and κ for the mixed L-OS 250/AS particles converged towards the values of pure AS for mixtures with ≥20% w/w AS. Surface tension measurements of bulk aqueous L-OS 250/AS solutions showed that L-OS 250 was indeed surface active, as expected from its molecular structure, decreasing the surface tension of solutions with 24% from the pure water-value at a L-OS 250 concentration of 0.0025 mol/L. Based on these surface tension measurements, we present the first concentration-dependent parametrisation of surface tension for aqueous L-OS 250, which was implemented to different process-level models of L-OS 250 hygroscopicity and CCN activation. The values of κ obtained from the measurements were compared with κ calculated applying the volume additive Zdanovskii-Stokes-Robinson mixing rule, as well as κ modelled from equilibrium Köhler theory with different assumptions regarding L-OS 250 bulk-to-surface partitioning and aqueous droplet surface tension. This study is to our knowledge the first to investigate the hygroscopic properties and surface activity of L-OS 250; hence it is an important first step towards understanding the atmospheric impact of organosulfates.

1 Introduction

Atmospheric aerosols still account for major uncertainties in our understanding of global climate and predictions of future climate change (IPCC, 2013). ~~In particular~~Especially the indirect radiative effects of organic aerosols, i.e. their influence on cloud drop formation and cloud properties, remain insufficiently constrained for reliable model predictions of both thermodynamic and large scale general circulation levels (Hallquist et al., 2009). Part of the uncertainty relates to our incomplete ~~The intrinsic cloud condensation nuclei (CCN) activity of many organic aerosol components remain uncharacterized, just as our~~ understanding of the various effects of mixing interactions in the aerosol phase~~, is incomplete~~ perhaps in particular the effect of surface active organic molecules (surfactants) in aqueous droplets and how these influence the Cloud Condensation Nuclei (CCN) activity of particles~~. Part of the uncertainty relates to the effect of organic surface activity in aqueous droplets. Surface active organic molecules (surfactants)~~Surfactants are frequently observed in atmospheric aerosol and cloud and fog water samples (Facchini et al., 1999; Mochida et al., 2002; Cheng et al., 2004; Lin et al., 2010; Song et al., 2012) and their aqueous extracts (Dinar et al., 2006), collectively comprising a significant fraction of the organic aerosol mass. For example, Humic-Like

~~s~~Substances (HULIS)~~, which are surface active,~~ have been found to account for up to 60% of water-soluble carbon in rural aerosols (Kiss et al., 2005).

~~Organosulfates (organic sulfate esters) have been observed as constituents of atmospheric aerosols in a wide range of environments, such as southeastern U.S.~~ (Surratt et al., 2008; Lin et al., 2012)~~, northern Europe~~ (Iinuma et al., 2007; Froyd et al., 2010; Kristensen and Glasius, 2011; Nguyen et al., 2014)~~ and even the Arctic, where organosulfates have been found to comprise 7-15% of total organic matter and 9-11% of submicron organic matter in two independent studies~~ (Frossard et al., 2011; Hansen et al., 2014)~~. Some organosulfates derived from monoterpenes contain a hydrophobic carbon ring and are anticipated to preferably stay at the liquid/air interface in aqueous solution (e.i. exhibit surface activity); however, this has not been investigated.~~

Surface activity and how it is accounted for in the thermodynamic representation of aerosol water uptake has been found to significantly impact model predictions of CCN activity for some atmospheric organics (Prisle et al., 2008; Prisle et al., 2010b). Introducing these predictions in large-scale atmospheric modelling of cloud-climate interactions and radiative forcing have been demonstrated to translate into impacts of comparable magnitude to the existing uncertainty in climate modelling (Prisle et al., 2012). Hence it is increasingly important to understand the effect of surface activity on cloud droplet activation, ~~These effects have in turn been demonstrated to translate into impacts on large-scale atmospheric modelling of cloud-climate interactions and radiative forcing of comparable magnitude to the existing uncertainty in climate modelling (Prisle et al., 2012). H~~ however~~,~~ to this date only a limited number of organic aerosol systems have been characterized in terms of their surface activity and the impact on cloud activation.

The hygroscopicity parameter κ (kappa) was introduced by Petters and Kreidenweis (2007) as a single variable to account for chemical effects on aerosol water uptake in equilibrium Köhler predictions of droplet growth and cloud activation. The κ-value is defined as an operational parameter and can be obtained from measurements of either hygroscopic water uptake in the sub-saturated humidity regime, or from the critical point of cloud droplet activation at supersaturated conditions, i.e. the critical particle diameter defined as the dry particle diameter, where 50% of the particles can activate at a given supersaturation~~i.e. the supersaturation threshold or activation diameter.~~ As an operationally defined parameter, the κ-value can be seen as describing aerosol – water mixing interactions with respect to a volume-based reference state. As aerosol growth is a combined effect of water uptake properties of components within the aerosol mixture, a range of aerosol – water mixing states is spanned by the subsaturated and supersaturated measurements, respectively (Prisle et al., 2010a). Provided that interactions of the mixture of individual aerosol components with water remain unchanged (or "ideal", as defined with respect to a certain reference state) over the entire concentration range spanned by measurements, the κ-value determined at different humidities, and at sub- and supersaturated conditions in particular, should remain unchanged. However, (non-ideal) mixing interactions of especially organic aerosol components with water are largely unknown and may be very complex, in particular in the presence of inorganics in the mixture (Prisle et al., 2010a). In general, previous studies comparing κ-values at sub- and supersaturated conditions found that the subsaturated κ-values were lower than supersaurated κ-values for both ambient aerosols and laboratory-generated aerosols, especially in the case of secondary organic aerosol (Good et al., 2010; Massoli et al., 2010; Cerully et al., 2011; Dusek et al., 2011; Hersey et al., 2013; Hong et al., 2014; Pajunoja et al., 2015), however a few studies found the discrepancy to be insignificant for some aerosol compositions and particle sizes (Good et al., 2010; Dusek et al., 2011).

Organosulfates (OS, organic sulfate esters), have been observed as constituents of atmospheric aerosols in a wide range of environments, such as south-eastern U.S. (Surratt et al., 2008; Lin et al., 2012), northern Europe (Iinuma et al., 2007; Froyd et al., 2010; Kristensen and Glasius, 2011; Nguyen et al., 2014) and even the Arctic, where OS have been found to comprise 7-15% of total organic matter and 9-11% of submicron organic matter in two independent studies (Frossard et al., 2011; Hansen et al., 2014). Some OS derived from monoterpenes contain a hydrophobic carbon ring and may prefer to stay at the liquid/air interface in aqueous solutions (i.e. exhibit surface activity). Despite the apparent atmospheric abundance and widespread relevance of organosulfates, their cloud forming properties have not yet been investigated; this gap has motivated the present study, where an atmospherically relevant organosulfate is characterized in terms of surface activity and hygroscopic properties.

Here, an OS derived from limonene, with a molecular weight of 250 Da (L-OS 250) was synthesized. The hygroscopic properties of L-OS 250, ammonium sulfate (AS) and mixtures hereof were studied in the laboratory employing a unique custom-build setup, allowing parallel measurements at sub-and supersaturated conditions. Furthermore the surface tension of aqueous solutions of L-OS 250 and L-OS 250 in mixture with AS were measured. κ was derived from the measurements at sub- and supersaturated conditions as well as modelled based on the volume additive Zdanovskii-Stokes-Robinson (ZSR) mixing rule (Petters and Kreidenweis, 2007) and three different partitioning representations, which can be used to represent cloud activation in global climate models. The specific aims of the study are to investigate how κ is influence by humidity, particle size and L-OS 250/AS mixing ratio as well as to scrutinize whether the model representations can reproduce the experimental κ-values for the system. The ability of the models to reproduce hygroscopicity measurements on process level is very important for their applicability in global climate models. Finally the study aims towards evaluating the cloud forming properties of organosulfates.

