

Response to comments of anonymous referees # 1, acp-2021-577

General comments

In this paper, authors conducted a series of laboratory studies on the evolution of sub and super-saturated water uptake of secondary organic aerosol in chamber experiments from mixed precursors. The comparison of aerosol hygroscopicity under sub- and supersaturated conditions involves complex SOA characteristics are important for CCN predictions and understanding the RH effects (from sub-saturation to super saturation) on aerosol hygroscopicity and further improve aerosol hygroscopicity parameterizations. Therefore, the theme of this paper is scientifically meaningful, and the designed laboratory studies are also valid. However, more insightful analysis is required to better interpret the laboratory results.

Many thanks to the reviewer for the comments and suggestions. We have improved the manuscript accordingly. Please find a point-by-point response below.

Two main conclusions are drawn in this study.

The first one is that SOA composition played a second role in the kappa variations. I agree with the authors, and this is obvious considering that the well-known fact that inorganic aerosol is much more hygroscopic than SOA, thus, of course the SOA composition should play the second role. However, at the same MR_SOA/PM, considerable variations can be found, for example, at MR_SOA/PM ~0.4, the k_{HTDMA} varies from less than 0.2 to about 0.4, which demonstrates that the SOA compositions played significant roles in determining the apparent kappa. The authors should quantitatively derive the apparent/effective hygroscopicity parameter K_{OA} using the volume mixing rule under sub- and supersaturated conditions and discuss their differences with previous results (Kuang et al., 2020b), quantitatively present the relationships between K_{OA} and SOA oxidation levels under sub- and super-saturated conditions and discuss more about the controlling factors of K_{OA} variations based on AMS signals and VOC precursors (Wang et al., 2019). Otherwise, the authors are just talking about the sub- and super-saturated water uptake of mixed aerosol system includes organic and inorganic aerosols but not that of secondary organic aerosol, and is not consistent with the theme of the title.

As suggested by both reviewers, I calculated the κ_{org} with ZSR method, and included results/discussions including the suggested references into the manuscript. The paragraph has been rephrased as follows:

“Previous studies found the sub-saturated aerosol water uptake (κ) increases with chemical aging of SOA from single precursor oxidation and showed a positive relationship with SOA oxidation state (e.g. O:C ratio or f_{44} , fraction of m/z, 44 in total organic signal) (Jimenez et al., 2009; Massoli et al., 2010; Lambe et al., 2011; Zhao et al., 2016; Duplissy et al., 2011; Kuang et al., 2020a), but no clear relationship involving multiple precursors with various oxidation state (Alfarra et al., 2013; Zhao et al., 2016). In addition, Wang et al. (2019a) found that the positive relation between water uptake at the super-saturated conditions and oxidation state (O:C) is attributed to lower molecular weight of organic species other than higher solubility at higher oxidation level. To illustrate relation between κ of SOA and the oxidation state, the κ_{org} was deduced with ZSR method and the κ of ammonium sulphate from AIOMFAC assuming volume additivity. Two main messages are shown in Fig. S2. Firstly, the calculated κ_{org} from HTDMA and CCN counter varied with VOC systems ranging from -0.2 to 0.2. The ZSR method assumes that components are independent and the water uptake by individual components are additive. Therefore, the negative values of the κ_{org} indicates the existence of interactions between inorganic and organic substances and thus results in less water uptake than the case without interactions in ZSR method (Zardini et al., 2008). Secondly, the calculated κ_{org} at sub- and super-saturated conditions showed no clear relationship with oxidation state of SOA (f_{44}) in various VOC systems, which is consistent with previous studies involving multiple precursors (Alfarra et al., 2013; Zhao et al., 2016). Other factors might have influences but need further investigations, such as organic mass loading, molecular weight (Cappa et al., 2011; Petters et al., 2017), solubility (Petters et al., 2009; Ruehl and Wilson, 2014; Huff Hartz et al., 2006), surface tension (Ovadnevaite et al., 2017; Bzdek et al., 2020; Ruehl et al., 2016; Lowe et al., 2019) and co-condensation (Kulmala et al., 1993; Topping et al., 2013b; Hu et al., 2018) and will be discussed in Section 3.5.”

