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

Received and published: 18 September 2015

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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Responses to Referee #2

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 one-by-one responses to the comments and the corresponding changes to the manuscript. The original comments are shown in italics.

Anonymous Referee #2

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This manuscript explores the effect of mixed anthropogenic and biogenic SOA on CCN activity and droplet growth kinetics, compared to pure biogenic or anthropogenic SOA. The paper is well written and logical, and I would recommend publication, subject to a few comments:

Page 19913 section 3.1.1: It would add an interesting angle to refer to the study of Rickards et al (2013) in which a review of existing studies attempting to link kappa and O:C were combined. http://pubs.acs.org/doi/abs/10.1021/jp407991n. They found that systematic variability between κ parametrizations determined from different studies remains large, consistent with the O/C ratio providing only an approximate guide to aerosol hygroscopicity. They do however present a new parameterization based on collated laboratory/field data. Given the propensity to rely on simplified metrics, it would be useful to highlight where your results lie as compared to these parameterizations. Indeed, does this comparison confirm any of your findings?

Response:

We thank the reviewer for the supportive remarks and bringing about the reference.

In the revised manuscript, we have compared our data with the parameterization in Rickards et al (2013) (Fig. S5). Our data are generally in line with the parameterization proposed by Rickards et al (2013) while κ_{CCN} of BSOA is higher than those predicted by the parameterization. However, because the variations of kappa discussed by Rickards et al (2013) are large and the parameterization is based on various chemical systems and various conditions (consistent with this study), it is difficult to conclude from the comparison whether that study supports or contradicts our data. Note that in the manuscript we compared the kappa of BSOA and ASOA with previous studies, which showed consistency with our data.

In the revised manuscript, we have added the following sentence.

"The relationship between κ_{CCN} and O/C was further compared to the parameterization in the study by Rickards et al. (2013) (Fig. S5), which was obtained from their experimental data and a number of literature data and showed very large variability of κ versus O/C."

Page 19914 line 3 and figure 1: "The CCN activity of the three types of aerosol is generally similar at similar OH dose. In addition, with exception of BSOA, kCCN is largely invariant over a wide range of OH doses" But in the figure, kCCN appears to be slightly higher for BSOA than for ASOA or ABSOA at a given OH dose (particularly around molecules cm-3 s). Plus, it looks like there is a slight increase in kCCN with OH dose for ASOA. Are these differences not significant / important?

Response:

Overall, considering the variations of the κ_{CCN}, no distinctive difference between κ_{CCN} of BSOA and that of ASOA or ABSOA could be identified.

For ASOA, we guess that the reviewer referred to experiment A4. κ_{CCN} at the highest OH dose (1.6×10^{11} molecules cm^{-3} s) is similar to κ_{CCN} at the lowest OH dose of that experiment (1.6×10^{11} molecules cm^{-3} s). Also considering κ_{CCN} of all ASOA, there is no significant difference in κ_{CCN} over a range of OH doses.

Page 19914, second para and figure 2: In figure 2a it is hard to follow the same SS since they change very soon after the addition of BVOC. In 2b it looks to me like there is a slight increase in kCCN after addition of AVOC. Do you not consider this significant? Could you also please comment on how you decided the delay time between additions of the different VOCs?

Response:

In Figure 2a, the change of kappa can be tracked by the blue and green markers (SS: 0.51% and 0.68%), and at these two SS, there are data before and after BVOC addition. In the revised manuscript, we have clarified this issue.

In Figure 2b, there is a very slight increase after AVOC addition. However, such a minor change can also be attributed to the concurrent aging of SOA. Such increasing trend can be tracked by the data at 0.43% SS (light green marker). Immediately after AVOC addition, there are barely any ASOA formation (ASOA fraction ~0), but there was already a slight increase of kappa.

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

In the revise manuscript, we have explained this point.

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

Droplet growth kinetics. Section 3.1.2: Of course, this is an area gathering increased attention. With regards to the 'threshold droplet growth analysis', whether there is, or isn't, any kinetic mass transfer effects from the phase state of the aerosol might depend on how the aerosol have been treated. If there is sufficient water, or any plasticizer for that matter, in the particle then water uptake in the CCN counter is likely not going to be affected. Is the aerosol exposed to rapi/slow drying for example? It would help draw out potential effects with regards to this if more detail on the method was given rather than just referring to previous studies.

Responses:

We agree that the residual water in the particle may affect droplet growth kinetics. In this study, the aerosols were produced at typically 30-60% RH and were dried to ~10% RH using a silica gel diffusion drier with a residence time of around 3 s before they were measured by CCN set up. In the revised manuscript, we have added these details.

"Before entering the instruments, the particles were dried using a silica gel diffusion drier (gradually drying to ~10% RH) with a residence time of around 3s".

Section 3.3, line 13: 'an approximate cubic relationship between K and surface tension'. It is much easier to simply state that sensitivity to surface tension in the Kohler equation is increased at the point of activation. There is no need to reference a numerical approximation.

Response:

We have accepted the reviewer's suggestion. In the revised manuscript, we have modified this sentence as follows.

"κ_{CCN} is more sensitive to surface tension at the point of activation according to the Köhler equation."

Please could you add error bars to the diamonds in figure 7.

Response:

Accepted. In the revised manuscript, we have added the error bars to the diamonds.

Cloud Condensation Nuclei Activity, Droplet Growth Kinetics and Hygroscopicity of Biogenic and Anthropogenic Secondary Organic Aerosol (SOA)

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Abstract

Interaction of biogenic volatile organic compounds (VOC) with anthropogenic VOC affects the physicochemical properties of secondary organic aerosol (SOA). We investigated cloud droplet activation (CCN activity), droplet growth kinetics, and hygroscopicity of mixed anthropogenic and biogenic SOA (ABSOA) compared to pure biogenic SOA (BSOA) and pure anthropogenic SOA (ASOA). Selected monoterpenes and aromatics were used as representative precursors of BSOA and ASOA, respectively.

We found that BSOA, ASOA, and ABSOA had similar CCN activity despite the higher oxygen to carbon ratio (O/C) of ASOA compared to BSOA and ABSOA. For individual

reaction systems, CCN activity increased with the degree of oxidation. Yet, when considering all different types of SOA together, the hygroscopicity parameter, κ_{CCN}, did not correlate with O/C. Droplet growth kinetics of BSOA, ASOA, and ABSOA was comparable to that of $(NH_4)_2SO_4$, which indicates that there was no delay in the water uptake for these SOA in supersaturated conditions.

In contrast to CCN activity, the hygroscopicity parameter from hygroscopic tandem differential mobility analyzer (HTDMA) measurement, κ_{HTDMA}, of ASOA was distinctively higher (0.09-0.10) than that of BSOA (0.03-0.06), which was attributed to the higher degree of oxidation of ASOA. The ASOA components in mixed ABSOA enhanced aerosol hygroscopicity. Changing the ASOA fraction by adding BVOC to ASOA or vice versa AVOC to BSOA changed the hygroscopicity of aerosol, in line with the change in the degree of oxidation of aerosol. However, the hygroscopicity of ABSOA cannot be described by a simple linear combination of pure BSOA and ASOA systems. This indicates that additional processes, possibly oligomerization, affected the hygroscopicity.

Closure analysis of CCN and HTDMA data showed κ_{HTDMA} was lower than κ_{CCN} by 30%-70%. Better closure was achieved for ASOA compared to BSOA. This discrepancy can be attributed to several reasons. ASOA seemed to have higher solubility in subsaturated conditions and/or higher surface tension at the activation point than that of BSOA.

1 Introduction

Secondary organic aerosol (SOA) is an important class of atmospheric aerosol with impacts on air quality, human health and climate change (Hallquist et al., 2009; Kanakidou et al., 2005; Jimenez et al., 2009; Zhang et al., 2011; Verma et al., 2014). Despite substantial improvements in the understanding of SOA formation mechanisms and properties, considerable uncertainties remain about the regional and global budget of SOA (e.g. Goldstein and Galbally (2007)). Models often do not correctly predict the ambient concentrations of organic aerosol (OA) (e.g., Spracklen et al. (2011), Heald et al. (2005)), and usually the modeled concentrations underestimate the observed OA concentrations (Spracklen et al., 2011). Recent studies suggested that interactions between biogenic volatile organic compounds (VOC) and anthropogenic emissions can enhance SOA formation and often, ambient OA concentrations correlate with anthropogenic tracers such as CO or isopropyl nitrate (de Gouw et al., 2008; de Gouw et al., 2005; Weber et al., 2007; Shilling et al., 2013; Xu et al., 2015). However, ^{14}C carbon isotopic analysis showed that the SOA material itself is composed mostly of modern carbon, i.e. arises from biogenic sources, including biomass burning (Weber et al., 2007; Zotter et al., 2014). These observations suggest that a consideration of an anthropogenic enhancement can reduce the discrepancies between models and observations (de Gouw et al., 2005; Goldstein et al., 2009; Hoyle et al., 2011; Worton et al., 2011; Glasius et al., 2011).

Anthropogenic VOCs (AVOC), such as aromatic compounds are possibly important factors that lead to enhanced SOA formation as their oxidation products can interact with biogenic VOC (BVOC) oxidation products during SOA formation, as shown by several studies (Hoyle et al., 2011; Emanuelsson et al., 2013; Flores et al., 2014). In a recent study, Emanuelsson et al. (2013) found that anthropogenic SOA (ASOA) components reduce the volatility of biogenic SOA (BSOA) in a non-linear way with respect to the ASOA fraction, possibly by oligomerization or a phase change such as formation of a glassy state (Emanuelsson et al., 2013; Virtanen et al., 2010; Koop et al., 2011). The reduced volatility in the mixed SOA (anthropogenic-biogenic SOA, ABSOA) can enhance SOA persistence and concentrations in the atmosphere. Flores et al. (2014) investigated the optical properties of BSOA, SOA from simultaneous addition of BVOC and AVOC and SOA from sequential addition of BVOC and AVOC. They found that both SOA from mixed AVOC and BVOC show an increase of scattering component of the refraction index with aging (increase of the oxygen to carbon ratio (O/C)) and the increase is greater for SOA from simultaneous addition of BVOC and AVOC than SOA from sequential addition of VOC.

Besides the thermochemical and optical properties, cloud droplet activation (cloud condensation nuclei (CCN) activity) and hygroscopicity are important physicochemical properties that have critical implications for the impact of aerosol on climate. It is possible that enhanced oligomerization which happens in the mixed aerosol particles could modify its CCN activity and hygroscopicity (Xu et al., 2014). Given that CCN activity and hygroscopicity correlate with the aerosol O/C in many cases and given that ASOA tends to have a higher O/C (Chhabra et al., 2011; Emanuelsson et al., 2013), it is expected that ASOA components enhance the CCN activity and hygroscopicity of mixed SOA. However, to the best of our knowledge, the influence of the interaction of AVOC with BVOC on CCN activity and hygroscopicity of SOA has not been studies from the literature.