~~To our knowledge, atmospherically relevant OS have not yet been characterized in terms of their hygroscopic properties and in particular their intrinsic κ-values and effects of mixing interactions on the κ-values for particles comprising OS are not known, despite their apparent atmospheric abundance and widespread relevance. Here, we have synthesized an atmospherically relevant OS, derived from limonene with a molecular weight of 250 Da (L-OS 250), for systematic hygroscopicity characterization of this compound as a proxy for the many monoterpene-derived organosulfates observed in ambient air. We employed a unique setup, to simultaneously measure hygroscopic growth of different particle sizes at subsaturated conditions and CCN activation at supersaturated conditions on the same aerosol sample flow, in order to investigate the potential presence and direction of a discrepancy in κ-values between these humidity regimes. A similar approach has previously been used by Herich et al. (2009). Different relative L-OS 250 mixing ratios with ammonium sulphate (AS), an ubiquitous inorganic component in atmospheric aerosols were investigated with the setup. We also measured aqueous surface tension of bulk solutions of L-OS 250 and mixtures with AS, in particular to investigate the impact of a possible L-OS 250 surface activity on hygroscopic properties and cloud activation thermodynamics, as determined from equilibrium Köhler theory. Specifically, we aimed to establish whether the volume additive Zdanovskii-Stokes-Robinson (ZSR) mixing rule (Petters and Kreidenweis, 2007) is applicable for these particular particles, and whether there is any detectable change in the aerosol – water interaction properties with particle mixing state, in terms of humidity and particle composition and size.~~

2 Methods

2.1 Synthesis of limonene-derived organosulfates

L-OS 250 isomers were synthesized using the method presented ~~described in more details~~ by Cavdar and Saraçoğlu (2009) for synthesis of hydroxy sulfate esters by ring opening of epoxides with sodium hydrogen sulfate. Approximately 0.61 g limonene oxide was dissolved in 20 mL dried dichloromethane (CH_2Cl_2). Next, 1.10 g dried sodium bisulphate ($NaHSO_4$) was added to the reaction solution under magnetic stirring. The mixture was left at room temperature for 4-5 days for reaction, while the reaction environment was kept inert using nitrogen gas. The reaction scheme for the synthesis is given in Figure 1.

Following synthesis, the product was purified by solid phase extraction on an ion exchange hydrophilic column (Strata-X-A 33u polymeric strong anion, Phenomenex) using a solvent sequence of 10% acetonitrile in MilliQ water followed by acetonitrile and chloroform.

Based on analysis using an ultra-high performance liquid chromatograph coupled to a quadrupole time-of-flight mass spectrometer through an electrospray ionisation inlet (UHPLC-ESI-q-TOF-MS) running in either positive or negative ionization mode, it was estimated that an approximately 90(±5)% pure sample of L-OS 250 isomers was obtained in the acetonitrile fraction, the 10% impurities being by-products of organosulfates with MW 268 and MW 384 (chromatograms from the UHPLC-ESI-q-TOF-MS analysis are given in supplementary).

2.2 Measurement of surface tension

Aqueous solutions of L-OS 250 and mixtures of L-OS 250 and AS (Sigma-Aldrich $\geq$ 99 %), were prepared in MilliQ water (resistivity of 18.2 MΩcm at 25 ºC) for measurement of surface tension, σ. For each solute composition, 9 or more solutions of different concentrations were made to obtain measurements over a broad concentration range (see details in Table 1).

Surface tension of each solution was measured with a FTÅ 125 pendant drop tensiometer, with an overall uncertainty of ±2%. Measurements were done over a concentration range capturing the transition region of solution surface tension as it changes from the pure water value to the level of maximum obtainable surface tension reduction. Approximately 40 pictures were taken of each pendant drop and the surface tension was calculated based on the pictures by the programme FTA32. The surface tension reported here, resulted from analysis of three succeeding droplets, where the relative standard deviation of the surface tension did not exceed 1%. According to Noziere et al. (2014) surface tension of a pendant drop is reduced over time until the minimum equilibrium surface tension is reached, hence surface tension was measured for a L-OS 250 and a L-OS 250 with 80% AS solution (C(L-OS 250) = 0.005M) over a 30 min. time period. The surface tension was found to be stable after approximately 1 min., and the following measurements were thus initiated after 2 min. Measured surface tension was parametrized as a function of ternary solution composition according to the equation previously used by Prisle et al. (2010b), here in the form:

$$\sigma = \sigma_w - a \cdot R \cdot T \cdot Ln\left(1 + \frac{C_{L-OS\ 250}}{b}\right) \qquad (1)$$

where σ_w is the surface tension of water, $C_{L\text{-}OS\ 250}$ is the molar concentration of L-OS 250, R is the universal gas constant in $J \cdot K^{-1} \cdot mol^{-1}$, T is the temperature in Kelvin, Ln is the natural logarithm (to the base of e) and a and b are the Szyskowski equation fitting-parameters, which were fitted as dependent on solute mixing ratio, as:

$$a = a_1 + a_2 \cdot \frac{C_{AS}}{C_{AS} + C_{L-OS\ 250}} \qquad (2)$$

$$b = b_1 + b_2 \cdot \frac{C_{AS}}{C_{AS} + C_{L-OS\ 250}} \qquad (3)$$

where C_{AS} is the molar concentration of AS. The values for a_1, a_2 and b_1 and b_2 are given in paragraph 3.1.

2.3 Parallel H-TDMA/ CCNC measurements

To study the hygroscopic properties and the CCN activation of particulate L-OS 250 and their mixtures with AS, a unique custom-build laboratory set-up was built, enabling parallel measurements of both subsaturated water uptake and supersaturated cloud droplet activation for the same aerosol sample.

An atomizer (TOPAS ATM 220) was used to generate particles from aqueous solutions comprising L-OS 250 and AS in different relative mixing ratios. Each solution was prepared with de-ionized and purified water (resistivity of 18.2 MΩcm at 25 ºC). The solute compositions (relative L-OS 250 and AS mass fractions) and total solute concentrations (C, [g(solute)/L(solution)]) are given in Table 2. Following atomization, the aqueous aerosol was dried by passing through a diffusion dryer containing silica gel, resulting in a dry aerosol with relative humidity (RH) in the range 4-7%. It is assumed that particles at this RH are essentially water-free, and furthermore that their dry compositions reflect the relative solute mass fractions of the respective atomized solutions. At this point, the flow of dry particles was split two ways for parallel measurements of water uptake ability with a Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA) and cloud droplet activation with a Cloud Condensation Nuclei counter (CCNC). A schematic of the water uptake characterization setup is shown in Figure 2. Compressed air was applied after atomization to dilute the particle concentration in order to prevent coagulation.~~Dry gas (N_2) was applied after atomization to dilute the particle concentration.~~

The hygroscopic growth factor (HGF) of the generated particles was studied with the fifth generation University of Helsinki Volatility Hygroscopicity Tandem Differential Mobility Analyzer (VH-TDMA) (Hong et al., 2014), where the volatility mode was deactivated so the instrument functions solely in hygroscopicity mode. The dry particles were charged by a neutralizer and passed through a Differential Mobility Analyzer (DMA1, Hauke type), where a monodisperse aerosol distribution was selected, based on the electrical mobility of the particles. For each particle composition, four individual dry sizes were selected: 30 nm, 60 nm, 100 nm and 145 nm. The flow of monodisperse particles was then split into two ways, one going into a humidifier while the other one bypassing the humidifier. The humidifier exposed the particles to an environment with four different set RHs of 80%, 85%, 90% and 93%.

Number concentration size distribution data from both routines were measured using two similar systems, each including a Differential Mobility Analyzer (DMA, Hauke type), scanning the size distribution of the particles, and a condensation particle counter (CPC, TSI 3010 and TSI 3772), counting the number concentration of particles.

The HGF of the particles at each RH was obtained as the ratio of the size distribution of the humidified (D_{wet}) to dry (D_{dry}) particles (Cruz and Pandis, 2000):

$$HGF(RH) = \frac{D_{wet}(RH)}{D_{dry}} \tag{4}$$

The H-TDMA was calibrated prior to the measurements using pure ammonium sulfate particles with sizes 30 nm, 60 nm, 100 nm and 145 nm at dry conditions. The obtained data in dry condition was used to calibrate the measured raw data at RHs in other regimes based on the algorithm introduced by Gysel et al. (2009). Furthermore, the measured growth factor distribution data was inverted using the piecewise linear inversion approach (Gysel et al., 2009) by the software Igor Pro to obtain the HGFs.

For each particle dry size, four to six measurements of the HGF were made at each RH and the relative standard deviation between these measurements was below 3% for all compositions. This standard deviation accounts for uncertainties related to the experimental setup, including particle size selection and RH set point, as well as uncertainties connected with the data inversion process. Error bars presented in the following sections on reflect the variations between these measurements according to the observed relative standard deviations (± 2 standard deviation). The standard deviation found here are in line with a previous study, estimating uncertainties on HGFs to be below 5% (Massling et al., 2009).

The ability of the generated particles to activate into cloud droplets at supersaturated conditions was measured with a CCNC from Droplet Measurement Technologies (DMT, model CCN-100) attached with a Hauke-type DMA (DMA3). After passing through a neutralizer, the dried particles were transferred to DMA3 (see Figure 2~~1~~)~~.~~, which scanned over the particle sizes. This means that the specific particle size selected in DMA3 was changed every second minute. ~~from which a monodisperse particle distribution was obtained.~~ The particle flow was then split into two lines, one going into a CPC (TSI, 3010), counting the total number concentration of particles, and one going to the CCNC, counting the number concentration of particles that activate or become droplets larger than 1µm at a given supersaturation (SS). The nominal SS given by the CCNC was corrected to obtain the actual SS profile created in the instrument, based on measurements with AS following suggestions by Rose et al. (2008). Information regarding the calibration is given in supplementary material. CCN activation spectra were measured at thirteen different SSs, ranging from 0.099

to 0.922% (calibrated values, corresponding to 100.099 to 100.922% RH), by defining one supersaturation at the time and then scanning over the particle sizes (DMA3). 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. d50 for all SS was measured twice for all particle compositions except 90% L-OS 250, for which SS was only measured once.

