Responses to Referee #1

We thank the reviewer for the careful review of our manuscript; the comments and suggestions are greatly appreciated. All the comments have been addressed. In the following please find our responses to the comments one by one and the corresponding changes made to the manuscript. The original comments are shown in italics.

Anonymous Referee #1

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The manuscript "Cloud condensation nuclei activity, droplet growth kinetics and hygroscopicity of biogenic and anthropogenic Secondary Organic Aerosol (SOA)" by D.F. Zhao and co-authors deals with sub- and supersaturated hygroscopicity of chamber generated SOA from representative anthropogenic and biogenic precursors, relating observed differences to chemical variations in terms of oxidation state and mixing between each SOA component. The paper is interesting in relation to both aerosol thermodynamics, atmospheric chemistry and aerosol modelling accounting for effects of chemical ageing. It is well-written and the discussion is overall good. I do however have some additional suggestions for clarifications and to elaborate a bit further.

General comments*:*

Although I generally think the discussion is very good, the manuscript would benefit if some of the clarity in the conclusions section would be evident already at the discussion stage.

The consequences for atmospheric studies of exactly the processes (SOA mixing) and SOA types studied could be emphasized a bit further.

Response:

We thank the reviewer for the supporting remarks.

In the revised manuscript, we have accepted the suggestion and clarified the discussion. We have emphasized the consequences of the SOA mixing as follows.

"On the regional scale, when an air mass from regions influenced by anthropogenic emissions (e.g. an urban region) transports to regions influenced by biogenic emissions (e.g. a forest region), the physicochemical properties of the mixed SOA formed will likely shift to be BSOA-dominated due to the fast turnover of BVOC, i.e., decreasing hygroscopic growth compared with ASOA. In contrast, when an air mass from regions influenced by biogenic emissions transports to regions with anthropogenic emissions, the SOA properties will likely remain those of BSOA due to the slow turnover of AVOC."

Concerning the description of the experiments, it could be clarified whether the ageing processes are considered to occur in both the gas and aerosol phases, or only in the gas-phase. I was somewhat unsure of this in relation to the mixed A- and BSOA studies and it *certainly affects the interpretation of mixing and other thermodynamic effects vs. kinetics and the plausibility of oligomerization. What's the basis of the different time lags chosen for mixing A and B VOCs? Do you have homogeneous nucleation in the chamber, there is no mention of seeds?*

Response:

Although aging can occur in both the gas and particle phase, here we assume, based on the study by Donahue et al. (2012), that dominating aging occur in the gas phase. We used oligomerization explicitly when we discussed oligomerization. This point has been clarified in the revised manuscript as follows.

"Photochemical aging is thought to mainly happen in the gas phase (Donahue et al., 2012) and to affect the particle composition by partitioning, although heterogeneous oxidation and particle phase oxidation may also play a role."

The time lag in the experiments with sequential VOC addition was chosen in a way that particle mass concentration generated from the first VOC reached a maximum and after 1-2 h the second VOC was added. The time lag was longer when AVOC was added first due to its low reactivity. In the revised manuscript, we have added the following sentences.

"In experiments with sequential VOC addition, the second VOC was added 1-2 h after the SOA mass concentration generated from the first addition reached its maximum. Accordingly, the time lag was longer when AVOC was added first due to its lower reactivity."

We had homogenous nucleation in the chamber and no seed was used. In the revised manuscript, we have clarified these issues as follows.

"In all the experiments, particles formed by homogeneous nucleation and no seed aerosol was added."

I am not sure how well oligomer formation explains the hygroscopicity and CCN activity results. Is oligomerization the most plausible explanation for the non-linear response in K to A and BSOA fractions? It could also be non-ideal solution effects, such as codependent solubility, possibly also leading to evaporation of some SOA material. You could either explain in more detail what makes you believe there should be oligomers in the aerosol, e.g. give a few more references to previous work supporting this, or explore other explanations, such as solubility and co-solvation effects, in a bit more detail. These would be supported by the sub-unity K(HTDMA)/K(CCN) ratios? Instead of chemical pathways to reducing volatility, have you considered also thermodynamic explanations, such as Raoult's law mixing (see e.g. Asa-Awuku, 2009)? Alternatively, how would you make a future experiment to get a positive detection of these oligomers?