Several field studies found a delay in droplet growth kinetics of the aerosol from anthropogenic origin when compared with the aerosol from biogenic origin (Shantz et al., 2010; Shantz et al., 2012). ASOA, as an important anthropogenic aerosol, may contribute to this delay. In addition, a recent laboratory study suggests limited mixing in SOA formed by sequentially mixing a biogenic precursor (α-pinene) with an anthropogenic one (toluene) (Loza et al., 2013). It is possible that limited mixing could affect water uptake by ABSOA and delay droplet growth when the diffusion of water within aerosol particle was suppressed. Yet, no laboratory studies on the droplet growth kinetics of ASOA and ABSOA have been found.

In this study, we investigated the effect of the interaction of ASOA and BSOA on CCN activity and hygroscopicity of aerosol. We also studied the kinetics of droplet growth of ASOA, BSOA and mixed ABSOA.

2 Experimental

2.1 Experiment setup and instrumentation

The experiments were conducted in the atmosphere simulation chamber SAPHIR (Simulation of Atmospheric PHotochemistry In a large Reaction chamber). SAPHIR is a double-wall Teflon chamber with a volume of 270 m^3. Details of the chamber have been previously described (Rohrer et al., 2005; Bohn et al., 2005). The chamber uses natural sunlight for illumination and is equipped with a louvre system which can be used to simulate dark processes. For the experiments described here, various instrumentations were used to characterize gas phase and the particulate phase species.

Chamber parameters like temperature, relative humidity, flow rate, and photolysis frequencies were also recorded. The actinic flux and the corresponding photolysis frequencies were provided from measurements using a spectral radiometer (Bohn et al., 2005; Bohn and Zilken, 2005).

The number concentration and size distributions of aerosol were measured by a scanning mobility particle sizer (SMPS, DMA model 3081/CPC model 3785, TSI Shoreview, USA) and separate condensation particle counter (CPC, model 3786, TSI) to allow detection of nucleation particles down to 3 nm.

The chemical composition of aerosol was measured by a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research Inc., USA). To characterize the degree of oxidation of aerosol, the oxygen to carbon ratio (O/C) and f_{44} (fractional contribution of m/z 44 to the total organics signal) were obtained from the mass spectra. The O/C (corrected for the minor influence of gaseous components) was derived by the elemental analysis of mass spectra obtained in the high mass resolution mode (W-mode) of the mass spectrometer as described by Aiken et al. (2007) and Aiken et al. (2008). The contributions of gas phase CO_2 and water vapor to m/z 44 and to m/z 18, respectively, were characterized using a CO_2 and H_2O analyzer (Picarro, Santa Clara, USA). The values were subtracted to obtain the particle signals before the elemental analysis (Allan et al., 2004).

Droplet activation and droplet growth were measured using a size scanning CCN method as described previously (Buchholz, 2010; Zhao et al., 2010). This method, also known as Scanning Mobility CCN analysis (SCMA, (Moore et al., 2010)), has been successfully used in a number of previous studies (Asa-Awuku et al., 2008; Padro et al., 2007; Engelhart et al., 2008; Asa-Awuku et al., 2009; Asa-Awuku et al., 2010; Engelhart et al., 2011). The measurement was done by coupling a differential mobility analyzer (DMA, model 3081, TSI Shoreview, USA) with a cloud condensation nuclei counter (CCNC, Droplet Measurement Technique, USA) and condensation particle counter (CPC3786, TSI). Before entering the instruments, the particles were dried using a silica gel diffusion drier (gradually drying to ~10% RH) with a residence time of around 3s. Particles then passed through the DMA and the outgoing air was split into two paths connecting to the CCNC and CPC, which measure the CCN and cloud nuclei (CN) concentrations, respectively. The flow rate of the CCNC is around 0.5 L/min with a sheath to aerosol flow ratio of 10. The residence time in the CCN column is around 24 s with the time in the final supersaturation slightly shorter (Lance et al., 2006). The DMA scanned over a size range between 10 and 450 nm while the supersaturation (SS) remained constant. And four to five different supersaturations in the range of 0.1%-1.3% were used depending on the particle sizes. From the measurement, CCN activation fraction over size and the dry activation diameter (or critical dry diameter, D_{crit}) was obtained using a method as described in Buchholz (2010). Briefly, for each particle size, the CN and CCN concentrations measured were used to calculate the activation fraction (a_f = CCN/CN). Before a_f was calculated, the measured CN and CCN concentrations were corrected for multiple charged particles. To separate the single from the multiple charged particles, the fraction of multiple charged particles was calculated according to a Boltzmann charge distribution using the measured size distribution (Wiedensohler, 1988). Then, a_f was determined for each charge class separately and fitted with a Gaussian error function (Rose et al., 2008). The dry activation diameter at the set SS is the turning point of this function.

For each SS at least three full scans were performed and the resulting D_{crit} were averaged. For the calibration of SS, D_{crit} of ammonium sulfate at various SS was measured and compared to theoretical data in the literature (Rose et al., 2008). The set SS was corrected according to the theoretical data. From the CCN data, the hygroscopicity parameter κ_{CCN} was calculated according to the one parameter representation of the Köhler equation proposed by Petters and Kreidenweis (2007). The error bars of κ_{CCN} were estimated using the standard deviation of D_{crit} from three duplicate scans. A higher hygroscopicity parameter κ indicates a more hygroscopic material, i.e. cloud droplet activation at lower SS for particles of a given size or at smaller size for a given SS.

The hygroscopic growth of the aerosol was measured using a home-built hygroscopic tandem differential mobility analyzer (HTDMA). The details of the HTDMA were described previously (Buchholz, 2010; Zhao et al., 2010). Particles were selected using the first DMA and then were exposed to a prescribed relative humidity to measure the growth factor. Hygroscopic growth was measured at different RH. The sizes of the humidified particles were determined by the second

DMA which was operated in a scanning mode in combination with a CPC (model 3022A, TSI). The size selected aerosol flow and the sheath air flow of the second DMA were humidified at room temperature (25-30°C depending on the surroundings) to almost the same relative humidity (RH) with the sheath air at slightly higher RH. The second DMA was kept in a thermo-insulated box which was cooled to 20 °C. Both aerosol and sheath air flow were cooled down to the same temperature before entering the second DMA, and thus the RH increased to its final value. The residence time of particles at the final humidity is approximately 30 s before they entered the SMPS operated with sheath air of the same RH. The hygroscopic growth factor (*GF*) was calculated as the ratio of the size of the wet particle (D_{wet}) to the selected dry size (D_{dry}). The HTDMA was calibrated using ammonium sulfate aerosol by comparing with the theoretical growth curve (Rose et al., 2008). From hygroscopic growth factor at 90% RH, the hygroscopicity parameter, κ_{HTDMA}, was calculated according to Petters and Kreidenweis (2007). The error bars of κ_{HTDMA} were estimated using the standard deviation of the growth factor at (90±1) % RH of at least three duplicate scans.

SOA samples were collected on PTFE filters at the end of different experiments to obtain detailed insight into the chemical composition of the aerosol particles. The details of sample collection and analysis are described in Emanuelsson et al. (2013) and Kristensen and Glasius (2011). Before the filters, the air passed through an annular denuder coated with XAD-4 resin to remove gaseous organic species. The filters were extracted and analyzed using a Dionex Ultimate 3000 HPLC system coupled through an electrospray (ESI) inlet to a q-TOF mass spectrometer (micro-TOFq, Bruker Daltonics GmbH, Bremen, Germany), which was operated in both positive and negative mode. Pinonic acid, cis-pinic acid, terpenylic acid, diaterpenylic acid acetate (DTAA) and 3-methyl butane tri-carboxylic acid (MBTCA) were quantified using authentic standards.

For SOA from part of the experiments (experiment #B3, AB4, AB6 as in Table 1), samples were also collected on quartz fiber filters and analyzed by ultra-high resolution mass spectrometry (UHRMS). In this analysis, the aerosol samples were extracted as described elsewhere (Kourtchev et al., 2013). The extracts were analyzed using an ultrahigh resolution LTQ Orbitrap Velos mass spectrometer (Thermo Scientific, Bremen, Germany) equipped with a TriVersa Nanomate robotic nanoflow chip-based ESI source (Advion Biosciences, Ithaca NY, USA). The

Orbitrap MS instrument calibration, settings and mass spectral data interpretation are described in Kourtchev et al. (2014). The mass accuracy of the instrument was below 1.5 ppm and the instrument mass resolution was 100,000 at m/z 400. The negative ionization mass spectra were collected in three replicates and in this study, only ions that appeared in all three analytical replicates were kept for evaluation.

The VOC were measured by a high resolution proton transfer reaction-mass spectrometer (HR-PTR-MS, Ionicon, Innsbruck, Austria) (Jordan et al., 2009) and gas chromatography coupled to a mass spectrometer (GC-MS, PerkinElmer, Waltham, USA) (Apel et al., 2008; Kaminiski, 2014).

The OH concentration was measured directly using laser-induced fluorescence (LIF) (Fuchs et al., 2012). The OH radicals inside the chamber are mainly formed by the photolysis of HONO formed via a photolytic process on the chamber walls, and to a minor fraction by O_3 photolysis (Rohrer et al., 2005). From the OH concentration, the OH dose was calculated and used as a common abscissa in order to better compare different experiments. The OH dose is the integral OH concentration over time that gives the accumulated OH concentrations to which gases and particles were exposed in the course of experiment. One hour exposure to a typical atmospheric OH concentration of 2×10^6 molecules cm^{-3} is then equivalent to an OH dose of 7.2×10^9 molecules cm^{-3} s.

2.2 Experimental procedure

The experimental procedures have been described elsewhere in details (Emanuelsson et al., 2013; Flores et al., 2014) and only a short description is given here. The chamber was typically humidified to 60-70% RH in the beginning of the experiment and relative humidity can vary in the range of 30-70% due to the ambient temperature change and the dilution by the flow to compensate the sampling loss. In a typical experiment, VOC was added to the chamber and then the roof was opened to start the photooxidation. In some experiments, O_3 was added. In all the experiments, particles formed by homogeneous nucleation and no seed was added. In the BSOA experiments, a monoterpene mixture of α-pinene and limonene with a molar ratio of 1:1 was used as the representative BSOA precursors and its photooxidation induced BSOA formation. Ozone was added to initialize BVOC oxidation and particle formation. In the ASOA experiments, toluene or xylene was used as the representative ASOA precursors. In the mixed

SOA experiments (ABSOA), AVOC and BVOC were added, either simultaneously or sequentially to investigate the potential effect of adding order.