~~The nominel SS given by the CCNC was corrected to obtain the actual SS profile created in the instrument, based on measurements with AS following suggestions by Rose et al. (2008). Information regarding the calibration is given in supplementary material.~~ Regarding uncertainties on the measurements, it is estimated that the particle size-selection in the DMA has an uncertainty of 3% and based on previous studies it is estimated that the uncertainty on the SS in the CCNC after calibration has a maximum value of 5% of SS (Rose et al., 2008;Asa-Awuku et al., 2009). Error bars presented in the following sections on critical particle diameter reflect these uncertainties.

2.3.1 Calculation of κ

The critical diameters obtained from the CCN measurements and the HGFs obtained from the H-TDMA measurements were used to calculate an effective hygroscopicity parameter, κ, for all particle sizes, compositions, and humidity conditions. 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.~~Hence, κ for example also expresses the influence of chemical composition on CCN activity.~~

From the HGF (H-TDMA experiment), κ was calculated by the equation given below (Hong et al., 2014):

$$S(D_{wet}) = \frac{HGF^3 - 1}{HGF^3 - (1-\kappa)} exp\left(\frac{4\sigma MW_W}{RT\rho_W D_{dry} HGF}\right) \quad (5)$$

where $S(D_{wet})$ is the saturation ratio, here it is the RH set in the H-TDMA measurements, HGF is the hygroscopic growth factor obtained from H-mode measurements, D_{dry} is the particle dry diameter, σ is the droplet surface tension, ρ_W and MW_W are the density and molar mass of water, respectively, R is the universal gas constant, T is the inlet temperature.

From the H-TDMA measurements κ can be calculated by inserting the experimental HGFs into equation 5 and then isolate κ by re-arrange the equation.

For each dry size, RH and particle composition, HGF was measured four to six times, hence four to six κ-values were obtained. In the following sections κ for each composition at a given RH and dry size is represented as the mean κ-values from these measurements. The standard deviation on the mean κ-value was below 7 % for all compositions except for pure L-OS 250 where the standard deviation was up to 36 %. In the following sections error bars represent ± two standard deviations on the mean κ.

From the CCN measurements, κ was found using the equation (Petters and Kreidenweis, 2007; Rose et al., 2010).

$$S(D_{wet}) = \frac{D_{wet}^3 - D_{dry}^3}{D_{wet}^3 - D_{dry}^3(1-\kappa)} exp\left(\frac{4\sigma MW_W}{RT\rho_W D_{wet}}\right) \qquad (6)$$

where D_{wet} is the droplet diameter.

When the experimental critical particle diameter is inserted into equation 6 as D_{dry}, κ can be iterated by varying the droplet diameter, D_{wet}, and κ itself until the minimum difference between the theoretical supersaturation, $S(D_{wet})$, and the experimental supersaturation is obtained. Reported CCN κ-values are thus the κ-values resulting in minimum difference between theoretical and experimental supersaturation (Petters and Kreidenweis, 2007; Rose et al., 2010).

~~Equation 6 was used to solve critical supersaturation for each particle dry size found in the experiments by changing κ and droplet diameter, D_{wet}, until the difference between calculated and calibrated supersaturation was at a minimum. Reported CCN κ-values are the κ-values resulting in minimum difference.~~

We calculate κ assuming the surface tension of pure water in Equations 5 and 6 above. ~~Any effects of surface tension reduction in the droplets on water uptake and CCN activation are therefore captured in the variation of the corresponding effective κ-values determined from our measurements.~~ The uncertainty on the CCN-derived κ-values was estimated to 10% (double the uncertainty on SS) and error bars on CCN-derived κ presented in the following sections represent this uncertainty.

Volume additive κ-values were calculated for particles of mixed composition, based on the Zdanovskii–Stokes–Robinson (ZSR) relation (Stokes and Robinson, 1966), by applying the mean measured κ-values for pure AS and L-OS 250 according to their estimated respective bulk volume fractions as previously done by for example Gysel et al. (2007), Petters and Kreidenweis (2007), Swietlicki et al. (2008) and Kristensen et al. (2014).

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$$\kappa = \sum_i \varepsilon_i \kappa_i \qquad (7)$$

Here, ε_i is the volume fraction of component *i* in the particle and κ_i is the intrinsic κ-value for component *i* in its pure form. The volume fraction is calculated from the mass fraction and the density of each component. The bulk mass density of AS is well known as 1.77 g cm^{-3} but to the best of our knowledge the density of L-OS 250 is currently unknown. Ambient organic aerosol mass densities are generally observed to be between 1.2 and 1.7 g cm^{-3} (Hallquist et al., 2009) and a density of 1.176 g cm^{-3} was found for sodium dodecyl sulphate, SDS (Prisle et al., 2011 and references herein), a surfactant with a sodium sulfate group (SO_4Na) considered to be similar to the sulfate group (HSO_4) in organosulfates. Hence, here we calculate additive κ-values assuming a density of 1.176 g cm^{-3} and 1.7 g cm^{-3} for L-OS 250 to cover this potential range. The volume additive κ-values were calculated for the specific purpose of investigating the validity of the additivity assumption for calculating κ-values for the L-OS 250/AS system.

2.4 Köhler modelling

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. (2010b). The bulk-to-surface partitioning model is a development of the model from Sorjamaa et al. (2004) and returns results similar to the model presented by Topping (2010) (e.g. Prisle et al., 2012).

~~of the studied particles was modelled as described in (Prisle et al., 2010b). Following κ was calculated from the modelled HGF and SSc using Eqs. (5) and (6) respectively.~~

The Köhler equation (8) is analogous with Equation 5 and 6, but without the κ approach used to calculate water activity:

$$S(D_{wet}) = x_W \cdot \gamma_W \cdot exp\left(\frac{4\sigma MW_W}{RT\rho_W D_{wet}}\right) \quad (8)$$

Where x_w is the water mole fraction and γ_w is the activity coefficient of water, which is here set to unity. The dry particle size and composition and the droplet size are the input parameters, which means that HGF must be known; hence the equilibrium RH can be calculated. HGF is varied until equilibrium RH is equal to the experimental RH (80, 85, 90 or 93%). Similarly, when the dry size and composition are the input parameters, critical supersaturation (SSc) can be solved numerically by varying droplet size. In both cases, droplet composition is always known and it can be used to calculate droplet solution surface tension (Equation 1). In addition, surface tension can be fixed to that of pure water or the effects of surfactant bulk-to-surface partitioning on water mole fraction and the concentrations used to calculate surface tension can be accounted for.

The model thus returns HGF-values and SSc under different assumptions, which are used to calculate κ from Equation 5 and 6 respectively.

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Three different model approaches, previously introduced by Prisle et al. (2010b) were used to assess the effects of surface tension reduction and surfactant bulk-to-surface partitioning on the L-OS 250 water uptake. First, bulk-to-surface partitioning and surface tension effects are both ignored (σ_w), which in particular means that the droplet surface tension in Equation 6 is taken as that of pure water. Second, reduction of droplet surface tension from L-OS 250 is considered, but the influence of bulk-to-surface partitioning is still ignored (σ_b)~~.~~, thus bulk solution properties are assumed. This means using Equation 6 with the concentration dependent surface tension (Equation 1) according to the total droplet concentration of L-OS 250. Third, bulk-to-surface partitioning is considered in the evaluation of the droplet bulk phase composition and surface tension (σ_p). used to calculate surface tension and water mole fraction change when the surfactant partitions to the droplet surface. Additional details about the surfactant partitioning calculations are given in the Supplementary material.~~This means that bulk solution concentrations (κ and droplet surface tension) change when the surfactant partitions to the droplet surface.~~

Droplet solution concentrations are calculated from the number of moles of each species (water, AS and L-OS 250), while assuming partial dissociation for ammonium sulphate (ν~2.3 based on the parametrisation presented by Prisle (2006)) and no dissociation for L-OS250 (ν=1). Since L-OS 250 is a molecular species and expected to be a very weak acid it is assumed that L-OS 250 does not dissociate in solution but primarily is present in its molecular form. Both AS and L-OS 250 are assumed to be fully dissolved at all relevant droplet concentrations and droplet solutions are also assumed to be ideal, due to the current lack of explicit information on non-ideal solution interactions involving L-OS 250. Mass mean molecular weight of 255.3 Da was assumed for L-OS 250, based on the 10% impurities. Droplet surface tension is calculated using Equation 1 when surface tension effects are accounted for, using the L-OS 250 bulk concentration evaluated either with or without consideration of bulk-to-surface partitioning; otherwise the constant surface tension value of pure water is used. Since the fit (Equation 1) can give negative surface tension values at high L-OS 250 concentrations, the minimum surface tension have been limited to 0.020 N/m. When bulk-to-surface partitioning is accounted for, droplet bulk solution concentrations are solved from the Gibbs adsorption equation as described in detail by Prisle et al. (2010b). This requires that the surface tension gradient is well-defined and non-zero, which in this case specifically means that surfactant bulk-to-surface partitioning cannot be evaluated for solution compositions resulting in droplet surface tensions below 0.020 N/m. This corresponds to the physical situation of constant surface tensions obtained for solutions above the so-called critical micelle concentration, where the aqueous surface is saturated in adsorbed surfactant and no further bulk-to-surface partitioning takes place (for more details, see Prisle et al. (2010b)).