Response:

The solubility and co-solvation effects as discussed in Asa-Awuku et al. (2009) have been taken into account in the ASOA fraction calculation. Here the ideal mixing of ASOA components with BSOA components was assumed, i.e., a single phase and that the total SOA mass participate the partitioning of ASOA and BSOA components. In the case of non-ideal mixing, the ASOA fraction would be lower. The kappa of ABSOA will be lower than the linear combination to an even higher extent, i.e., stronger non-linear effects. Therefore, this co-solvation effect is less likely to explain our findings.

In the revised manuscript, we have clarified the mixing of ASOA and BSOA components in Sect. 2.2.

"In the ABSOA experiments, the mass fraction of ASOA in the total aerosol was estimated using a method based on the aerosol mass yield and VOC consumed as described by Emanuelsson et al. (2013), where ideal mixing of ASOA and BSOA components was assumed."

In the future experiments, conditions that can form comparable fractions of both ASOA and BSOA, thus favorable to ASOA and BSOA interaction such as oligomerization are preferred. Therefore, relatively higher AVOC concentration and higher OH concentration (as in experiment AB5) are desirable. This point has been added in Sect 3.2 of the revised manuscript.

In the revised manuscript, we have further supported the discussion of effects of oligomer formation using more references and our filter data as follows.

"We observed the oligomer formation in these samples (Fig S6). Oligomer in SOA has been found by a number of studies (Gao et al., 2004; Noziere et al., 2015; Tolocka et al., 2004; Kalberer et al., 2004; Kourtchev et al., 2015; Kourtchev et al., 2014). Small multi-functional products from aromatics oxidation (Hamilton et al., 2005; Jenkin et al., 2003; Johnson et al., 2005) may promote oligomerization between ASOA and BSOA components."

Why would oganic-organic interactions decreasing particle volatility and SOA persis-tence lead to increases in CCN activity? In fact, ideal mixing of organic components (organic phase) would indicate strong similarities between the different SOA types and therefore potentially an unchanged CCN activity of their mixtures, as indeed observed.

Response:

By "the interaction between ASOA and BSOA", we mainly refer to the oligomerization and morphology changes (glassy states). These interactions can decrease the volatility and decrease the CCN activity.

The ideal mixing only indicates some similarities between different SOA. Yet, even if different OA components can mix well forming single phase, they could still have different detailed chemical composition and different components can still interact physically and chemically (e.g. oligomerization). For example, oligomer can be formed in pure BSOA or ASOA particles.

In the revised manuscript, we have clarified this interaction in Sect 3.1.1.

"We conclude that the interaction of AVOC with BVOC oxidation products, such as potential oligomerization during the photochemical oxidation does not affect CCN activity of the resulting ABSOA."

Similar droplet growth kinetics doesn't necessarily mean particles are internally well mixed.The presence of water could lead to melting of one organic phase which could then facilitate melting of another organic aerosol phase. Maybe you could clarify a bitwhat significance you put on the similar growth kinetics?

Response:

We agree with the reviewer's comment and we did not claim that growth kinetics data indicates that particles are internally mixed. In the revised manuscript, we have clarified this issue.

It reads now:

"Based on the droplet growth kinetics of the ABSOA (Fig. 3) observed in this study, no matter whether ASOA and BSOA components are well mixed in the particles, mixing issues did not seem to affect the water uptake of particles in supersaturated conditions. Hence, the kinetics of ABSOA, ASOA and BSOA activation may be regarded to be similar when cloud activation is considered."

How are the error bars shown on K values estimated? These K values are fairly low (<0.1), but it still seems that differences are significant and outside uncertainty limits?

Response:

The error bars of κ_{CCN} were estimated using the standard deviation of D_{crit} from three duplicate scans. The error bars of κ_{HTDMA} were also estimated using the standard deviation of the growth factor at (90±1) % RH of at least three duplicate scans.

We are not sure which kappa the reviewer referred to. We guess the reviewer referred to κ_{HTDMA} and the differences of κ_{HTDMA} between BSOA and ASOA. The differences between κ_{HTDMA} of ASOA and BSOA are significant and beyond the uncertainty limits.

In the revised the manuscript, we have clarified how the error bar was estimated.

Specific comments:

19913 l. 18-20: "Since different SS correspond to different critical sizes, this dependence indicates a size dependent chemical composition of aerosol (Zhao et al., 2015a)." Couldn't it also be dilution state and concentration dependent behavior in the aqueous phase. What would be the mechanism for size dependent composition?