In total, three BSOA experiments (including one using α-pinene as precursor), seven ASOA experiments, and six mixing experiments (ABSOA) with biogenic and anthropogenic precursors were analyzed in detail and the summary for these experiments is given in Table 1. In two experiments (#AB1, AB2), AVOC was added 6.3 h before the BVOC. 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. In two experiments (#AB3, AB4), BVOC was added 2.5 h and 5 h before the AVOC, respectively. In the other two experiments (#AB5, AB6), BVOC and AVOC were added simultaneously into the chamber. 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. Assuming the same density for ASOA and BSOA, the mass fraction of ASOA is equal to its volume fraction.

3 Results and discussion

3.1 Droplet activation of BSOA, ASOA and ABSOA

3.1.1 Comparison of droplet activation of BSOA, ASOA and ABSOA

Droplet activation of BSOA, ASOA and ABSOA at various supersaturations (SS) was parameterized by applying the hygroscopicity parameter κ_{CCN} (Petters and Kreidenweis, 2007). Generally, κ_{CCN} was found to increase slightly with time in the light periods and remained relatively constant or slightly decreased in the dark periods (overview in Fig. S1). The increase of κ_{CCN} with time in the light period is attributed to photochemical aging, which leads to functionalization, i.e. the formation of oxidized compounds with hydroperoxide, hydroxyl, carbonyl, and carboxylic acid groups (Kroll and Seinfeld, 2008; Zhao et al., 2015b). Photochemical aging is thought to mainly happen in the gas phase (Donahue et al., 2012) and affect the particle composition by partitioning, although heterogeneous oxidation and particle phase oxidation may also play a role. The formation of oxidized compounds with polar functional groups is also supported by the our filter sample analysis of SOA, showing the formation of a number of organic acids, carbonyl compounds and multi-generation compounds such as 3-methyl butane tricarboxylic acid (3-MBTCA), a tracer for photochemical ageing (Zhang et al. (2010), see also Table 3 of Emanuelsson et al. (2013)). This functionalization increases the SOA average polarity and thus enhances hygroscopicity (Duplissy et al., 2008; Topping et al., 2005; Suda et al., 2014). We found that κ_{CCN} depended on SS. Since different SS correspond to different critical sizes, this dependence indicates a size dependent chemical composition of aerosol (Zhao et al., 2015a). When comparing CCN activity of different SOA, κ_{CCN} at similar supersaturation was examined.

The droplet activation of BSOA, ABSOA, and ASOA particles represented by κ_{CCN} is compared for two SS (0.51% and 0.34%) in Fig. 1. Different experiments required different ranges of SS because of the achievable particle size ranges. Usually ASOA particles were smaller and thus higher SS were needed to get a proper range of activation fraction to derive D_{crit}. Therefore, we choose κ_{CCN} at two SS in the medium range, 0.34% and 0.51%, to compare between experiments thus maximizing experiments with overlapping SS. In order to compare CCN activity of different SOA particles from different experiments, κ_{CCN} is plotted as a function of OH dose (Fig. 1a), the integral OH concentration over time to which the particles were exposed. The CCN activity of the three types of aerosol is generally similar at similar OH dose. In addition, with exception of BSOA, κ_{CCN} is largely invariant over a wide range of OH doses, equivalent to 1-4 days of OH exposure in the atmosphere (assuming average OH concentration 2×10^{6} molecules cm^{-3} and 12 h sunlight per day).

Similarity in CCN activity of ASOA, BSOA and ABSOA was also observed in the ABSOA experiments with sequential VOC addition, independent of the order of addition of AVOC or BVOC. When BVOC was added after AVOC to the chamber, besides the reaction with OH, BVOC also reacted with O_3 formed previously from photochemical reactions of AVOC. The reaction products from both ozonolysis and OH oxidation helped to convert ASOA rapidly to ABSOA reaching significant fractions of BSOA (e.g. 70% within 2.5 h, Fig 2a). However, κ_{CCN} remained largely unchanged within the experimental uncertainty upon the formation of ABSOA (green and blue markers). Note that κ_{CCN} should be compared at similar SS because κ_{CCN} depended on SS and the SS range changed due to the particle size shift after BVOC addition.

Such invariance was also observed when BVOC was added first to form BSOA and then AVOC was added to form ABSOA (Fig. 2b). Therefore we conclude that BSOA, ASOA and ABSOA have similar CCN activity.

For BSOA, κ_{CCN} increased with photochemical aging at all SS. For ASOA and ABSOA, κ_{CCN} increased with photochemical aging only at higher SS while κ_{CCN} remained relatively stable at low SS (Fig. S2). The increase of κ_{CCN} with aging is a result of oxidation to form oxygenated compounds with higher affinity for water. At the same time, the volatility of BSOA, ASOA, and ABSOA in these experiments decreased with the OH dose (Emanuelsson et al., 2013), indicating that these hygroscopic components were at the same time less volatile than the initial aerosol components.

Figure 1b shows κ_{CCN} as a function of O/C. Although the O/C of ASOA and ABSOA was generally higher than that of BSOA (Fig. 1b), there is no significant difference between the CCN activity of ASOA, ABSOA, and that of BSOA. This suggests that although ASOA components increased the O/C of ABSOA and decreased its volatility (Emanuelsson et al., 2013), it did not enhance its CCN activity. 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. Decreasing volatility and invariant CCN activity at higher O/C induced by presence of ASOA components indicates different effects of oligomerization and photochemistry on volatility and CCN activity of aerosol. While both oligomerization and photochemical aging reduce the volatility (Emanuelsson et al., 2013), they have counterbalancing effects on CCN activity. Oligomerization increases the molar volume and decreases the molar concentration of solutes, which results in an increase of water activity and thus the saturation ratio. Therefore, oligomerization reduces CCN activity, while photochemical aging enhances the CCN activity by producing more oxygenated compounds via functionalization (Zhao et al., 2015b). 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). 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 (Petters et al., 2009;

Tritscher et al., 2011). In this study we did not observe a significant difference in CCN activity between ABSOA and other SOA, indicating that the effects of possible oligomerization on the CCN activity of ABSOA are likely compensated by the effects of photochemical aging.

For BSOA and ABSOA, κ_{CCN} generally increases with O/C at a given SS (Fig. S2). For ASOA, the relationship between κ_{CCN} and O/C is not so apparent. The κ_{CCN} values of BSOA (0.11-0.19) are consistent with κ_{CCN} values obtained in previous studies (Massoli et al., 2010; Lambe et al., 2011; Frosch et al., 2011). An increase of κ_{CCN} with O/C of SOA has been reported by a number of previous studies (Massoli et al., 2010; Lambe et al., 2011). Yet, other studies reported that κ_{CCN} of SOA is largely independent of O/C or $f_{44,}$ another proxy of the degree of oxidation of organic aerosol (Frosch et al., 2011; Alfarra et al., 2013). The inconclusive results in the literature may be attributed to the differences in reaction conditions including the VOC type and concentration, NO_x concentration, photochemical aging (OH dose) and O/C range. In this study, the observation that κ_{CCN} is invariant on O/C in ASOA may be associated with the relatively high and narrow range of observed O/C for ASOA. Emanuelsson et al. (2013) proposed that first generation products of AVOC (mainly carbonyls) may have higher vapor pressure compared to BVOC products. Therefore, AVOC need a higher OH dose and more oxidation steps before a significant amount of material starts to condense on the particles. As a result, once SOA started to form, ASOA had already reached a relatively high O/C due to aging in the gas phase (Fig. 1b). As a consequence, a further increase of O/C in ASOA is likely slower and less pronounced.

Considering all types of SOA investigated here, κ_{CCN} did not correlate with O/C here (Fig. 1b), which is in agreement with the findings of Alfarra et al. (2013) that water uptake is independent of f_{44} as a metric of the degree of oxidation for multiple biogenic precursors. This is because O/C affects the solubility of the solute but other effects such as molecular weight, surface tension and density are also important. Massoli et al. (2010) also showed, the correlation between κ_{CCN} derived from CCN and O/C is less significant than in individual systems, when considering all systems together including α-pinene, trimethylbenzene, and m-xylene. The relationship between κ_{CCN} and O/C was further compared to the parameterization in the study by Rickards et al. (2013) (Fig. S5), which was obtained from their experimental data and a number of literature data and showed very large variability of κ versus O/C.

For ASOA systems, particle formation was studied for different aromatic precursors at low NO_x (NO_x<1 ppb) and high NO_x concentrations (10 ppb of NO added). The CCN activity of ASOA from different precursors including toluene, xylene, and benzene was found to be similar. Although NO_x levels affect the overall SOA particle composition and yields (Ng et al., 2007a; Hildebrandt et al., 2009; Zhang et al., 2014; Presto et al., 2005; Eddingsaas et al., 2012; Ng et al., 2007b), they had no significant effect on the CCN activity of ASOA comparing the low NO_x (NO_x <1 ppb) with high NO_x (10 ppb NO added) condition (Fig. S3). The CCN activity of ASOA generally agreed with the range obtained from a number of previous studies (Massoli et al., 2010; Prenni et al., 2007; Lambe et al., 2011). Similarly, NO_x level has been found to not influence the CCN activity of SOA from α-pinene ozonolysis and subsequent photochemical aging (Frosch et al., 2011).

3.1.2 Droplet growth kinetics

Droplet growth kinetics was investigated using the method of ‘threshold droplet growth analysis’ (TDGA), which has been used successfully in many field and laboratory studies (Engelhart et al., 2008; Asa-Awuku et al., 2009; Asa-Awuku et al., 2010; Bougiatioti et al., 2011). In this method, the droplet growth kinetics was assessed by comparing the droplet sizes from various SOA with that from ammonium sulfate, which is highly hygroscopic and rapidly grows under supersaturated conditions. When two particles are exposed to the same SS, they will grow to droplets of similar size, if their critical SS *and* the mass transfer of water vapor are similar. In this study, the TDGA method was applied to the size-resolved CCNC data and droplet size was compared for activated particles with SS_{crit} equal to the instrument SS (i.e. particles with a size of D_{crit}) (Asa-Awuku et al., 2009; Asa-Awuku et al., 2010; Bougiatioti et al., 2011).

Droplet size as a function of SS for BSOA, ASOA and ABSOA were compared with that of ammonium sulfate (Fig. 3). The droplet sizes of BSOA, ABSOA or ASOA are similar to those of ammonium sulfate. This indicates the absence of a kinetic barrier for the water uptake of these SOA during droplet activation. Our study is in agreement with several previous studies showing comparable droplet growth kinetics of SOA from monoterpenes with that of ammonium sulfate (Engelhart et al., 2008; Frosch et al., 2011). For SOA from toluene or xylene, no report on droplet growth kinetics was found in the literature. The droplet growth of aerosol from anthropogenic sources in the field containing both organics and ammonium sulfate has been shown to be slower than that of the pure ammonium sulfate, using a static diffusion cloud condensation chamber (Shantz et al., 2010; Shantz et al., 2012). Based on our study, ASOA from common aromatics, does not explain such delay and the observations by Shantz and co-workers must have been caused by other aerosol components (Shantz et al., 2010; Shantz et al., 2012).