3 Results and discussion

3.1 Surface tension

Figure 3 shows the surface tension of aqueous solutions of L-OS 250 and five mixtures of L-OS 250 and AS, as a function of the L-OS 250 molar concentration. L-OS 250 decreased the surface tension of aqueous solution from that of pure MilliQ water (73 mN/m at 20 ºC) considerably. Even at a concentration of 0.0025 mol/L the surface tension was decreased to 55.5 mN/m. The surface tension further decreased to 39.4 mN/m when the L-OS 250 concentration increased to 0.24 mol/L. Surface tension of the mixed L-OS 250 and AS solutions with ≤ 50% w/w AS converges toward the surface tension of pure aqueous L-OS 250, while the surface tension for the mixed solutions with ≥ 80% AS was lower than for the solutions of pure L-OS 250 with the same aqueous concentration. Previous studies have shown that addition of AS to pure water increased the surface tension (Lee and Hildemann, 2013; Matubayasi, 2013), however a decrease in surface tension of an organic solution when AS is added has been observed. For example, Ekström et al. (2009) found the surface tension of solutions of mannitol and methylerythritol to decrease with addition of 17% w/w AS, whereas the surface tension of solutions of adipic acid and methylthreitol increased with the same mass addition of AS. 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.~~The difference between their observations and the present can be qualitatively explained by differences in surface activity, impact on aqueous surface tension and effects interactions with the inorganics of the different organics involved.~~ The additional surface tension reduction observed at high AS concentration in the present study is consistent with a salting out effect, where the presence of AS in solution decreases the solubility of L-OS 250, hereby forcing L-OS 250 towards the solution surface.

For the investigated system, the lowest surface tension was observed for the L-OS 250 solutions with 90% AS at all L-OS 250 concentrations, where the surface tension dropped from approximately 73 to 33 mN/m over the concentration range of 0.0001 to 0.05 mol/L L-OS 250. Interestingly, the surface tensions of the L-OS 250 solutions with 95% w/w AS were increased compared to the 90% w/w AS of the same L-OS 250 concentration, over the full concentration range probed and converged towards the surface tension of pure L-OS 250 at concentrations lower than 0.005 mol/L. These observations suggest the presence of nonadditive effects of L-OS 250 and AS affecting solution surface tension, since the surface tension at a given L-OS 250 concentration does not decrease monotonically with AS concentration over the full range of L-OS 250/AS mixing ratios from 100 to 0% L-OS 250~~1–0~~. At 90% AS, salting out of the organic by AS appears to be the dominant effect causing surface tension to decrease below the additive effects of each solute components separately in solution, whereas at 95% AS the increase in surface tension caused by AS is no longer fully counteracted by surfactant salting out.

Measured surface tensions were parametrized as a function of ternary solution composition according to Equation 1. The fits are plotted in Figure 3 together with measured data and the fitting parameters are a_1 = 1.86E-6 mol/m^2, a_2 = 5.78E-7 mol/m^2, b_1 = 1.30E-4 mol/L, b_2 = 1.67E-6 mol/L. From Figure 3 it is evident, that there are 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 difficulty to capture~~ the composition-dependent surface tension variation over the full range of concentrations again indicates that the combined influences of L-OS 250 and AS on ternary aqueous surface tension are not linearly additive, as is also clear from the trend in the measurements. This might be expected for two components of very different molecular structures and behaviour in respective binary aqueous solutions.

3.2 Hygroscopic growth factor

Figure 4 shows HGF of laboratory generated particles of L-OS 250, AS and their mixtures as a function of RH. The HGF is shown for particles of four dry sizes (30, 60, 100 and 145 nm) being exposed to 80 – 93 % RH.

All six particle compositions showed hygroscopic growth at the selected RHs, and the HGF increased with increasing RH in each case, as expected for particles with non-vanishing hygroscopicity.

Only weak hygroscopic growth was observed for the pure L-OS 250 particles with HGF increasing from approximately 1.0 (no growth) at 80% RH to 1.2 at 93% RH, where the water uptake occurs smoothly over the given RH range. 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. ~~.~~There are no indications of deliquescence, as water uptake occurs smoothly over the given RH range. To the best of our knowledge the aqueous solubility of L-OS 250 is currently not characterized. Our present data are consistent with a modest L-OS 250 solubility, leading to a saturated solution with a water activity of about 0.85 at the onset of hygroscopic growth. The HGF of pure AS particles on the other hand increased from approximately 1.4 to 1.9 over the same RH range, consistent with the high water solubility and well-documented hygroscopic properties and deliquescence RH (DRH) of AS of 79.9 (±0.5) % at 295 K (Seinfeld and Pandis, 2006).

For the mixed particles, the HGF corresponding to a given dry particle size and RH increased with increasing weight percentage of AS, in accordance with an increasing contribution of the more hygroscopic component. For mixtures with ≥ 20% w/w AS, the overall HGF converged towards the HGF of pure AS for all particle sizes, thus the system shows a non-linear composition dependency. It must be kept in mind, that when a particle with presumably 80% w/w of L-OS 250 or some other organic demonstrates the same HGF as a pure AS particle, it does not imply that the organic has no intrinsic hygroscopicity in the mixture, but rather, that the resulting impact of the organic in the mixed particle is similar to the hygroscopic properties that would arise from the same particle fraction being composed purely of AS. In accordance with Köhler theory, any reduction of droplet surface tension from L-OS 250 should increase particle hygrocopicity. This therefore means that surface tension effect of L-OS 250 in our experiments appear to compensate for a possible decrease in direct impact on water activity from the larger molecular size, lower solubility and lower dissociation degree of L-OS 250, compared to AS.

Non-linear composition dependency has previously been observed for particles of mixed organic and inorganic compounds. Hämeri et al. (2002) found an overall particle hygroscopicity close to that of pure AS, when measuring the HGF for particles of malonic acid and succinic acid with 50% w/w AS. In our experiments the non-linear composition dependency is more pronounced as HGF-values of the mixed particles already coincide with the ones for pure AS at as low as 20 % w/w AS which could be caused by differences in surface activity of the organic compounds and their interaction with AS. For example, the acids considered by Hämeri et al. (2002) are hygroscopic and only weakly surface active in contrast to L-OS 250 showing significant surface activity, pointing to the significance of surface tension reduction effects for increasing the organic contribution to particle hygroscopicity. 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 non-linear composition dependency towards the hygroscopic properties of AS observed.

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In general, the dry size of the particles were observed to have little or modest influence on the measured HGF, however, for the particles of pure L-OS 250 and L-OS 250 with 10% w/w AS, the largest HGF was observed for the smallest particle sizes compared with the larger particles. For the pure AS particles and particles with ≥ 20% w/w AS, the opposite behaviour was seen, where the largest HGFs were measured for the largest particles. This further supports our inferences related to effects of organic solubility vs. surface activity: for particles with the highest fractions of L-OS 250, there could be kinetic effects of dissolution present, increasing the amount of dissolved material in the smallest particles, compared to the larger ones. Conversely, for particles with larger amounts of AS relative to L-OS 250, the hygroscopicity of the inorganic likely negates any effects of limited organic solubility. The size dependency for these particles may be related to effects of organic depletion from bulk-to-surface partitioning decreasing the relative amount of hygroscopic material in the droplet bulk of the smallest particles, compared to the larger ones (Prisle et al., 2010b).

~~Hämeri et al. (2002) have previously observed a similar effect of mixed organic and inorganic particles showing an overall particle hygroscopicity close to that of pure AS, in that the HGF measured for particles of malonic acid with 50% w/w AS and succinic acid with 50% w/w AS coincided with HGF for pure AS. The acids studied by Hämeri et al. (2002) are however hygroscopic and only weakly surface active, hence this behaviour is likely due to the coincidence of the effects of different mechanisms than in this work, in particular the relative effects of the organic and inorganic on droplet water activity. In our experiments the HGFs already coincide with the ones for pure AS at as low as 20% w/w AS, pointing to the significance of surface tension reduction effects for increasing the organic contribution to particle hygroscopicity, since L-OS 250 is a much stronger surfactant than the acids studied by Hämeri et al. (2002).~~

3.3 Critical particle diameter

Figure 5 shows the measured critical supersaturation (SSc) as function of dry particle diameter (D_{dry}) for the six different dry particle compositions studied. Unfortunately measurements at SSc 0.099 and 0.442 % resulted in negative values of the dry diameters for the pure L-OS 250 particles; hence these data points are absent.