Response:

The size-dependent kappa is plausibly attributed to the size-dependent chemical composition, although dependence of the deviation from ideality with concentration could also contribute. But this question is beyond the scope of this manuscript. The details of the size-dependent kappa and its causes are discussed elsewhere (Zhao et al., 2015). The possible mechanisms of the size-dependent kappa include the Kelvin effect, heterogeneous oxidation and the effects of the higher generation products.

19915 l. 13-16: "Functionalization does not significantly change the molar volume of organics, but it increases the van't Hoff factor due to both its interaction of polar functional groups with water and additional dissociation effects by carboxylic and hydroxyl group (as in Eq. A6) (Petters et al., 2009; Tritscher et al., 2011)." What do you mean by the first part of this statement? Which interactions and how do they change the van't Hoff factor? How do you define the van't Hoff factor?

Response:

kappa is affected by the molar volume of organics and the van't Hoff factor as shown in Eq. A6. van't Hoff factor, i, is the ratio of the measured value of a colligative property to the expected value if the solute is a nonelectrolyte (Petrucci and Herring, 2007; McDonald, 1953; Low, 1969). It is the ratio of the actual concentration of molecules or ions produced when a substance is dissolved to the concentration of the substance if it does not dissociate. When a molecule dissociates, it can increase i. The interaction of polar groups with water decreases the repulsive force between organics and water, which therefore increases i. The relationship of van't Hoff factor and kappa is discussed in previous studies (Petters et al., 2009; Tritscher et al., 2011).

In the revised manuscript, we have clarified this sentence as follows and added more background information of i in the Appendix A.

"As shown in Eq. A6, κ is affected by the molar volume of organics and by the van't Hoff factor (the ratio of the actual concentration of molecules or ions produced when the substance is dissolved to the concentration of the substance if it does not dissociate)."

19915 l. 19: Here you briefly mention the effects of oligomerization on surface tension effects. I was a bit confused until reading on and you may consider mentioning this either in relation to the other surface tension discussion or after discussion oligomers in more detail. Maybe also clarify exactly what compensating effects of surface tension you are discussing here?

Response:

We have realized that it is not proper and closely relevant to discuss the effects of oligomerization and photochemical oxidation on surface tension here. In the revised manuscript, we have omitted this sentence.

19916 l.18: less significant as / less significant than?

Response:

We have corrected this to “less significant than” in the revised manuscript.

19917 l.17: similar with / similar to?

Response:

We have changed to “similar to” in the revised manuscript.

19918 l.1-7: The paragraph concerning mixing and the work of Hildebrandt et al. (2011): here it is not entirely clear if you are talking about an ideal organic-organic mixture or an ideal aqueous mixture with respect to each of the organics. For the latter option, I wonder what you consider the phase of the particles to be? For high viscosity or solid particles, it could of course affect the mixing state upon sequential addition to the reaction mixture. Also, I assume you are aware of that there is no reason to expect that an ideal organic mixture would entail that either organic would behave ideally in aqueous solution, but it is unclear from this paragraph, so I suggest you elaborate a bit on this very interesting issue.

Response:

In this paragraph we referred to organic-organic mixing. In an extreme case, the organics in the outer layer may hinder water uptake by organics in the inner layer. Our findings indicate that no matter whether the organics are well mixed or not, the water uptake in supersaturated conditions seemed not to be affected. We agree with the reviewer’s comment that well mixed organics do not entail the ideality in the solution. In the revised manuscript, we have clarified this point as follows.

“A recent laboratory study by Loza et al. (2013) suggests limited mixing of different types of SOA components in the particles formed ... yield. Based on the droplet growth kinetics of the ABSOA (Fig. 3) observed in this study, no matter whether ASOA and BSOA components are well mixed in the particles, the mixing issue did not seem to affect water uptake of particles in supersaturated conditions. The kinetics of ABSOA, ASOA and BSOA activation may be regarded to be similar when cloud activation is considered.”

19920 l. 2-3: What exactly is meant by simple linear mixing and a non-linear response, respectively? You do explain this, but I would define it rigorously before using these terms simply. What is the measured response, change in K(HTDMA)? Is it linear with respect to amount of AVOC and BVOC, or ASOA and BSOA? Also, is it ASOA and BSOA mass or volume fraction?

Response:

In the revised manuscript, we have defined it clearly. It reads now:

"Such a graph can help to detect whether the κ_{HTDMA} of ABSOA can be described by a simple linear mixing of the κ_{HTDMA} of BSOA and ASOA components with respect to their volume fraction or where non-linear response of κ_{HTDMA} is effective."