A recent laboratory study by Loza et al. (2013) suggests limited mixing of different types of SOA components in the particles formed from BSOA precursor α-pinene and ASOA precursor toluene added sequentially. In contrast, the study of Hildebrandt et al. (2011) supported the pseudo-ideal mixing of BSOA and ASOA components according to the aerosol mass 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, 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.

3.2 Hygroscopicity of SOA from HTDMA measurement

Figure 4 shows the hygroscopicity (κ_{HTDMA}) of BSOA, ASOA, and ABSOA. κ_{HTDMA} of BSOA was between 0.03 and 0.06, and increased slightly with OH dose. κ_{HTDMA} of ASOA was around 0.09-0.1, significantly higher than that of BSOA. Subsaturated hygroscopic growth of ASOA and BSOA was obviously different whereas their CCN activity was basically similar. The influence of the SOA types on the hygroscopic growth is different from their influence on CCN activity. The comparison between the water uptake in the subsaturated conditions from hygroscopic growth and that in the supersaturated conditions from CCN activity is discussed in the Sect 3.3. κ_{HTDMA} of ASOA did not change much with the OH dose and κ_{HTDMA} of ASOA from different aromatic precursors (toluene, xylene, and benzene) were similar (#A1, 2, 4, 5 in Fig. 4).

The higher κ_{HTDMA} of ASOA can be related to the chemical composition represented by O/C. The O/C of BSOA was about 0.3-0.5, distinctively lower than that of ASOA (0.7-0.8). O/C has been found to correlate with κ_{HTDMA} for various SOA systems (Jimenez et al., 2009; Massoli et al., 2010; Duplissy et al., 2008; Duplissy et al., 2011; Lambe et al., 2011). The same arguments as for CCN activity apply here. ASOA reached much higher O/C at the same OH dose compared to BSOA (Fig. S4) (Emanuelsson et al., 2013) because first generation products of AVOC have a smaller carbon number and higher vapor pressure compared to BVOC. Thus, first generation products of AVOC need thus more oxidation steps before starting to condense significantly on particles as discussed in Sect 3.1. In addition, constituents of aromatic ASOA generally have lower molecular weights than BSOA molecules here. We can expect that ASOA components have on average a lower molar volume and thus ASOA has higher κ_{HTDMA} assuming all other parameters are the same for ASOA and BSOA (c.f. Appendix A), since κ is by definition the ratio of the molar volume of water to the average molar volume of the solute.

The κ_{HTDMA} observed for ABSOA formed with AVOC and BVOC added in various orders were in the range 0.03 - 0.06, close to or slightly higher than the κ_{HTDMA} of BSOA. The observed O/C range of ABSOA was slightly higher than the O/C range of BSOA, but partly overlapping. Since ASOA had much higher κ_{HTDMA} than BSOA, ASOA enhanced the κ_{HTDMA} of ABSOA and the extent of enhancement depended on its fraction.

The enhanced κ_{HTDMA} due to ASOA fraction was also reflected clearly in the ABSOA experiments when AVOC and BVOC were sequentially added. In the experiment when ASOA was formed first, the SOA showed higher κ_{HTDMA}, around 0.09 (Fig. 5a). When BVOC was added to the system, ASOA was converted to ABSOA with a significant BSOA fraction (e.g., 70% within 2.5 h) and κ_{HTDMA} decreased from 0.09 to 0.04 with the formation of the BSOA components. Meanwhile the degree of oxidation of ABSOA decreased significantly as indicated by the decrease of f_{44} (from 0.23 to 0.1). For the experiments when AVOC was added to BSOA system, an effect was recognizable, however κ_{HTDMA} only increased slightly (Fig. 5b). This was because the reaction of aromatics with OH and SOA formation was slow and the fraction of ASOA did not exceed 10%. Accordingly, only a slight increase of f_{44} was observed (from 0.10 to 0.12) even with concurrent aging, consistent with the minor effects of the ASOA component on the chemical composition of ABSOA due to its low fraction.

Since ASOA has higher κ_{HTDMA}, mixing of ASOA with BSOA may directly enhance κ_{HTDMA} due to a simple linear mixing. In order to understand the role of ASOA components in enhancing κ_{HTDMA} of ABSOA, κ_{HTDMA} was also examined as a function of the ASOA fraction (as shown in Fig. 6). In the ABSOA experiment, two main factors affect the hygroscopicity: aging of the BSOA components and increasing fraction of ASOA components. Therefore, the OH dose is examined to account for the effect of aging. In Fig. 6, the dashed lines connect the κ_{HTDMA} of pure BSOA and pure ASOA of the same OH dose at a series of OH doses varying from fresh to aged SOA. 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. For each OH dose, a dashed line connects pure BSOA and pure ASOA at the given OH dose (represented by the size of marker). This line defines the expected κ_{HTDMA} range of ABSOA with varying ASOA fraction at given OH dose. 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 should be on the line corresponding to the given OH dose of that data point and should increase with ASOA fraction along the line due to the higher κ_{HTDMA} of ASOA. If a succession of points from one experiment cross dashed lines (i.e. points beyond the line corresponding to the OH dose of those points) would indicate κ_{HTDMA} cannot be explained by a linear combination.

For ABSOA, several cases with non-linear effects were observed. For the ABSOA in the experiment #AB1 and #AB2 where AVOC was added first, κ_{HTDMA} were significantly lower than the values from the linear combination of pure ASOA and BSOA components (much below the lines corresponding to the OH doses of the data points). For ABSOA in the experiment #AB5 when AVOC and BVOC were added together, κ_{HTDMA} did not change significantly in spite of a significant increase of ASOA fraction. In the beginning, κ_{HTDMA} of ABSOA was higher than the value from a linear combination, whereas in the end, κ_{HTDMA} was lower than the value from a linear combination of pure systems. These cases indicate that the observed κ_{HTDMA} of ABSOA cannot be explained by a simple linear combination of pure ASOA and BSOA systems. There seems to be some additional effects such as oligomerization, which altered the chemical composition of ABSOA and thus affected κ_{HTDMA}. Moreover, for the ABSOA in the experiment #AB5, κ_{HTDMA} remained largely unchanged in spite of continuous oxidation and increase of ASOA fraction, both enhancing hygroscopicity. This further indicates that the possible oligomerization, which should decrease the Raoult term and thus hygroscopicity, compensates the effect of photochemical aging which enhances hygroscopicity, consistent with the discussion in Sect. 3.1.

Morphological effects can also play a role. If the ASOA and BSOA components were not well mixed in the aerosol particles in the experiments with sequential VOC additions, there would be more BSOA components on SOA particle surface in the experiments #AB1 and #AB2. This could affect the κ_{HTDMA} and contributed to the non-linear effect. But this cannot explain the non-linear effect in the experiment with VOCs added simultaneously. 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.

The ABSOA filter samples from experiment #AB4 and #AB6 were extracted and analyzed for oligomers. 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. But we did not find indications that ABSOA contained more dimers compared to BSOA. This can be attributed to the low ASOA fraction ≤5% in experiments #AB4 and #AB6 (estimated using the method as in Emanuelsson et al. (2013)). The low ASOA fraction was caused by the low OH concentration and low chemical turnover of the aromatics in these experiments because high concentrations of VOC were used in order to generate enough particle mass for optical measurement (Flores et al., 2014). The low fraction of ASOA resulted in little oligomer formation by the interaction between the ASOA components and BSOA components. 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.

3.3 Closure between the hygroscopicity parameter from CCN and HTDMA

The hygroscopicity parameter κ was obtained from CCN and HTDMA measurements in supersaturated and subsaturated conditions, respectively. For all SOA types studied here, there is a significant gap between κ_{HTDMA} and κ_{CCN}. κ_{HTDMA} was significantly lower than κ_{CCN} with

$\kappa_{HTDMA}/\kappa_{CCN}$ around 0.3-0.7 (Fig. 7). The ratio of $\kappa_{HTDMA}/\kappa_{CCN}$ for BSOA and ABSOA was lower than that of ASOA, which is closer to 1. This means that there is a smaller gap between κ_{HTDMA} and κ_{CCN} for ASOA compared to BSOA and ABSOA.

The closure between κ_{CCN} and κ_{HTDMA} of SOA has been studied and discussed by a number of previous studies with varying results (Dusek et al., 2011; Alfarra et al., 2013; Good et al., 2010; Duplissy et al., 2008; Juranyi et al., 2009; Prenni et al., 2007; Massoli et al., 2010; Hansen et al., 2015; Wex et al., 2009; Whitehead et al., 2014). The discrepancy between κ_{CCN} and κ_{HTDMA} found here can be attributed to several possible reasons as discussed in the literature (Prenni et al., 2007; Massoli et al., 2010; Frosch et al., 2011; Good et al., 2010; Alfarra et al., 2013; Wex et al., 2009; Whitehead et al., 2014; Petters et al., 2009; Dusek et al., 2011). An important reason is the presence of slightly soluble compounds. These compounds only dissolve partly in the subsaturated condition while they can dissolve completely in the supersaturated conditions due to more water available. Therefore, κ is underestimated to varied extent in the subsaturated condition. ASOA components here seemed to have higher solubility compared to BSOA components, and thus the gap between κ_{CCN} and κ_{HTDMA} was smaller than that of BSOA.

Surface tension can also play a role in this discrepancy. κ was calculated using the surface tension of pure water (0.073 N m^{-1}). If the surface tension of the droplets is lower than that of water, κ would be overestimated. While κ_{HTDMA} is not so sensitive to the change of surface tension, κ_{CCN} is more sensitive to surface tension at the point of activation according to the Köhler equation (Petters and Kreidenweis, 2007). The surface tension under the subsaturated conditions is assumed to be lower than that under the supersaturated conditions due to the more concentrated organics in the droplets under the subsaturated condition (Prisle et al., 2008). 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 conditions 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}. However, surface active organics can be enriched at the surface to such a high extent that the Raoult term is significantly diminished (Prisle et al. 2008). This difference can compensate the overestimation by using the surface tension of water and the compensating effects make using surface tension of water be a reasonable choice.

Furthermore, the κ-Köhler model does not account explicitly for changes in non-ideality of a solution as a function of saturation ratio i.e. water activity. Instead, κ might be not constant through the whole range of water activity (Petters and Kreidenweis, 2007). In addition, different aerosol behaviors such as evaporation and condensation of organics in HTDMA and CCN instrument and limited diffusivity of water in case of glassy particles can contribute to the discrepancy (Whitehead et al., 2014; Asa-Awuku et al., 2009; Irwin et al., 2010; Topping and McFiggans, 2012; Topping et al., 2013; Duplissy et al., 2009).