Particles of all compositions could activate into cloud droplets in the investigated SS range and the SSc for activation decreased with increasing dry particle diameter as expected from equilibrium Köhler theory. Pure L-OS 250 particles activated at larger dry diameters compared to particles of pure AS at all selected SS, for example at a SS of 0.16 % pure L-OS 250 activated at a dry diameter of 170 nm whereas AS activated at a dry diameter of 93 nm. The curves for all six compositions ~~follow the~~have slopes close to the Köhler slope of approximately -3/2 in log-log space. According to equilibrium Köhler theory~~, this~~ a slope of -3/2 means that no explicit size-dependent effects are present in the obtained CCN spectra (Seinfeld and Pandis, 2006). Pure AS and L-OS 250 with 80% w/w AS, 50% w/w AS and 20% w/w AS had a slope of -3/2, whereas the slope for pure L-OS 250 and L-OS 250 with 10% w/w AS were slightly smaller (approximately -1.4), consistent with the presence of a modest size-dependent effect attributed to L-OS 250.

As was also observed for the measured subsaturated HGF, supersaturated activation properties of the mixed particles were dominated by AS, where the activation dry diameter at all SSs decreased with increasing weight percentage of AS. For particles with ≥ 20% w/w AS the activation dry diameter is essentially the same as for pure AS.

Previous studies of mixed organic and inorganic particles showed similar observations of a decrease in activation dry diameter with increasing amount of inorganics. For example, Prisle et al. (2010b) found the activation diameters of mixed surfactant (e.g. sodium octanoate, sodium decanoate, sodium dodecanoate and sodium dodecyl sulfate) and sodium chloride (NaCl) particles to decrease with increasing NaCl mass fraction in the particles, when investigating surfactant/NaCl systems with 5 to 80% w/w NaCl. However in contrast to the present study, the activation diameters did not coincide for any of the different surfactant/NaCl compositions investigated, indicating that the full cancellation of different opposing effects did not occur in their study.

3.4 κ-values

κ-values were calculated based on the H-TDMA measurements using Equation 5 and based on the CCN measurements using Equation 6 as well as using the ZSR-based additive formula (Equation 7). Furthermore, CCN experiments were modelled from equilibrium Köhler theory employing three different sets of assumptions, as explained in section 0 above, and the corresponding κ-values were calculated from the modelled critical supersaturations using Equation 6.

3.4.1 H-TDMA derived κ

Figure 6 shows $\kappa_{\text{H-TDMA}}$ as function of RH and dry particle size (D_{dry}) for the six compositions of L-OS 250 with AS investigated. The obtained κ-values for particles of all six chemical compositions at the four RHs showed a consistent size dependence, where κ decreased with increasing particle size. 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. To our knowledge, this is the first time that a decrease in $\kappa_{\text{H-TDMA}}$ with increasing dry particle size has been reported for particles of the same chemical composition.

Some studies of ambient aerosols have on the contrary showed that κ-values increase with particle size. For example, Holmgren et al. (2014) and Wu et al. (2013) found $\kappa_{\text{H-TDMA}}$ to increase with particle size during field campaigns in France and Germany, respectively. However, for field measurements, the chemical composition of the particles with all likelihood changes with size and with time, hence the change in κ observed with increasing particle size in the field studies is probably a result of changing chemical composition. In this study, particles of different size were formed from atomization of the same solution, hence, ideally they should have the same chemical composition. If this is the case, then the observed trend implies that the smaller particles are more hygroscopic than larger ones of the same chemical composition. This dependence may in turn be a true size dependence, resulting from a change in surface effects or dissolution kinetics with particle size. It should be mentioned, that the observed size dependence could potentially be an indirect effect of a changing chemical composition or from an artefact in our experiments. From the HGF measurements a bi-modal size distribution was observed for the mixed L-OS 250/AS particles, indicating that the particles may be externally mixed, thus it is possible that droplets formed with the atomizer from mixed L-OS 250/AS solutions have different chemical composition due to the surface activity of L-OS 250. The same could in principle be true for the pure L-OS 250 particles, since approximately 10% impurities (of two other organosulfates) were present here, however, these impurities are very similar in structure to L-OS 250. On the other hand it cannot explain the observed size dependence of the pure AS particles which should be fully soluble and not surface active in any case. We therefore do not believe that changing particle composition is the main cause of the observed particle size dependency in measured κ-values. Based on our results alone and the relatively modest size dependence observed, we cannot give the conclusive statement that smaller particles are more hygroscopic than larger ones of the same chemical composition. However the results present the possibility and further studies should be conducted.

Regarding RH, $\kappa_{\text{H-TDMA}}$ for pure L-OS 250 increased significantly ($\triangle\kappa/\kappa_{\text{RH93\%}}\cdot 100\% = 44\%$, 72%, 92% and 95% for 30 nm, 60 nm, 100 nm and 145 nm particles respectively), when RH increased from 80 to 93% humidity. This increase in $\kappa_{\text{H-TDMA}}$ could be caused by increased dissolution of L-OS 250. At low RH (here 80%), the water content in the droplets may not be high enough to dissolve the L-OS 250 particle entirely, resulting in a mixed liquid- and solid-phase droplet. Both Henning et al. (2012) and Zardini et al. (2008) have previously suggested that phase separation could make aerosol hygroscopicity RH dependent and Henning et al. (2012) found that soot particles coated with solid succinic acid resulted in no hygroscopic growth whereas soot particles coated with liquid/dissolved succinic acid resulted in hygroscopic growth, suggesting that the increase in $\kappa_{\text{H-TDMA}}$ observed here could also be caused by gradual dissolution of L-OS 250 with increasing RH. This effect will be discussed further in section 0.

For the pure AS particles and the L-OS 250 particles with 10%, 50% and 80% w/w AS, increasing subsaturated RH showed no clear effect on $\kappa_{\text{H-TDMA}}$. For these compositions, the $\kappa_{\text{H-TDMA}}$ appeared to be within in a stable range, independent of RH. For L-OS 250 particles with 20% w/w AS, $\kappa_{\text{H-TDMA}}$ decreased with increasing RH. This changing behaviour of κ with respect to RH for the different particle compositions may be due to a change in interactions between AS and L-OS 250 with changing mass fraction, which could influence the particle water activity.

$\kappa_{\text{H-TDMA}}$ showed a clear increase with increasing mass fraction of AS, where $\kappa_{\text{H-TDMA}}$ for mixtures with $\geq$ 20% AS converged towards the values of pure AS. As discussed by Sjögren et al. (2008), interaction of inorganic and organic species can increase the overall particle hygroscopicity and thus the apparent hygroscopicity of organic compounds, hence the high κ-values observed for the mixed particles with $\geq$ 20% w/w AS, that cannot be explained by increasing AS fraction alone is expected to be a result of such interactions. The $\kappa_{\text{H-TDMA}}$ for pure L-OS 250 (0.002 to 0.09) correspond to weakly hygroscopic organic compounds according to Petters and Kreidenweis (2007). L-OS 250 contains an alcohol group and a sulfate group, which are both polar; however the molecule contains a hydrophobic ring structure, hence it is not surprising that the hygroscopicity of L-OS 250 is modest. The $\kappa_{\text{H-TDMA}}$ for pure AS was here measured to be between 0.42 and 0.58, in line with previous studies, where κ for AS is in the range 0.33 to 0.72 (Clegg et al., 1998; Koehler et al., 2006; Carrico et al., 2008).

$\kappa_{\text{H-TDMA}}$ showed a clear increase with increasing mass fraction of AS, where $\kappa_{\text{H-TDMA}}$ for mixtures with $\geq$ 20% AS converged towards the values of pure AS. As discussed by Sjögren et al. (2008), interaction of inorganic and organic species can increase the overall particle hygroscopicity and thus the apparent hygroscopicity of organic compounds, hence the high κ-values observed for the mixed particles with $\geq$ 20% w/w AS, that cannot be explained by increasing AS fraction alone is expected to be a result of such interactions. The $\kappa_{\text{H-TDMA}}$ for pure L-OS 250 (0.002 to 0.09) correspond to weakly hygroscopic organic compounds according to Petters and Kreidenweis (2007). L-OS 250 contains an alcohol group and a sulfate group, which are both polar; however the molecule 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., ~~hence it is not surprising that the hygroscopicity of L-OS 250 is modest.~~ The $\kappa_{\text{H-TDMA}}$ for pure AS was here measured to be between 0.42 and 0.58, in line with previous studies, where κ for AS is in the range 0.33 to 0.72 (Clegg et al., 1998; Koehler et al., 2006; Carrico et al., 2008).