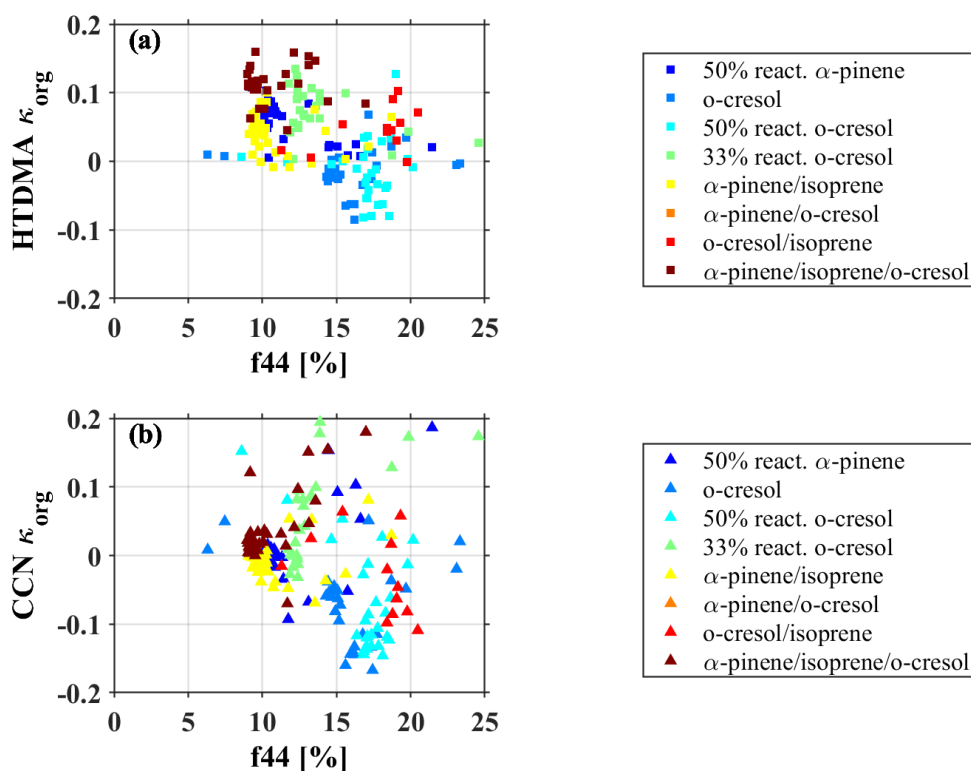


Figure S2. (a) relation between κ_{org} calculated from HTDMA and the fraction of m/z 44 in total organic signal, f_{44} . (b) relation between κ_{org} calculated from CCN counter and f_{44} in all investigated VOC systems.

The second one is “ K_{HTDMA}/k_{CCN} increased as a function of SOA mass fraction, independent of initial VOC concentrations and sources, the mean k_{HTDMA} can be 60% higher than k_{CCN} on average when aerosol fraction approached 0.8”. This finding is quite interesting but the explanation is not very convincing. The authors conclude that this finding is possibly attributable to the non-ideality of solutes at different RH or different cocondensation of condensable organic vapors within the two instruments. At L397, the authors claim that water increase in CCN set-up is not favorable for co-condensation of semi-volatile vapors. However, the condensation of these vapors such as HNO_3 is influenced by both water vapor content and temperature. Although the temperature in CCN is higher than the temperature in HTDMA which seems not favorable for cocondensation, however, the aerosol water content in the CCN is much higher than in the HTDMA due to the super-saturated conditions. Thus, I cannot agree upon this argument. As to the possible role of non-ideality, the authors cited two papers published by Brechtel and Kreidenweis (2000a) and Brechtel and Kreidenweis (2000b) and said “the interactions of inorganic ions and organic molecules can exert both positive and negative effects in the water uptake, depending on the organic fraction

and inorganic species”. The organic fraction and inorganic species are clear in this study, can authors perform some quantitative analysis? or at least deliver a clear qualitative result that the interactions of inorganic ions and organic molecules exerted a positive or a negative effect on the water uptake.