4 Conclusions and implications

We investigated the droplet activation, droplet growth kinetics and hygroscopicity of the BSOA, ASOA, and ABSOA formed from monoterpenes and aromatics used as representative BVOC and AVOC.

We found that BSOA, ASOA and ABSOA had similar CCN activity although ASOA had a higher O/C. Adding BVOC after ASOA formation, or adding AVOC after BSOA formation did not significantly change the CCN activity of SOA. The similar CCN activity of BSOA, ASOA and ABSOA suggests that ASOA components and the interaction of ASOA with BSOA did not significantly change the CCN activity of SOA. This was likely due to compensating effects of potential oligomerization (reducing effect) and photochemical aging (enhancing effect) on CCN activity.

κ_{CCN} generally increased slightly with photochemical aging, using OH dose as a proxy of photochemical aging and increased with O/C of aerosol for individual reaction systems. But when taking all the SOA types into account, κ_{CCN} did not correlate with O/C.

Analysis of the droplet growth kinetics shows that the droplet sizes from BSOA, ASOA, and ABSOA in supersaturated conditions were similar to those obtained with ammonium sulfate, indicating that none of these SOA has a kinetic barrier for water uptake. The fast water uptake of ASOA indicates that ASOA formed by aromatic precursors is not responsible for the droplet growth delay found in field studies (Shantz et al., 2010; Shantz et al., 2012). This finding also suggests that potentially limited mixing between BSOA and ASOA reported in the literature does not hinder the water uptake in supersaturated conditions.

In contrast to CCN activity, the hygroscopicity of ASOA was distinctively higher than that of BSOA. The higher hygroscopicity was related to the higher O/C of ASOA compared to BSOA. Therefore, the ASOA component in ABSOA enhanced the hygroscopicity of aerosol and the extent depended on the ASOA fraction. Adding BVOC to ASOA or AVOC to BSOA changed the aerosol hygroscopicity, which was consistent with co-occurring changes in the ASOA fraction and the degree of oxidation of the aerosol represented by f_{44}. However, the hygroscopicity of ABSOA cannot be described by a linear combination of pure BSOA and ASOA systems. This indicates that additional processes such as oligomerization suppressed the hygroscopicity, which is in agreement with the interpretations for CCN activity.

Comparing hygroscopicity parameter κ obtained from CCN and HTDMA measurement shows a discrepancy between κ from the two methods. κ_{HTDMA} was significantly lower than κ_{CCN} for all SOA types studied here, by 30%~70%. This discrepancy could not be resolved but can be attributed to the presence of slightly soluble materials, possible surface tension effect, or non-ideality of solutions and different behaviors of aerosol in the instruments. Better closure between HTDMA and CCN was found for ASOA than BSOA and ABSOA. ASOA seemed to have higher solubility in the subsaturated condition and/or lower surface tension at the activation point compared to BSOA.

This study has important implications for assessing the impact of SOA formed by the interaction of biogenic VOC with anthropogenic VOC emissions on the radiative forcing and climate. Since the interaction of AVOC with BVOC reduces the volatility (Emanuelsson et al., 2013), it prolongs particle persistence, which further enhances the particle concentration. Yet, based on this study, the CCN activity is not significantly affected. Therefore, models to assess the climatic effects of SOA formed through the interaction of biogenic VOC with anthropogenic VOC emissions could use single series of hygroscopicity parameter κ_{CCN} for BSOA, ASOA, and ABSOA to predict CCN concentration. However, significant mixing of ASOA and BSOA components can change the hygroscopic growth factor of the particles, which further affects the optical properties of SOA.

Comparing emission rates of aromatic compounds and isoprenoids (Lamarque et al., 2010; Guenther et al., 2012) and considering the turnover rates with OH and O_3 suggest that ABSOA should be dominated by BSOA components in most cases, as in most of our experiments. Thus globally droplet activation and hygroscopic growth may be determined by BSOA. 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.

Appendix A: Equations related to κ-Köhler theory

Based on κ-Köhler theory (Petters and Kreidenweis, 2007), the following equations are tenable,

$$\frac{1}{a_w} = 1 + \kappa\frac{V_s}{V_w} \qquad \text{(A1)}$$

$$\frac{1}{a_w} = 1 + i\,\frac{n_s}{n_w} \qquad \text{(A2)}$$

where a_w is water activity, and V_s and V_w are the volume of solute and water, respectively. n_s and n_w are the amount of solute and water in moles, respectively. I is the 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.

From Eq. (A1) and Eq. (A2) one can get

$$\kappa = i\,\frac{V_w/n_w}{V_s/n_s} \quad . \qquad \text{(A3)}$$

In addition, the amount of water and solute is described by

$$n_w=V_w\rho_w/M_w \qquad \text{(A4)}$$

$$n_s=V_s\rho_s/M_s \qquad \text{(A5)}$$

ρ_s and ρ_w are the density of solute and water, and M_s and M_w are the molecular weight of solute and water, respectively.

Substituting Eq. A4 and A5 into Eq. A3 yields

$$\kappa = i\frac{M_w/\rho_w}{M_s/\rho_s} \qquad \text{(A6).}$$

Assuming i is constant, κ is the ratio of molar volume of water to the average molar volume of the solute. Thus, a compound with lower molecular weight at similar density has lower molar volume and tends to have higher κ provided that other factors are constant.

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Table 1 Summary of the experiments in this study

Experiment #	Experiment type	Experiment description	BVOC (ppb)	AVOC (ppb)	Ozone added (ppb)
B1	BSOA	BVOC only	α-pinene, limonene (20, 20)	N.A	50
B2	BSOA	BVOC only	α-pinene (40)	N.A	160
B3	BSOA	BVOC only	α-pinene, limonene (48, 48)	N.A	200
A1	ASOA	AVOC only	N.A	toluene (85)	0
A2	ASOA	AVOC only	N.A	toluene (85)	0
A3	ASOA	AVOC only	N.A	p-xylene (30)	0
A4	ASOA	AVOC only	N.A	p-xylene (30)	0
A5	ASOA	AVOC only	N.A	benzene (280)	0
A6	ASOA	AVOC only	N.A	benzene (280)	0
A7	ASOA	AVOC only	N.A	p-xylene-d_{10} (200)	200
AB1	ABSOA	AVOC added 6.3 h before BVOC	α-pinene, limonene (20, 20)	p-xylene (30)	0
AB2	ABSOA	AVOC added 6.3 h before BVOC	α-pinene, limonene (20, 20)	toluene (85)	0
AB3	ABSOA	BVOC added 3 h before AVOC	α-pinene, limonene (20, 20)	toluene (85)	50
AB4	ABSOA	BVOC added 5 h before AVOC	α-pinene, limonene (39, 39)	p-xylene-d_{10} (51)	200
AB5	ABSOA	AVOC and BVOC added together	α-pinene, limonene (4, 4)	toluene (85)	60
AB6	ABSOA	AVOC and BVOC added together	α-pinene, limonene (42, 42)	p-xylene-d_{10} (90)	200

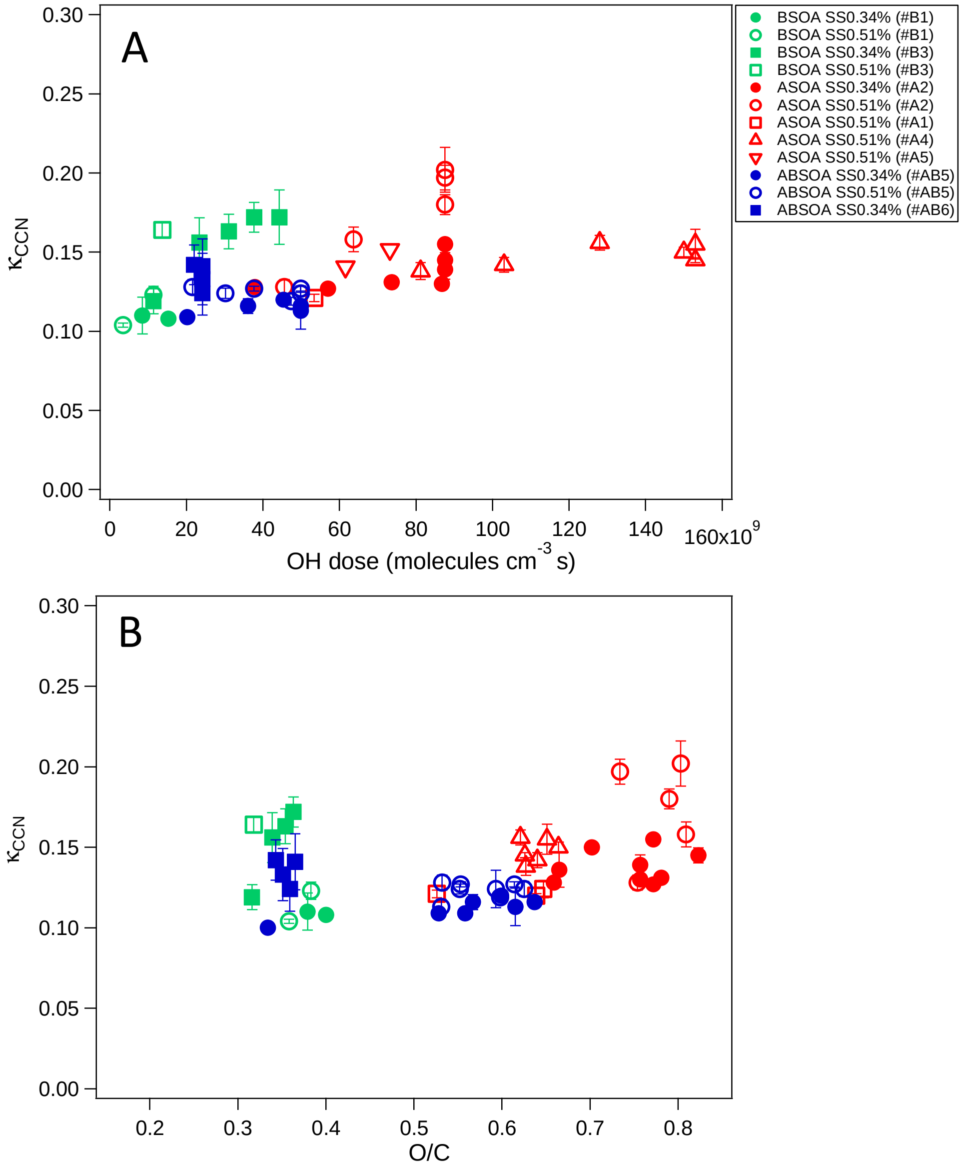

Figure 1. CCN activity of BSOA, ASOA, and ABSOA as a function of OH dose (A) and O/C of aerosol (B). κ_{CCN} at two supersaturations (SS) 0.34% (solid markers) and 0.51% (open markers) is shown. The green, red and blue colors indicate BSOA, ASOA and ABSOA, respectively. κ_{CCN} at similar SS is compared since κ_{CCN} depended on SS. BSOA, ASOA, and ABSOA showed no significant difference at a given SS. Although ASOA had higher degree of oxidation (O/C) than BSOA, ASOA components did not enhance κ_{CCN}.

