Interactive comment on "Measurement Report: Distinct size dependence and diurnal variation of OA hygroscopicity, volatility, and CCN activity at a rural site in the Pearl River Delta (PRD) region, China" by Mingfu Cai et al.

Summary:

This work demonstrates the hygroscopicity, volatility and CCN activity of OA particles at a rural environment of PRD. The manuscript fits well to the scope of ACP. However, I think more evidences or discussions should be included if possible. This paper is worth to be published, but not in its current form. Thus I recommend it to be accepted after the following comments listed below have been adequately addressed.

Comments:

1. Section 2.2.2: Please give more information of reference data used in the Köhler theory when performing the CCNC calibration with ammonium sulfate particles. This is very important because different parameterizations will retrieve different critical supersaturations (Rose et al., 2008).

Reply: We appreciate the reviewer for this suggestion. We have modified the sentence in lines 179-181 and added a section in the supplementary about the calibration as follows:

"Before the measurement, the SMPSs were calibrated with PSLs (20, 50 and 200 nm) and the CCNc was calibrated with ammonium sulfate ($(NH_4)_2SO_4$) particles at selected SSs (0.1%, 0.2%, 0.4%, 0.7%, 0.9%, and 1.0%, Sect. S1).

Text in the supplement. Section S1 Supersaturation calibration of the CCNc

Before and after the measurement, the CCNc was calibrated with ammonium sulfate ($(NH_4)_2SO_4$) particles. The critical supersaturation (Sc) was calculated by Köhler theory:

$$Sc = exp\left[\left(\frac{4A^3}{27B}\right)^{1/2}\right], A = \frac{4\sigma_{s/a}M_w}{RT\rho_w}, B = \frac{6i_s n_s M_w}{\pi\rho_w} \qquad \text{(S1)}$$

where $\sigma_{s/a}$ is the surface tension of the solution/air interface and is assumed to be pure water (0.0728 N m^{-1} at 298.15 K) for simplicity, M_w is the molecular weight of water (0.018 kg mol^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the thermodynamic temperature in Kelvin (298.15 K), ρ_w is the density of water (about 997.04 kg m^{-3} at 298.15 K), i_s is the van't Hoff factor and is assumed to be 2.5, n_s is the molality of $(NH_4)_2SO_4$, $n_s = \frac{\pi\rho_s D_{50}^3}{6M_s}$, D_{50} is the critical diameter, ρ_s is the density of ammonium sulfate (1769 kg m^{-3}), and M_s is the mole mass of ammonium sulfate (0.132 kg mol^{-1})."

2. Line 340, I understand the decomposition of particles is hard to quantify. Could you roughly estimate the uncertainty?

Reply: We appreciate the reviewer for this valuable suggestion. We have added some sentences in section 2.3.4 in lines 349-352 and a discussion in the supplement:

"We roughly estimated uncertainty caused by the decomposition and found that ignoring the decomposition of organics would lead to an underestimation of SVOA, while the decomposition of $(NH_4)_2SO_4$ played a minor role in the simulation (Sect. S2). However, the exact effects are still highly uncertain.

Text in the supplement. Section S2 Estimation of the uncertainty caused by the decomposition

During the heating process, ammonium sulfate ($(NH_4)_2SO_4$) would decompose to ammonium bisulfate (NH_4HSO_4) or triammonium hydrogen sulfate $(NH_4)_3H(SO_4)_2$, and ammonia (NH_3). Meanwhile, extremely low volatile OA (ELVOA) would decompose into semi-volatile or low-volatile OA. This could lead to uncertainty in the simulation. To estimate the uncertainty, we simulate the campaign average data based on the following assumptions:

Case 1. All $(NH_4)_2SO_4$ would decompose to $(NH_4)_3H(SO_4)_2$ at 150°C and then sublimation, while the decomposition of organics is ignored.

Case 2. All ELVOA would decompose to SVOA at 100°C, while the decomposition of ammonium sulfate is ignored.

Case 3. All $(NH_4)_2SO_4$ would decompose to $(NH_4)_3H(SO_4)_2$ and sublimation at 150°C, and all of EVLOA would decompose to SVOA at 100°C.