3.4.2 CCN-derived κ

Figure 7 shows the CCN-derived κ-values as a function of SSc for the different particle compositions. In general, κ_{CCN} increased with increasing mass fraction of AS in the particles, and those with ≥ 20% w/w AS have κ-values converging towards those of pure AS, exactly as was also found for $\kappa_{H\text{-}TDMA}$. This trend is therefore consistent over the whole humidity range investigated. κ_{CCN} for the pure L-OS 250 particles showed a weak increase with SS, implying a corresponding decrease of κ with increasing particle size, as the larger particles of a given composition activate at lower supersaturation conditions. κ_{CCN} increased from 0.095 to 0.145 when the SSs increased from 0.168 to 0.922 %, corresponding to particle diameters 170 and 47 nm, respectively (see Figure 7). κ_{CCN} for the L-OS 250 particles with 10 % w/w AS also show a weak increase with SS, rising from 0.18 to 0.23 over the selected SS range. However, including the uncertainty on $\kappa_{CCN,}$ the increasing trend for L-OS 250 and L-OS 250 with 10% w/w AS is likely not significant. For the pure AS particles and the particles with ≥ 20% w/w AS, κ_{CCN} showed no clear sign of increasing or decreasing trend with SS, but fluctuated within a range for each particle composition (0.49 to 0.57 for L-OS 250 with 20 % w/w AS, 0.50 to 0.59 for L-OS 250 with 50% w/w AS, 0.50 to 0.60 for L-OS 250 with 80% w/w AS and 0.51 to 0.59 for pure AS), where the individual κ_{CCN} fell within the uncertainty range of each other. Since the size dependency is strongest for pure L-OS 250, this suggests relation to properties of the organic, such as surface activity effects. We argue that a mean κ_{CCN} for each particle composition can be used to represent κ_{CCN} over the entire SS range of 0.099 – 0.922% investigated, as the individual κ_{CCN} fall within the overall uncertainty, and since the Köhler slopes obtained from the SSc curves are approximately -3/2 for all particle compositions, indicating the absence of significant size-dependent effects on SSc. Hence, in the following, κ_{CCN} for each composition is given as the mean κ_{CCN} (± 1 standard deviation) over the investigated SS range. In Table 3, the mean, minimum and maximum κ_{CCN} as well as standard deviation of κ_{CCN} is given.

3.4.3 Comparison of H-TDMA and CCN derived κ

Comparing $\kappa_{H\text{-}TDMA}$ and κ_{CCN} of each of the six particle compositions (see Figure 8), it is clear that κ-values for pure L-OS 250 are higher for supersaturated (CCN) than for subsaturated (H-TDMA) conditions. This is observed for all RH and particle dry sizes measured with the

H-TDMA. We note that the difference in κ between the two methods became smaller with increasing RH, meaning that at higher RH, $\kappa_{\text{H-TDMA}}$ for L-OS 250 approach κ_{CCN}, as expected if there is indeed a dissolution effect present. As mentioned in section 3.4.1, the increase in $\kappa_{\text{H-TDMA}}$ for L-OS 250 with increasing RH could be caused by increased dissolution of L-OS 250, which would be consistent with the indications of its modest water solubility discussed above. This explanation is supported by the observation of $\kappa_{\text{H-TDMA}}$ approaching κ_{CCN} with increasing RH. It is therefore suggested that the low $\kappa_{\text{H-TDMA}}$ for L-OS at 80%, 85% and 90% RH is caused by incomplete dissolution of L-OS 250 resulting in a mixed solid-/aqueous-phase system.

The $\kappa_{\text{H-TDMA}}$ for L-OS 250 with 10% AS coincide with κ_{CCN} for 30 nm and 60 nm particles whereas 100 nm and 145 nm particles have κ-values below the corresponding κ_{CCN}. For L-OS 250 particles with ≥ 20% w/w AS, it was generally observed that $\kappa_{\text{H-TDMA}}$ for 30 nm particles were a bit higher than κ_{CCN}, whereas $\kappa_{\text{H-TDMA}}$ for 145 nm particles were lower than κ_{CCN} and finally $\kappa_{\text{H-TDMA}}$ for 60 nm and 100 nm particles were essentially the same as the obtained κ_{CCN}. An exception is found for pure AS at 90% RH, and L-OS 250 with 20 to 80% w/w AS at 93% RH, where $\kappa_{\text{H-TDMA}}$ were below κ_{CCN} for the three larger particle sizes.

The trend of $\kappa_{\text{H-TDMA}}$ being smaller than κ_{CCN} has previously been observed in other laboratory studies investigating secondary organic aerosol hygroscopicity (Prenni et al., 2007; Petters et al., 2009; Massoli et al., 2010; Wex et al., 2010; Pajunoja et al., 2015), as well as in field measurements of ambient aerosol (Cerully et al., 2011; Hersey et al., 2013; Hong et al., 2014). The discrepancies between $\kappa_{\text{H-TDMA}}$ and κ_{CCN} found in the field studies were discussed by Hong et al. (2014), outlining different effects that could influence κ, first, the different degrees of dissolution of organics at sub- and supersaturated conditions, as well as potential phase separation of the particle and secondly the difference in instrumental design of the H-TDMA and CCNC, such as the residence time in the humidifying unit of the instrument relative to the aerosol equilibration time at the sub- and supersaturated conditions. In the setup used here residence times in the humidifying units were assessed to 1s in the H-TDMA and 10 s in the CCNC.

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The difference between $\kappa_{\text{H-TDMA}}$ and κ_{CCN} observed here can primarily be explained from the first-mentioned dissolution effect, since the discrepancy is mainly observed for the pure L-OS 250 particles, whereas the L-OS 250 particles with ≥20% w/w AS in general had the same κ-

values measured in the two saturation regimes, hence the interactions between AS and L-OS 250 are similar at sub- and supersaturation conditions at ≥20% w/w AS. Close agreement between $\kappa_{H\text{-}TDMA}$ and κ_{CCN} have previously been found for ambient aerosols with high mass fraction of ammonium and sulfate ions (e.g. Good et al., 2010). This could imply that a given amount of organics in aerosols may influence the aerosol hygroscopicity to a different extend at sub- and supersaturated conditions and that application of a single κ-value for a specific aerosol chemical composition many not be sufficient for describing particle hygroscopicity over the entire sub- and supersaturated humidity range.

3.4.4 Modelled κ

HGF and SSc values for L-OS 250, AS and four mixtures hereof investigated in our experiments were modelled from equilibrium Köhler theory employing 3 different sets of assumptions concerning surface tension and bulk-to-surface partitioning. These assumptions are briefly summarized below:~~as described in section 0 above:~~

1) Bulk-to-surface partitioning and surface tension effects are both ignored (σ_w)
2) Reduction of surface tension from the organic is considered, but effects of bulk-to-surface partitioning on droplet concentration are ignored (σ_b).
3) bulk-to-surface partitioning is considered in the evaluation of the droplet bulk phase composition, and the impact on surface tension according to the resulting bulk concentrations is included (σ_p)

κ-values were then calculated from the modelled HGF- and SSc-values using Equation 5 and 6, respectively. The purpose was to examine if surface tension or surfactant partitioning can explain the observed hygroscopic behaviour for the investigated L-OS 250 containing particles. Furthermore, κ-values for the four L-OS 250/AS mixtures corresponding to κ at sub- and supersaturated conditions were modelled using the volume additive ZSR mixing rule (Equation 7), using the measured mean κ-values of pure L-OS 250 and pure AS and the respective volume fractions of the two compounds. To obtain particle volume fractions from experimental mass fractions, we ideally need the mixed particle density, estimated as the volume additive bulk mass density of different particle components. The density of L-OS 250 ($\rho_{L\text{-}OS\ 250}$) is to the best of our knowledge unknown; hence the calculation was done using two different density cases for L-OS 250, 1.176 g cm^{-3} and 1.7 g cm^{-3}, as explained in section 2.3.1. κ was modelled this way for both sub- and supersaturated conditions~~ (see Figure 9)~~.

Figure 9 shows the κ-values resulting from the different model assumptions. The upper left panel~~The left panel of Figure 9~~ shows the additivity representation of κ (κ_{ZSR}) together with the measured values of $\kappa_{H\text{-}TDMA}$ and κ_{CCN}. κ_{ZSR} calculated using $\rho_{L\text{-}OS\ 250}$ = 1.176 g cm^{-3} (κ_{ZSR_1}) resulted in κ-values closer to the measured values than did κ_{ZSR} calculated using $\rho_{L\text{-}OS\ 250}$ = 1.7 g cm^{-3} (κ_{ZSR_2}) for all L-OS 250/AS compositions. κ_{ZSR_1} for L-OS 250 with 10% w/w AS and 80% w/w AS were reasonably close (± 10%) to $\kappa_{H\text{-}TDMA}$ for 145 nm particles and $\kappa_{CCN;}$ however, for L-OS 250 with 20% w/w AS and 50% w/w AS, $\kappa_{H\text{-}TDMA}$ and κ_{CCN} fall in the range of 0.4 – 0.6, whereas κ_{ZSR_1} have values of 0.17 and 0.32 for H-TDMA and 0.23 and 0.37 for CCN respectively. For these compositions, the additivity formula thus yields a very poor representation of the variations in measured κ-values, suggesting that the additivity formula should only be used for compositions very close to pure L-OS 250 or pure AS.