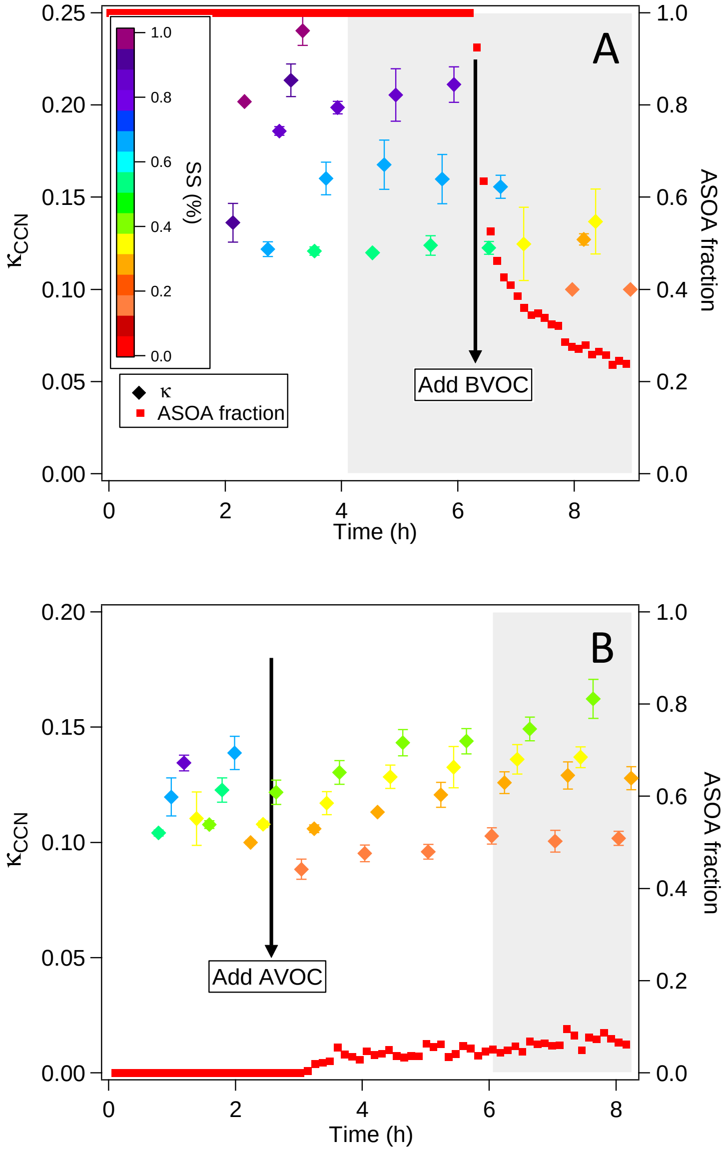

Figure 2. CCN activity of ABSOA from sequential VOC addition at various supersaturations (SS). (A) Toluene was added first and monoterpenes were added 6 h afterwards as indicated by the vertical arrow. The shaded areas show dark periods. ASOA fraction (red dots, right axis) decreased remarkably upon BVOC addition but κ_{CCN} showed no significant change. (B) Monoterpenes were added first and toluene was added 2.6 h afterwards as indicated by the vertical arrow. κ_{CCN} showed no significant change upon the addition of AVOC to BSOA. Note that time series of κ_{CCN} should be followed at similar SS because κ_{CCN} depended on SS and the SS range may change due to the particle size change.

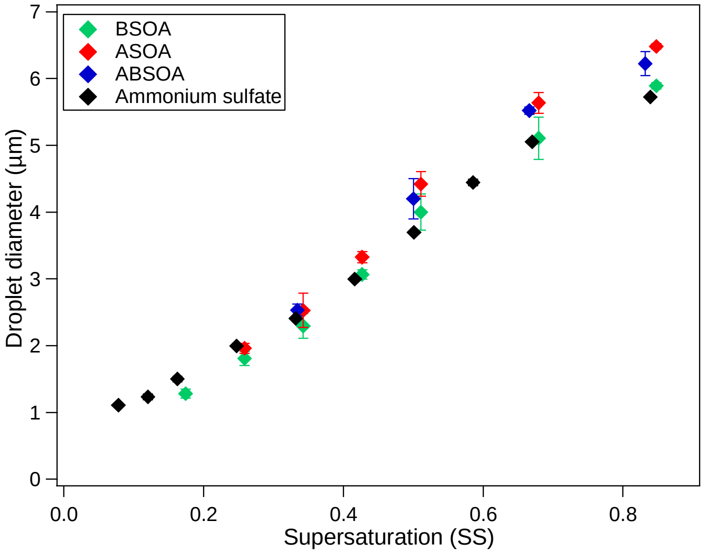

Figure 3. Droplet sizes of BSOA, ASOA, ABSOA and ammonium sulfate aerosols at various supersaturations (SS). In the CCNC, all SOA particles reached comparable droplet sizes compared to ammonium sulfate.

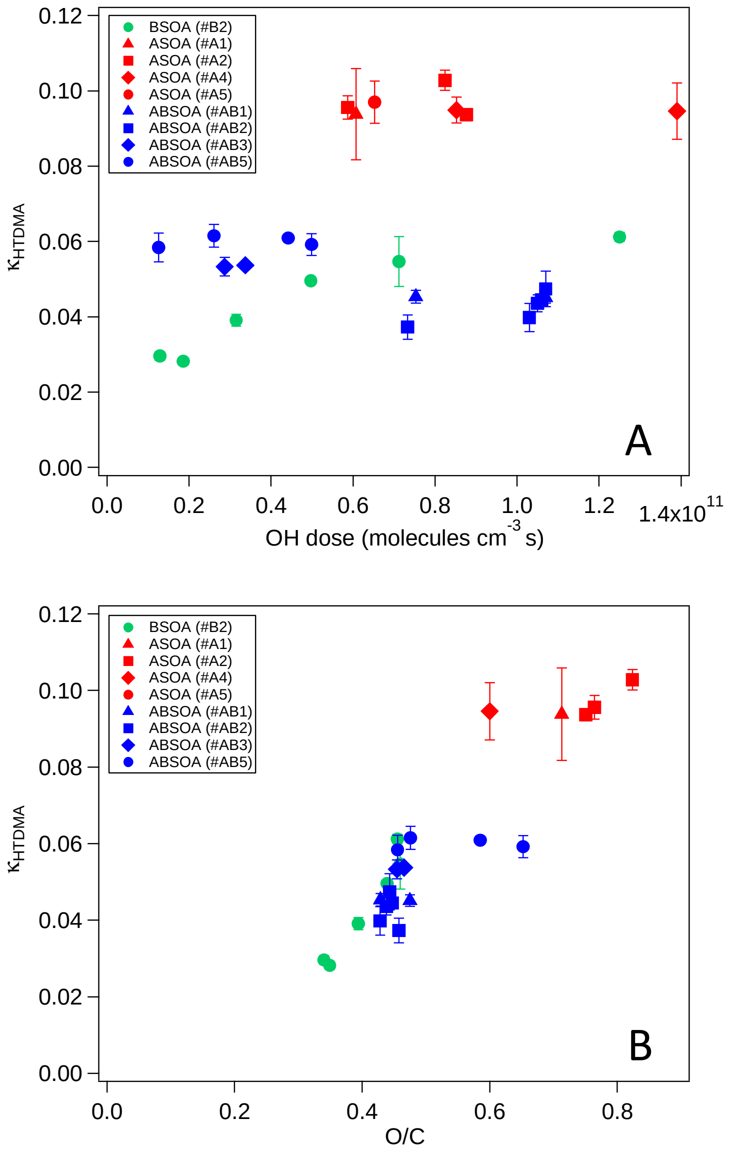

Figure 4. κ_{HTDMA} for BSOA, ASOA and ABSOA as a function of OH dose (A) and O/C of aerosol (B). ASOA had a distinctively higher κ_{HTDMA} and O/C than BSOA.

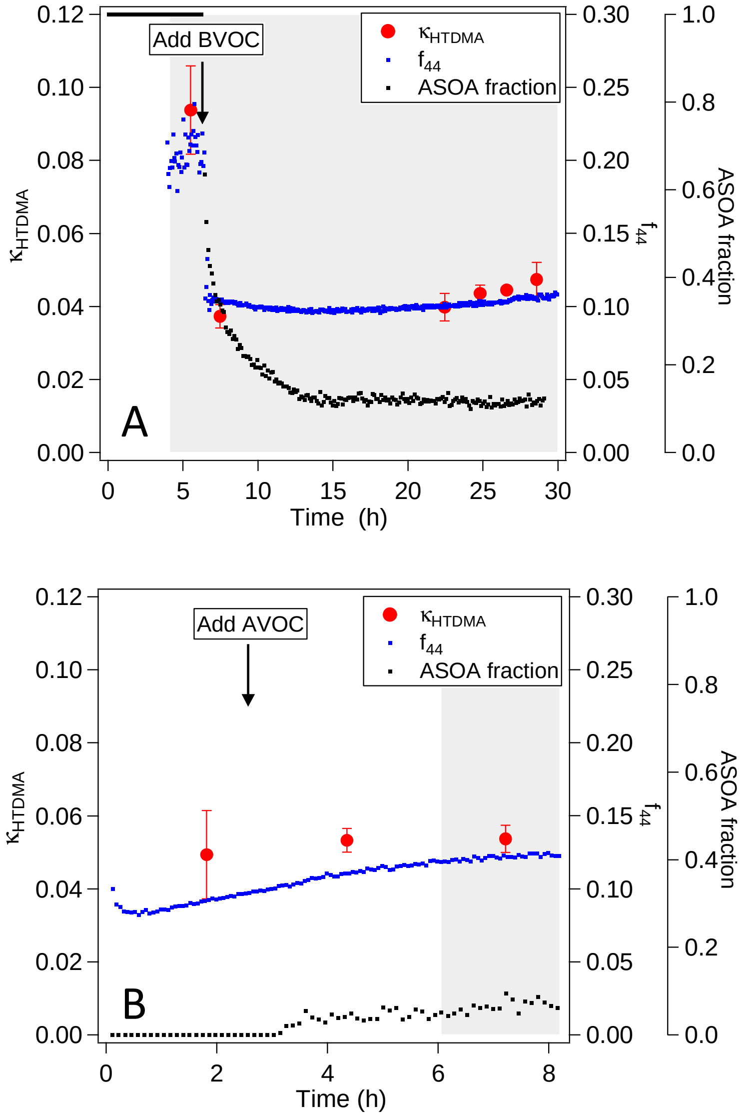

Figure 5. κ_{HTDMA} of ABSOA from experiments when AVOC and BVOC were added sequentially (same experiments as in Fig. 2). (A) Toluene was added first and the monoterpenes were added 6 h afterwards as indicated by the vertical arrow. The shaded areas indicate the dark periods. κ_{HTDMA} decreased significantly with the decrease of ASOA fraction due to the addition of BVOC. At the same time, f_{44} decreased distinctively. (B) Monoterpenes were added first and toluene was added 2.6 h afterwards as indicated by the vertical arrow. κ_{HTDMA} increased slightly as only a minor fraction (<10%) of ASOA was formed. At the same time, f_{44} also increased slightly.