"… If the κ_{HTDMA} of ABSOA can be described by a linear combination of the κ_{HTDMA} of pure ASOA and BSOA components in respect of their volume fraction, the κ_{HTDMA} data point …"

19921, l. 1-6: Regarding morphology, considering the growth kinetic results, is this really a plausible explanation? If both types of SOA have similar growth kinetics to ammonium sulphate, how would morphology explain non-linear effects on mixed particle K? I understand the experiments are made in different humidity regimes, but wouldn't any differences be enhanced at CCN conditions? You may want to explain this further.

Response:

Morphology effects may contribute to non-linear effects. As the reviewer noticed, the similar kinetics was obtained in supersaturated conditions. In subsaturated conditions, water uptake flux to particles might be low and water diffusivity in the more concentrated solution may be slower than in supersaturated conditions thus limiting hygroscopic growth of the particle. This may be the reason that some studies observed kinetic delays in water uptake at low SS but no kinetic delay at high SS (Engelhart et al., 2008).

In the revised manuscript, we have improved this discussion as follows.

"In addition, if ABSOA forms a glassy state, the lower diffusivity in the particle may hinder water uptake thus decreasing κ_{HTDMA}. Although similar growth kinetics of SOA to $(NH_4)_2SO_4$ was observed in supersaturated conditions, in subsaturated conditions the water diffusivity in the particle may be limited thus limiting water uptake."

19922, l. 9: Regarding the interpretation of potential surface tension effects, if the surface tension effect of BSOA would be greater than for ASOA, in the sense that surface tension is lower at CCN activation for BSOA, this should in my opinion lead to a smaller observed discrepancy between K(HTDMA) and K(CCN) for BSOA, since at both humidity conditions there would then be a positive bias on K. Also, if surface tension effects were significant for BSOA, then I would expect subsaturated hygroscopicity of BSOA to be greater than for ASOA, opposite to what is reported. However, surface tension effect are complex and maybe you can clarify your line of reasoning a bit further?

Response:

If the surface tension effect of BSOA is greater, i.e., surface tension is lower than ASOA, κ_{CCN} of BSOA would be higher. Although low surface tension also cause a positive bias to κ_{HTDMA}, the surface tension effect in subsaturated conditions is fairly small, i.e., κ_{HTDMA} is relatively stable. Therefore, the $\kappa_{HTDMA}/\kappa_{CCN}$ would be smaller for BSOA, i.e. a bigger gap between κ_{HTDMA} and κ_{CCN}.

We agree that when all other parameters are the same, if surface tension effects were larger for BSOA, κ_{HTDMA} of BSOA would be greater than ASOA. However, the chemical composition (functional groups and degree of oxidation) and the molecular mass of ASOA and BSOA were different. For example, ASOA components here have an average lower molar volume and higher O/C, both enhancing $\kappa_{HTDMA.}$ This was discussed in our manuscript (Sect. 3.2 page 19919 lines 1-5).

In the revised manuscript, we have improved the discussion of this part. Now it reads:

"… If the surface tension effect for BSOA would be larger than for ASOA, i.e. lower surface tension in supersaturated conditions, this would lead to a higher κ_{CCN} for BSOA. While the surface tension effect in subsaturated condition is small, i.e. κ_{HTDMA} is relatively constant, higher κ_{CCN} of BSOA results in a larger discrepancy between κ_{HTDMA} and κ_{CCN}."

19922, l. 24: Concerning evaporation and condensation causing potential artifacts, what are the respective residence times at sub- and supersaturated water uptake? Again, I don't immediately see how the limited diffusivity would be a plausible explanation for the K discrepancy when the growth kinetics are similar?

Response:

The residence time is around 30 s in the HTDMA measurement, which was described in Sect. 2.1 and around 24 s in the CCN measurement with the time in the final SS slightly lower (Lance et al., 2006), which has been added in the revised manuscript.

As we discussed above, the similar growth kinetics of SOA to $(NH_4)_2SO_4$ was obtained in supersaturated conditions. In subsaturated conditions, diffusivity of water in glassy particles could be the limited and could possibly limit the water uptake thus decreasing kappa.

Reference:

Asa-Awuku, A. et al. Mixing and phase partitioning of primary and secondary organic aerosols, Geophys. Res. Lett.36 (15), 10.1029/2009GL039301, 2009.

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