From figure 9 it is clear that the model representations σ_w, σ_b and σ_p results in similar κ-values in the subsaturated regime ~~κ-values, modelled using the σ_w, σ_b and σ_p representations, are similar in the sub-saturated range ~~and the values are practically independent of dry size and supersaturation. This behaviour is seen, because surface tension changes have negligible effect on the equilibrium relative humidity and surfactant bulk-to-surface partitioning is limited due to the low surface area to volume ratio for droplets conditioned at subsaturated humidities. As a result, the Köhler representation κ-values are similar to the ZSR κ-values and equally poor in representing the observed non-linear weight fraction dependency. This suggests that the non-linear composition dependency is caused by dissolution and non-ideal internal droplet mixture effects ~~droplet interaction effects ~~of L-OS 250, which are not accounted for in the Köhler models, rather than being a consequence of L-OS 250 surface activity.

One striking feature is that the bulk surfactant representation σ_b is clearly not able to predict measured aerosol water uptake and droplet activation in the supersaturated humidity range, where σ_b predicts a significant increase in κ with supersaturation for all particles comprising L-OS 250. This has been found consistently in previous studies of both pure surfactant and mixed surfactant/salt systems (Prisle et al., 2008; Prisle et al., 2010b; Prisle et al., 2011). ~~Based on equilibrium Köhler theory, water uptake is increased, when droplet solution surface~~

~~tension is decreased according to the bulk solution surface tension parametrisation, which leads to unrealistically large modelled κ-values for particles comprising L-OS 250.~~ The σ_w representation is much better at reproducing experimental data, but again the model is not able to predict the non-linear composition dependency, since also this model is purely a bulk solution representation. Finally, the σ_p model is able to predict the magnitude of the pure L-OS 250 κ_{CCN}-value and also the increasing trend with increasing SS, but again the model is not able to predict the non-linear composition dependency. This strongly suggests that partitioning effects do in fact influence activation thermodynamics of L-OS 250, even if the overall κ-values may be subject to cancellation effects, as was found for other atmospheric surfactants (Prisle et al., 2008; Prisle et al., 2010b), however partitioning does not seem to drive the variation in water uptake between the sub- or supersaturated regimes.~~but is not a driver of variation in the water uptake in the sub- or supersaturated regimes.~~

These findings are in good agreement with those from Prisle et al. (2010b), who showed that bulk solution surface tensions should not be used for microscopic droplets without accounting for bulk-to-surface partitioning.

4 Cloud-forming effects of organosulfates

Atmospheric aerosols are very complex, often consisting of many thousand organic compounds (Hamilton et al., 2004;Hallquist et al., 2009), thus the two-component particles studied here are properly not fully representative for atmospheric aerosols. However investigation of simplified systems can reveal the important interactions between complex organic compounds and common inorganics, which may influence cloud activation as well as expose how κ is influenced by the mixing ratio of organics to inorganics. Based on the results presented in the previous sections, we here try to evaluate the cloud-forming potential of organosulfates and the possible implications of our results for climate models.

~~We have here outlined the hygroscopic properties and aqueous surface activity of L-OS 250.~~ From our measurements, it was clear that L-OS 250 is indeed surface active and decreases the surface tension of water considerably, even for mixtures where the L-OS 250 concentration were as low as 5% of total solute concentration. However, the low intrinsic κ-values for L-OS 250 showed the organosulfate to be modestly hygroscopic, hence in terms of water uptake, the significant surface activity must be countered by other effects in the droplets, such as limited water solubility. Based on the results presented here, the intrinsic cloud forming properties of pure L-OS 250 thus appear to be limited. On its own, L-OS 250 particles require significantly higher SS to activate into cloud droplets compared to the inorganic salts such as AS. On the other hand, L-OS 250 does not appear to inhibit the CCN activity of very active inorganics such as AS beyond displacing the AS mass in the aerosol, since he hygroscopic properties of mixtures of L-OS 250 and AS, converged towards the properties of pure AS, when AS composed ≥ 20% w/w of the mixture. In fact, when particles with as much as 80% by mass of L-OS 250 display the same water uptake properties as pure AS particles of the same size, it shows a significant contribution of the organic and/or its interactions with the inorganic. The discrepancy between $\kappa_{H\text{-}TDMA}$ and κ_{CCN} for L-OS 250 shows that extrapolation of κ from the subsaturated to the supersaturated range is connected with significant uncertainties. In regard to the cloud forming potential of L-OS 250 it should therefore be emphasised that the CCNC measurements are of greater importance as clouds are supersaturated with water.

The results presented in section 3.4.4 are important for global climate models, as the partitioning representations, σ_w, σ_b and σ_p, tested here, may be used in such models. From figure 9 it is clear that σ_b in particular fails to represent the experimental data at supersaturated conditions. When the partitioning representation σ_b is implemented in global simulations of droplet activation, the predicted cloud droplet number is much larger, than when σ_w or σ_p is used (Prisle et al., 2012), hence σ_b predicts a greater indirect aerosol effect than the two other representations. Our results imply that σ_b should not be used in global simulations to represent cloud droplet activation as it cannot reproduce experimental data on process level. Introducing σ_b in climate models would thus result in even larger uncertainties on the future climate.

Concerning global climate models it is of high interest to consider whether organosulfates can be merged with other organics and represented by one common κ-value. The κ-values found here are within the range of other organics (approximately 0.0 to 0.3 for CCNC measurements), including carboxylic acids, sugars and HULIS (Petters and Kreidenweis, 2007;Chan et al., 2008;Jing et al., 2015). Hence considering κ alone, it would seem that organosulfates can be merged with other organics, however this study reveals how organosulfates behave on their own and in mixture with inorganics, but this is not necessarily representative for complex organic mixtures. For example a recent study by Jing et al. (2015) shows that κ of organic mixtures can be much higher compared to what was expected by considering κ of the individual compounds, hence we do not think that all organics can be represented in climate models by one common κ-value based on the mean of individual κ-values.

L-OS 250 is but one of many organosulfates found in the atmosphere, but we believe that the hygroscopic properties found for L-OS 250 in this study is a good representation for (at least some of the) other monoterpene-derived organosulfates, for example OS 250 derived from α-/β-pinene, L-OS 252 and L-OS 268, since they have structural similarities and few functional groups (see Figure 10). Many organosulfates of atmospheric relevance contain additional hydroxyl groups or carboxylic acid groups and are composed of fewer carbon atoms than L-OS 250, for example OS 200 and OS 216 derived from isoprene (see Figure 10). These organosulfates with additional hydroxyl/carboxylic acid groups are likely to be more hygroscopic, and therefore more prone to activate into cloud droplets, according to the recent study by Suda et al. (2014), showing that hygroscopicity of organics increases with addition of hydroxyl groups, carboxylic acid groups and hydroperoxide groups, in the given order. There is thus a need for further hygroscopicity measurements to investigate the atmospheric impact and cloud forming potential of smaller and more polar organosulfates, e.g those derived from isoprene.

5 Conclusions

We have here presented the first ~~measurements~~ characterization of an atmospherically relevant organosulfate, derived from limonene (L-OS 250), in terms of surface activity and hygroscopic properties.~~of hygroscopic properties, CCN activity and aqueous surface tension properties for an atmospheric organosulfate.~~ Surface tension measurements showed L-OS 250 to be surface active with the capacity to decrease the surface tension of bulk aqueous solutions considerably. The surface tension of L-OS 250 solutions decreased even further with the addition of AS, suggesting a salting out effect in bulk solutions. The significant surface activity of L-OS 250 suggests that L-OS 250 could act as a CCN.