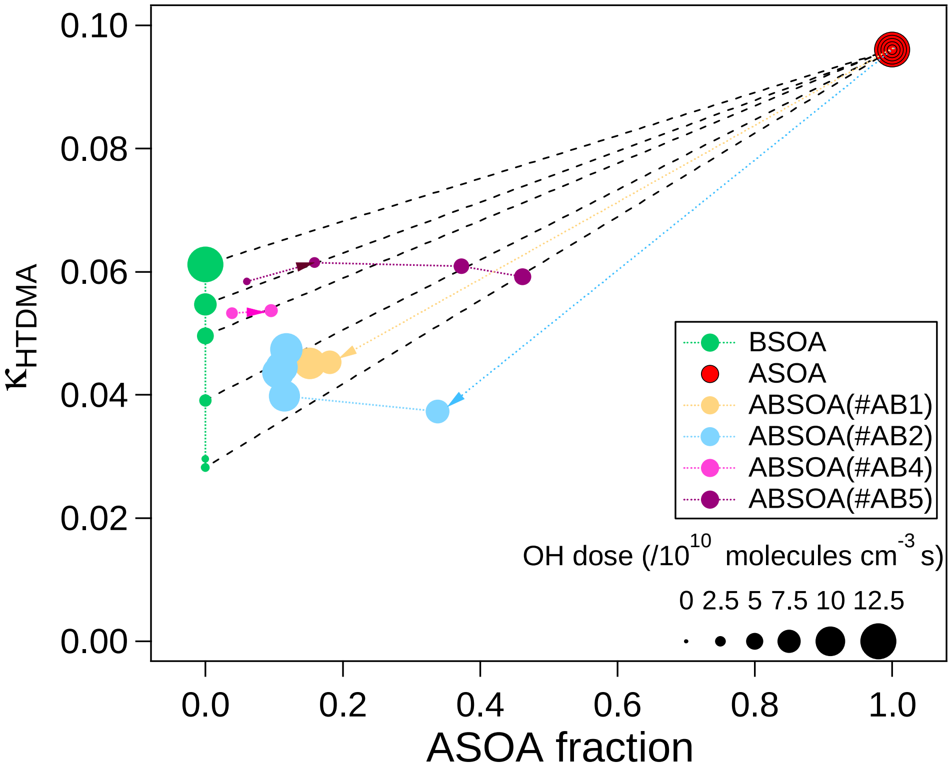

Figure 6. κ_{HTDMA} of ABSOA as a function of ASOA fraction. The size of the marker denotes the OH dose. For ASOA, κ_{HTDMA} is largely independent of OH dose and the average value was used, shown as the same point for different OH dose. The dashed lines connecting the pure BSOA and ASOA of the same OH doses stand for the linear combination of the κ_{HTDMA} of pure BSOA and pure ASOA at that given OH dose. A data point beyond the line corresponding to the OH dose of that point indicates a non-linear effect. The cases of non-linear effect can be found for ABSOA #AB1, #AB2 and #AB5. The dotted lines with arrow of ABSOA show the time order of data points.

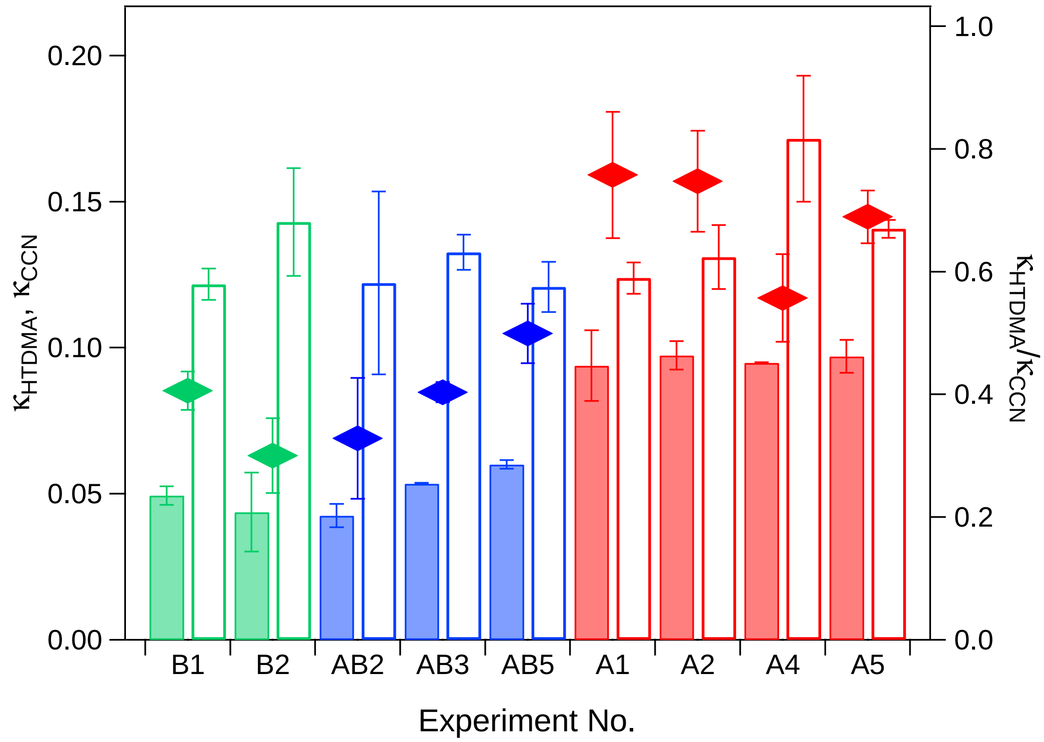

Figure 7. Comparison of κ_{HTDMA} and κ_{CCN} from HTDMA and CCN measurements for BSOA, ASOA, and ABSOA. The solid bar denotes the κ_{HTDMA} and the open bar denotes κ_{CCN} (left axis). The diamond denotes the ratio of κ_{HTDMA} to κ_{CCN} (right axis). The green, blue and red color indicates the BSOA, ABSOA and ASOA, respectively. For all SOA here, there was a discrepancy between κ_{HTDMA} and κ_{CCN}. For ASOA, the gap between κ_{HTDMA} and κ_{CCN} (low $\kappa_{HTDMA}/\kappa_{CCN}$) was smaller compared to BSOA.

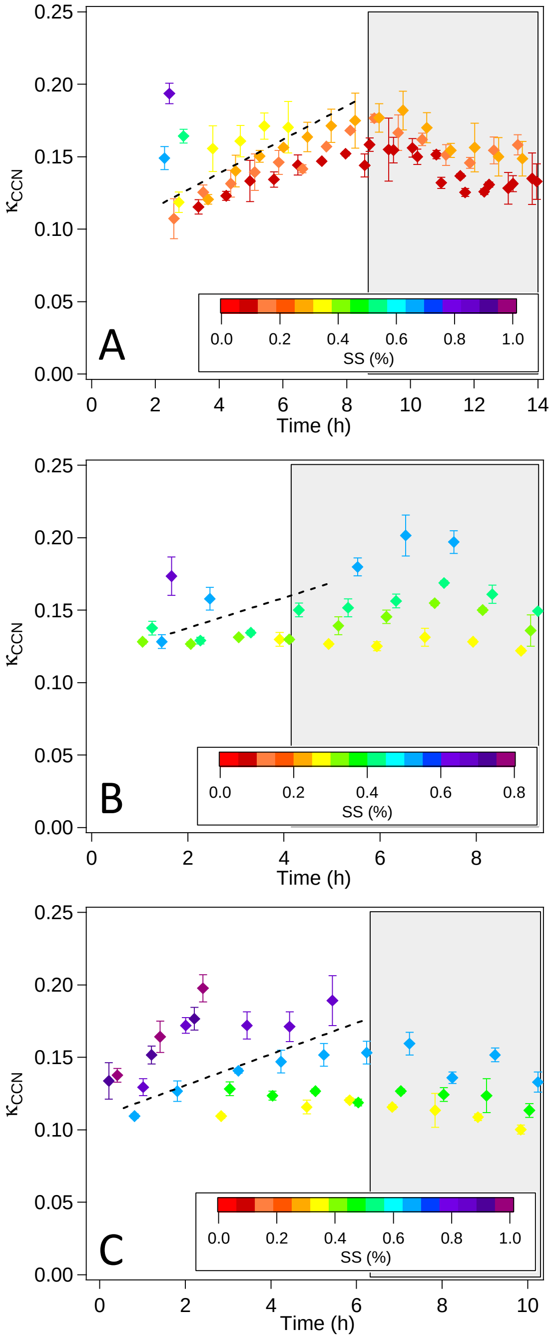

Figure S1. CCN activity of BSOA (A), ASOA (B) and ABSOA (C) at various supersaturations (SS). BSOA was formed by ozonolysis of monoterpene (mixture of α-pinene and limonene with a molar ratio of 1:1) followed by photooxidation. ASOA was formed by photooxidation of toluene. ABSOA was formed by the photooxidation of a mixture of toluene and monoterpenes (α-pinene:limonene =1:1). The shaded areas indicate dark periods.