The results show that the decomposition of $(NH_4)_2SO_4$ plays a minor role in the simulation if the decomposition of organics was ignored (Case 1). It is probably owing to the fact that $(NH_4)_2SO_4$ starts to volatilize at about 100°C and completely sublimate at about 200°C (Hong et al., 2017). The decomposition of organics would significantly increase the fraction of SVOA (Case 2 and 3) by about 0.15-0.54. However, the SSR increases from 0.0216 in the standard simulation (ignore decomposition) to 0.5277 and 0.6626 in the case 2 and 3, respectively, suggesting that the model fails to reproduce the MFR based on the adopted parameters ($\Delta H\_vap=80$ kJ mol-1 and $\alpha=0.09$). Thus, the results in case 2 and 3 are highly uncertain. In short summary, the decomposition of $(NH_4)_2SO_4$ would lead to a minor uncertainty in the simulation, while the decomposition of organic matter would significantly affect the model results by increasing the fraction of SVOA, for which the exact effects were still unclear. Further investigations are needed to better understand the decomposition of particles during the heating processes.

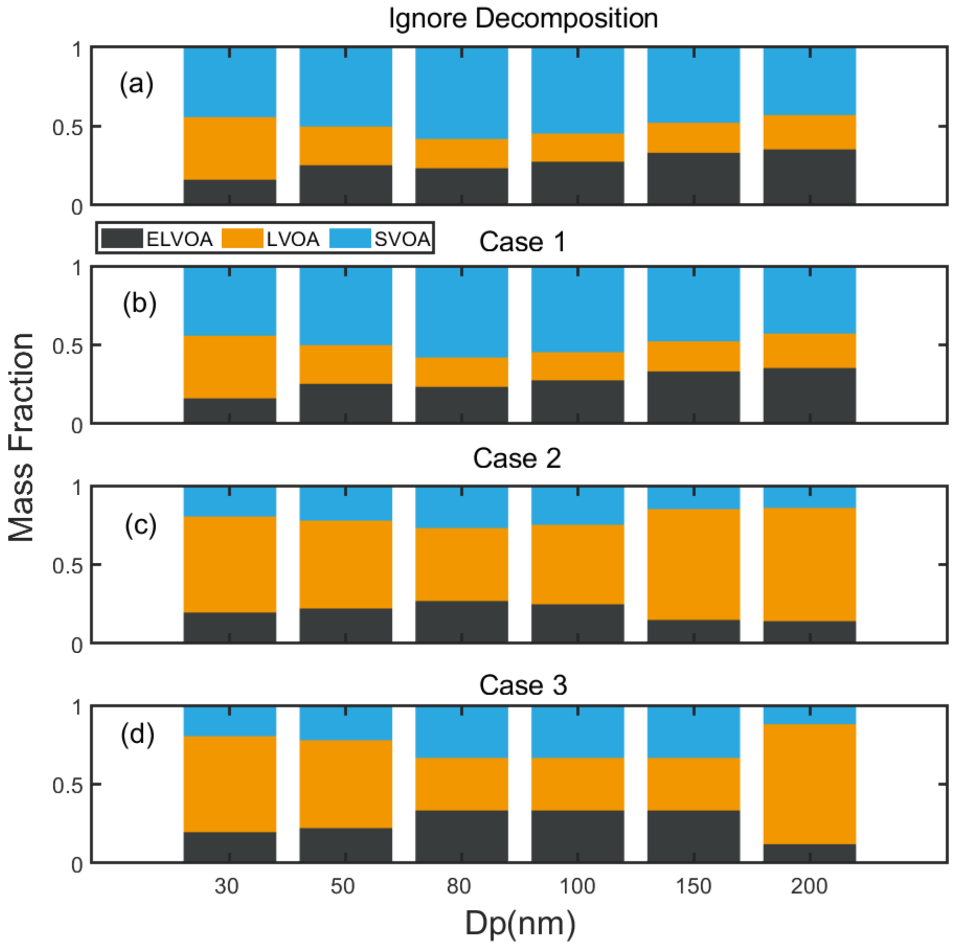

Figure S2.1. The mass fraction distribution of SVOA, LVOA and ELVOA of the campaign averaged MFR based on different assumptions.