Thanks for the reviewer. We agree that the evidence is ambiguous, and the discussion is not adequate. To better understand the role of non-ideality (and potentially co-condensation) in κ discrepancy between HTDMA and CCN, we performed AIOMFAC thermodynamic model calculations. Based on comparison between model results and the observation, a new section 3.5 has been added to understand how non-ideality and co-condensation influence sub- and super-saturated water uptake. Please find details in Section 3.5.

Towards the condensation of semi-volatiles (including HNO₃), we agree with the reviewer that both temperature and water content influence this process. The competition of increasing temperature and dilution in aerosol phase due to increasing water content will influence the condensation/evaporation of the semi-volatiles in CCN counter. This discussion has been included into the updated manuscript.

The influence of non-ideality has been discussed in the updated manuscript. But the thermodynamic model cannot give information on organic/inorganic interactions as the reviewer suggested, which needs further explicit molecular information and worthwhile deeper investigations in the future.

Specific comments:

1. L45-L50, just a suggestion: the first two sentences of the introduction lack continuity in logic, the authors jumped from aerosol-cloud interaction to the reliability of CCN prediction, I suggest a sentence that claim the accurate CCN prediction is essential for investigating aerosol-cloud interactions in climate models might be needed between the original two sentences.

A sentence has been added as suggested: “Thus, an accurate prediction of cloud condensation nuclei (CCN) number from aerosol properties is essential for investigating aerosol-cloud interactions in climate models.”

2. L53, the SOA can be formed not just through gas-phase partitioning, but also aqueousphase reactions (Ervens et al., 2011;Kuang et al., 2020a).

The sentence has been updated as suggested:

“A large portion of organic aerosols are secondary organic aerosol (SOA) (Zhang et al., 2007; Jimenez et al., 2009), formed from oxidation of gaseous volatile organic compounds (VOCs) via gas-particle partitioning (Hallquist et al., 2009) and aqueous-phase reactions (Ervens et al., 2011; Kuang et al., 2020).”

3. L58, about the role of organic aerosol hygroscopicity in climate and aerosol cloudinteractions, references such as (Liu and Wang, 2010;Rastak et al., 2017) might be better choices.

The sentence has been revised as suggested:

“Although the organic aerosol components are less soluble and consequently less hygroscopic than the referenced inorganic compounds (e.g. sulphate, nitrate) (Alfarra et al., 2013; Mcfiggans et al., 2006; Kreidenweis and Asa-Awuku, 2014; Huff Hartz et al., 2005; King et al., 2009), they can play an important role in the cloud formation globally (Liu and Wang, 2010; Rastak et al., 2017) due to its ubiquitous large fraction

(20 ~ 90 %) in fine particulate matter mass (Kanakidou et al., 2005; Jimenez et al., 2009; Zhang et al., 2007)."

4. L164 more details about the DMA-CCN set-p should be given, for example, the detailed supersaturation points and time schedule

Thanks for your suggestion.

More information about the setup has been added:

"During the experiments, DMA scans from 20 to 550 nm with 20 size bins. The selected aerosol particles will separate and go through the CCN counter and a CPC to measure the CCN and total particle number concentrations, respectively. The supersaturation ratio of CCN counter usually set to 0.5 % at the beginning of experiments. With the ongoing of SOA formation, the aerosol particles grow up. To derive a reliable activation curve with enough particle number concentration around the activation size, the set supersaturation ratio decreases accordingly down to 0.1 % during experiments, depending how fast the SOA is formed. The time resolution for each measurement is 10 mins."