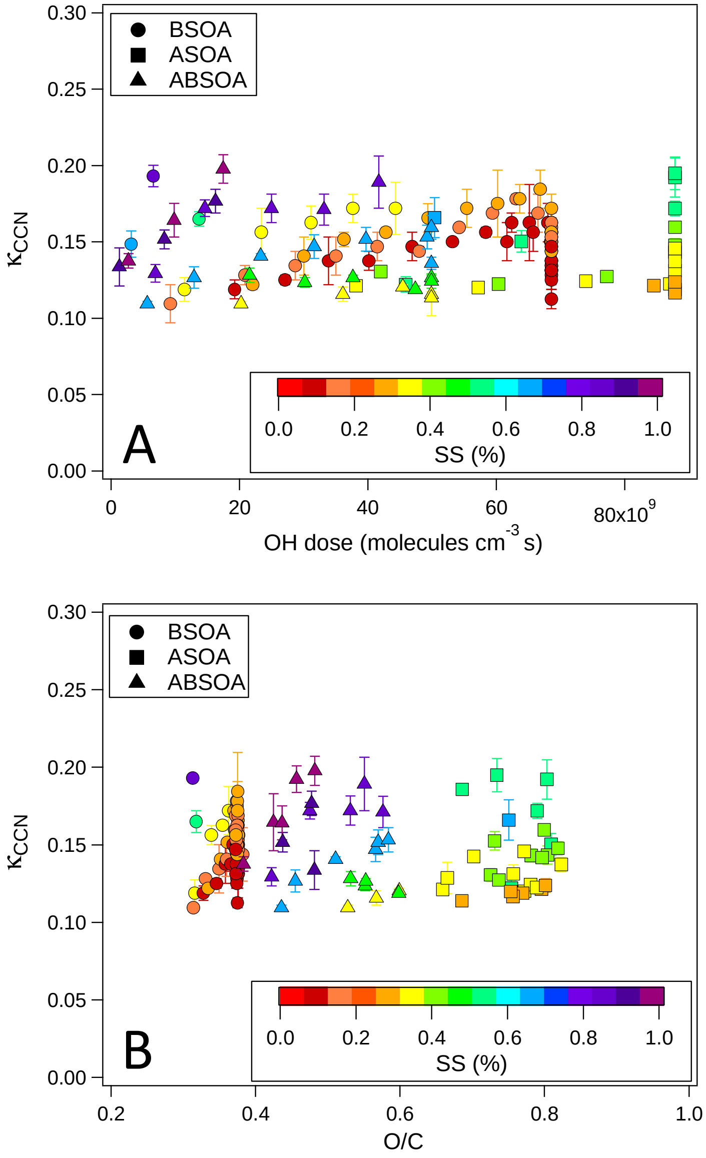

Figure S2. CCN activity of BSOA, ASOA and ABSOA represented by κ_{CCN} at various supersaturations (SS) as a function of OH dose (A) and O/C of aerosol (B). The points lining vertically for each aerosol type in panel A are from the dark period.

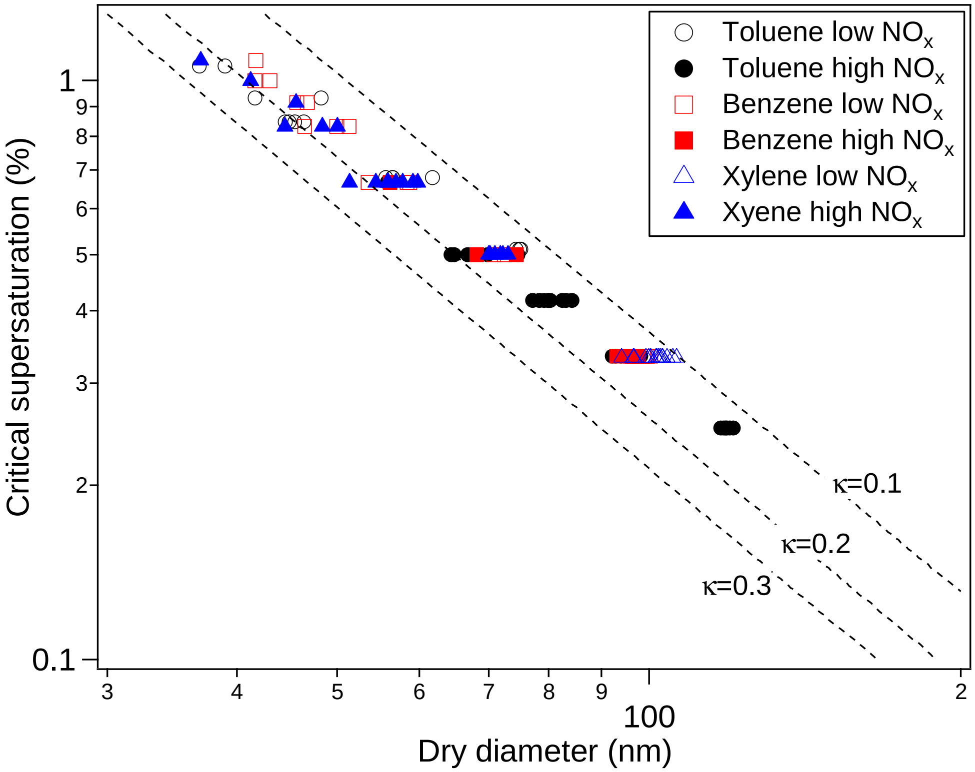

Figure S3. Critical supersaturation as a function of dry particle diameter of ASOA formed from toluene, benzene, and xylene photooxidation in the low NO_x (<1 ppb) and high NO_x condition (10 ppb NO added). ASOA from different precursors show similar CCN activity. ASOA produced at low NO_x and high NO_x show similar CCN activity.

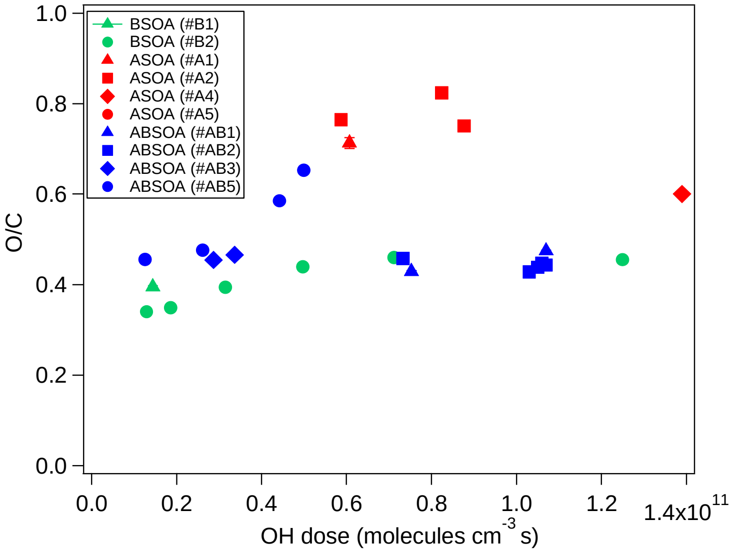

Figure S4. O/C of BSOA, ASOA and ABSOA as a function of OH dose.

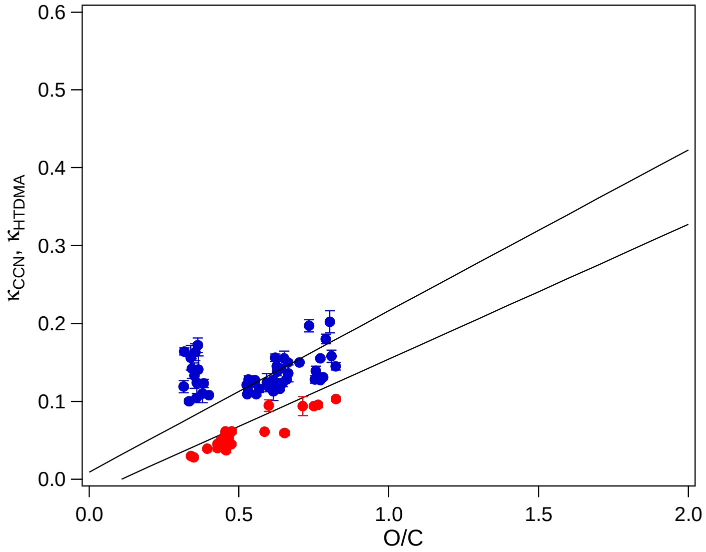

Figure S5. Comparison of κ in this study with the parameterization of the relationship between κ and O/C in the literature (Rickards et al., 2013). The blue markers show κ_{CCN} and the red markers show κ_{HTDMA}. The lines show the upper and lower limits of the parameterization in Rickards et al. (2013).

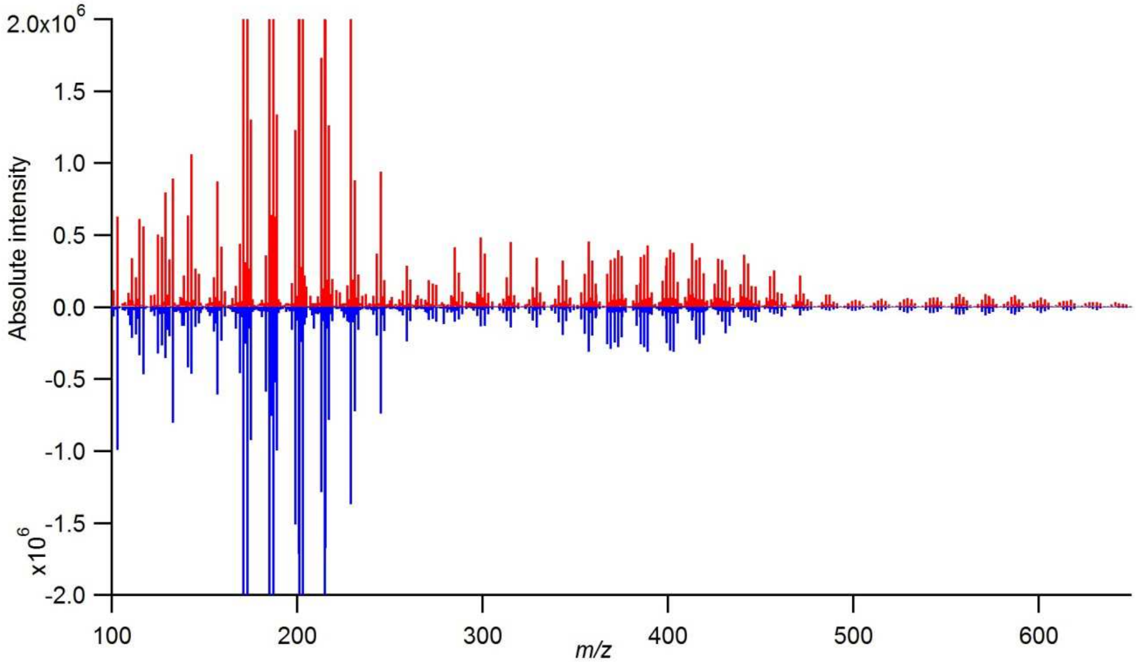

Figure S6. Mass spectra from nano ESI UHRMS of BSOA (red sticks, from experiment #B3 using α-pinene + limonene mixture as precursor) and ABSOA (blue sticks, from experiment #AB6 using α-pinene+limonene+p-xylene mixture as precursor).