The~~se~~ ~~water interaction~~hygroscopic properties of particles containing L-OS 250, AS and mixtures hereof were examined in the laboratory at sub- and supersaturated conditions~~,~~ using a custom-build setup, allowing ~~an instrumental setup that allows~~ parallel measurements of HGF (with an H-TDMA) and of CCN activation (with a CCNC). HGF for L-OS 250 was

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found to increase from 1.0 (no growth) to 1.2 over the measured subsaturated humidity range from 80% to 93%, showing that L-OS 250 can take up water in the subsaturated range. However compared to AS (HGF = 1.4 at 80% RH and 1.9 at 93% RH), the investigated L-OS 250 particles only showed weak hygroscopic growth. Measurement with the CCNC showed the ability of L-OS 250 to activate into cloud droplets; the critical diameters for L-OS 250 particles were 55 – 83% larger than for pure AS, which is comparable to critical diameters for other atmospheric organics, that have previously been characterized. The hygroscopic properties of the L-OS 250/AS system showed a non-linear composition dependency, as both HGF-values and d50 of the mixed particles with ≥ 20% w/w AS converged toward the values of pure AS. This implies that L-OS 250 actually contribute to the overall hygroscopicity of these mixed particles. The hygroscopicity parameter, κ, was calculated for the L-OS 250/AS system, revealing L-OS 250 to be weakly hygroscopic, κ derived from the H-TDMA measurements was found to vary with particle size for all particle compositions, increasing with decreasing particle dry diameter. However, whether $\kappa_{H\text{-}TDMA}$ is truly size dependent, or an experimental artefact has caused this tend cannot be concluded from these experiments alone. κ_{CCN} was larger than $\kappa_{H\text{-}TDMA}$ for L-OS 250, which is probably caused by differences in the degree of dissolution of L-OS 250 at sub- and supersaturated conditions. For AS and mixed L-OS 250/AS particles κ_{CCN} and $\kappa_{H\text{-}TDMA}$ were in the same range. κ also displayed the non-linear composition dependency observed for HGF and d50.

It was investigated if the hygroscopic properties of the L-OS 250/AS system could be reproduced by model calculations under different assumptions concerning surface tension effects and bulk-to-surface partitioning. Based on the model calculations, κ was calculated and compare with the experimental κ-values. None of the three model calculations or the ZSR mixing rule were able to capture the observed non-linear composition dependency for the mixed particles, indicating that L-OS 250 solubility and non-ideal droplet interactions could be important for mixtures of the L-OS 250/AS system, as these were not account for by the model. The bulk partitioning model, σ_b, was especially erroneous in reproducing the κ- values of the system, underlining that σ_b should not be used in global climate models to represent cloud activation.

~~At both sub- and supersaturated conditions, the water uptake properties of mixed particles with ≥ 20% w/w AS became similar to those of pure AS, showing that the contribution of L-~~

~~OS 250 to the overall hygroscopicity of these mixed particles is not insignificant. The hygroscopicity parameter, κ, was calculated for the L-OS 250/AS system from both H-TDMA measurements and the CCN measurements, respectively, and $\kappa_{\text{L-OS 250}}$ was in the range 0.002 – 0.14, corresponding to weakly hygroscopic organics, whereas κ_{AS} was in the range 0.42 – 0.59, as expected for a hygroscopic salt. $\kappa_{\text{H-TDMA}}$ was found to vary with particle size for all particle compositions, increasing with decreasing particle dry diameter. However, whether $\kappa_{\text{H-TDMA}}$ is truly size dependent, or the size dependency is a result of an experimental artefact, cannot be concluded from these experiments alone. κ_{CCN} was larger than $\kappa_{\text{H-TDMA}}$ values obtained from all RH and particle dry sizes for L-OS 250, which we explain by differences in the degree of dissolution of L-OS 250 in the particles at sub- and supersaturated conditions. For AS and mixed L-OS 250/AS particles κ_{CCN} and $\kappa_{\text{H-TDMA}}$ were in the same range.~~

~~Surface tension measurements showed L-OS 250 to be surface active with the capacity to decrease the surface tension considerably in bulk aqueous solution. At an L-OS 250 concentration of 0.0025 mol/L, the surface tension of water was decreased by 24% from the pure water value. The surface tension of L-OS 250 solutions with a given organic concentration decreased with addition of AS, suggesting a salting out effect in bulk solutions.~~

~~Modelled κ, calculated from the volume additive ZSR mixing rule and from model predicted HGF and critical supersaturations, were not able to capture the observed non-linear composition dependency upon mixing with AS in the particle phase. The models accounted for different surface tension effects, so these are not the main reasons for the observations. This indicates that L-OS 250 solubility and droplet solution are non-ideal, which were not accounted for by the models, could be important for mixtures of the L-OS 250/AS system.~~

~~The study evaluates the cloud forming properties of atmospheric organosulfates derived from monoterpenes, but in order to cover the hygroscopic properties of the full range of atmospheric organosulfates more experiments are needed, especially with the smaller and more polar ones derived from isoprene.~~

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Table 1: Composition and concentration range of the solutions used for surface tension measurements.

Composition [% wt/wt]		# solutions	Concentration range [mol/L]	
L-OS 250	**AS**		**L-OS 250**	**AS**
100	0	12	0.0001 – 0.24	–
80	20	10	0.0001 – 0.20	0.00005 – 0.10
50	50	9	0.0001 – 0.10	0.0002 – 0.20
20	80	9	0.0001 – 0.05	0.0007 – 0.37
10	90	9	0.0001 – 0.05	0.0017 – 0.85
5	95	9	0.0001 – 0.07	0.0035 – 2.7

Table 2: Solutions of L-OS 250, AS and mixtures hereof for measurement of hygroscopic growth factor and CCN activation.

Composition [%wt/wt]		**Total solute concentration [gL^{-1}]**
L-OS 250	**AS**	
100	0	0.21
90	10	0.21
80	20	0.20
50	50	0.22
20	80	0.19
0	100	0.25

Table 3: Mean, minimum and maximum values of the hygroscopicity parameter, κ, obtained from the CCN measurements, as well as standard deviations.

	κ_{CCN}			
	Mean	**Std.Dev**	**Minimum**	**Maximum**
L-OS 250	0.120	0.017	0.095	0.145
L-OS 250 (10% w/w AS)	0.207	0.013	0.182	0.229
L-OS 250 (20% w/w AS)	0.510	0.022	0.486	0.566
L-OS 250 (50% w/w AS)	0.519	0.028	0.496	0.589
L-OS 250 (80% w/w AS)	0.532	0.027	0.501	0.597
AS	0.538	0.026	0.509	0.594

Figure 1: Synthesis of limonene-derived organosulfates with a molecular mass of 250 Da (L-OS 250) by ring opening of limonene epoxides with sodium hydrogen sulfate. The reaction is based on Cavdar and Saracoglu (2009).

Figure 2: Schematic illustration of the experimental set-up for the dual H-TDMA and CCN measurements.

Figure 3: Surface tension as a function of the concentration of limonene organosulfate (L-OS 250) for six mixtures of L-OS 250 and ammonium sulphate (AS). Note that the data is plotted in semi-log space. Lines represent parametrisation curves and error bars show the 2% instrumental uncertainty.

Figure 4: Hygroscopic growth factor (HGF) as a function of relative humidity (RH) for particles of pure L-OS 250, pure AS and mixtures hereof. Growth factor is given for four dry particle diameters of each chemical composition. Each dot represents the mean HGF obtained from 4 to 6 measurements, and the error bars express ± two standard deviations as described in section 2.3~~0~~.

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.

Figure 6: Hygroscopicity parameter, κ, obtained from the H-TDMA measurements, as a function of RH for the six mixtures of L-OS 250 and AS. Error bars represent ± two standard deviations on κ as described in section 2.3.1

Figure 7: Hygroscopicity parameter, κ, derived from the CCN measurements, as a function of SSc for six mixtures of L-OS 250 and AS. Error bars represent an estimated uncertainty of 10% on κ and uncertainty on the SSc is estimated to be 5%/% as described in section 2.3.1.

Figure 8: Hygroscopicity parameter, κ, derived from the H-TDMA measurements, ~~as a function~~plotted against~~ of~~ κ obtained from the CCN measurements, for six mixtures of L-OS 250 and AS. A mean κ-values for each composition was found for the CCN-derived κ and error bars denote the uncertainty as explained in section 2.3.1.

Figure 9: Measured and modelled hygroscopicity parameter, κ, as a function of RH for six mixtures of L-OS 250 and AS. Markers represent the measured values of κ and lines represent the modelled values of κ. The light grey area denotes humidity in the supersaturated range (CCN) and the white area denotes humidity in the subsaturated range (H-TDMA). For subfigure ZSR the solid lines represent additive κ calculated using a density of 1.176 g cm^{-3} for L-OS 250 whereas a density of 1.7 g cm^{-3} is represented with the dotted lines. For subfigure σ_w, σ_b and σ_p,~~σ_p~~, the subsaturated range, the solid line is modelled κ for 30 nm particles, the dash-dotted line is modelled κ for 60 nm particles, the dotted line is modelled κ for 100 nm particles and the dashed line is modelled κ for 145 nm particles. Error bars represent the uncertainty on the κ-values obtained from the measurements (±10% on κ_{CCN} and ± two standard deviation on $\kappa_{H\text{-}TDMA}$). Please note that the y-axis in subfigure σ_b is different form the other subfigures.

Figure 10: Selected organosulfates derived from monoterpenes and isoprene (Surratt et al., 2007; Surratt et al., 2008). Note that isomers are possible for the given structures.