5. L175 Please report how the AMS vacuum aerodynamic diameter is converted to the mobility diameter, and estimate potential MR_SOA/PM uncertainties associated with this respect due to that obvious size-dependent chemical composition is observed. L226, a smaller particle size is not specific (compare to which size range), please presents diameter range directly

For the conversion of AMS vacuum aerodynamic diameter to mobility diameter. Firstly, I estimate the density of the nonrefractory aerosol particles using simple mixing rule shown in equation [1] assuming the density of ammonium sulphate (1.77 g/cm^3) and SOA (1.4 g/cm^3 as used). $F_{m,SOA}$ is the mass fraction of the SOA. Then, this estimated density is used to calculate the mobility diameter as shown in equation [2] (Zhang et

al., 2005).

$$\rho_{est} = \rho_{AS}(1 - F_{m,SOA}) + \rho_{SOA}F_{m,SOA} \quad [1]$$

$$D_m \approx \frac{D_{va}}{\rho_{est}} \quad [2]$$

For the potential $MR_{SOA/PM}$ uncertainty, the selection of SOA density can introduce uncertainty to the ρ_{est} , further on mobility diameter. Previous studies found that the SOA density can be different, with a range from 1.2 to 1.65 g/cm³ (Kostenidou et al., 2007; Alfarra et al., 2006; Varutbangkul et al., 2006; Nakao et al., 2013). For examples, Kostenidou et al. (2007) reported that the estimated density of SOA from α -pinene, β -pinene, d-limonene are 1.4-1.65 g/cm³. Nakao et al. (2013) investigated the SOA from 22 different precursors with a wide range of carbon number (C5-C15) and found their density ranges from 1.22 to 1.43, negatively related to their molecular size. In this study, considering the three precursors we used, we take a medium value of density (1.4 g/cm³) in the literature. To calculate the uncertainty of the SOA density on $MR_{SOA/PM}$, I recalculate with the minimum (maximum) density, 1.2 (1.65) g/cm³, the $MR_{SOA/PM}$ changes within +/- 10%. The discrepancy of $MR_{SOA/PM}$ between 100 nm and 200 nm is outside of the uncertainty, which indicates the difference of chemical composition between these two sizes.

A new paragraph describing the diameter conversion and the uncertainty of density on MR_{SOA} has been added to the method sec. 2.2:

“For the conversion of AMS vacuum aerodynamic diameter to mobility diameter. Firstly, I estimate the density of the nonrefractory aerosol particles using simple mixing rule shown in equation [1] assuming the density of ammonium sulphate (1.77 g/cm³) and SOA (1.4 g/cm³ as used).

$$\rho_{est} = \rho_{AS}(1 - F_{m,SOA}) + \rho_{SOA}F_{m,SOA} \quad [1]$$

$F_{m,SOA}$ is the mass fraction of the SOA. Then, this estimated density is used to calculate the mobility diameter as shown in equation [2] (Zhang et al., 2005).

$$D_m \approx \frac{D_{va}}{\rho_{est}} \quad [2]$$

For the potential MR_SOA/PM uncertainty, the selection of SOA density can introduce uncertainty to the ρ_{est} , further on mobility diameter. Previous studies found that the SOA density can be different, with a range from 1.2 to 1.65 g/cm³ (Kostenidou et al., 2007; Alfarra et al., 2006; Varutbangkul et al., 2006; Nakao et al., 2013). For examples, Kostenidou et al. (2007) reported that the estimated density of SOA from α -pinene, β -pinene, d-limonene are 1.4-1.65 g/cm³. Nakao et al. (2013) investigated the SOA from 22 different precursors with a wide range of carbon number (C5-C15) and found their density ranges from 1.22 to 1.43, negatively related to their molecular size. In this study, considering the three precursors we used, we take a medium value of density (1.4 g/cm³) in the literature. To calculate the uncertainty of the SOA density on MR_{SOA/PM}, I recalculate with the minimum (maximum) density, 1.2 (1.65) g/cm³, the MR_{SOA/PM} changes within +/- 10%.”

The sentence has been rephrased to clarify the size.

“Moreover, a size-dependent chemical composition was observed, with a higher MR_{SOA/PM} for particles at 75/100 nm than the 200/300 nm in all investigated VOC systems (as shown in Figure 2).”

References from the reviewer:

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References for response:

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