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3. Lines 409-413: I agree that the surfactant effect is crucial to explain the discrepancy in hygroscopicity closure study. Could you provide any chemistry evidence about that? Maybe from the AMS data or filter sample if this had been done in the campaign. Also, the difference between κCCN and κhtdma may also due to the parameterizations used in the CCNC and HTDMA calibration. See Wang et al., (2017). Please consider it and give more information as suggested in comment 1. Many studies (Petters et al., 2009;Wex et al., 2009;Hersey et al., 2013;Wu et al., 2013;Hong et al., 2014;Hansen et al., 2015;Mikhailov et al., 2015;Pajunoja et al., 2015;Zhao et al., 2016) have reported the different hygroscopic properties from CCNC and HTDMA measurements. I would suggest more discussions should be added.

Reply: We thank the reviewer for valuable suggestions. We totally agree that the discrepancy between κ_{HTDMA} and κ_{AMS} could be caused by many factors, including the surfactant effect, parameterizations used in the CCNc and HTDMA calibration, the solubility of organics, and liquid-liquid phase separation (Liu et al., 2018;Petters and Kreidenweis, 2013;Rose et al., 2008;Pajunoja et al., 2015;Renbaum-Wolff et al., 2016). The decrease of surface tension was positively correlated with the concentration of water-soluble organic aerosol (WSOA) (Facchini et al., 2000). Humic like substances (HULIS) were found to be a major group of surface-active species (Sugo et al., 2019;Dinar et al., 2006). Unfortunately, identifying such surface-active species at the molecular level is still a challenge by using AMS data. We collected $PM_{2.5}$ filter samples in this campaign, while all the samples have been analyzed in other purpose. Thus, it is difficult to provide any direct chemical evidence about these surface-active species in this campaign. Alternatively, we analyzed the ratio of atomic oxygen to atomic carbon (O:C), which was associated with the occurrence of LLPS (Bertram et al., 2011). Once LLPS occurred, the organic film on the droplet surface would decrease surface tension and enhance water uptake (Liu et al., 2018). For particles of organic/inorganic mixtures, the LLPS can occur when the O:C is low than 0.8 (Bertram et al., 2011;Song et al., 2012a, b;Schill and Tolbert, 2013). During this campaign, the average O:C obtained by the AMS measurement is ～0.53, suggesting that the LLPS likely occurred at supersaturation conditions, which could lead the discrepancy between κ_{HTDMA} and κ_{CCN}. We have modified some sentences and added some discussions in lines 415-439:

"This significant discrepancy between the measured κ_{CCN} and κ_{HTDMA} values might suggest that the water uptake behavior is different under super- and sub-saturation conditions, which is likely attributed to the surfactant effect. It was reported that organic matter in the particles could serve as surfactant and lower surface tension by about 0.01-0.032 N m^{-1}, leading to a higher CCN activity and thus a higher κ_{CCN} (Petters and Kreidenweis, 2013; Ovadnevaite et al., 2017; Liu et al., 2018). According to Eqs. (4) and (5), the κ_{CCN} was more susceptibly affected by the value of surface tension than that of κ_{HTDMA}, which would lead to the discrepancy between κ_{CCN} and κ_{HTDMA} values. The surfactant effect is closely related to the presence of liquid-liquid phase separation (LLPS) for organic-containing particles at high RH (Renbaum-Wolff et al., 2016; Ruehl and Wilson, 2014). Once LLPS occurred, the organic film on the droplet surface would decrease surface tension and enhance water uptake. For particles of organic/inorganic mixture, the LLPS can occur when the O:C is lower than 0.8 (Bertram et al., 2011; Song et al., 2012a, b; Schill and Tolbert, 2013). The average O:C obtained using AMS is about 0.53 in this campaign, suggesting that the LLPS likely occurred at supersaturation conditions. Meanwhile, the variation of the discrepancy between κ_{CCN} and κ_{HTDMA} is statistically insignificant during clean and polluted periods (Fig. S7b and S7c), implying that the surfactant effect was hardly affected by pollution condition. Note that surface tension effect is not the only factor which leads to a higher κ_{CCN}. It was found that κ_{CCN} could be higher than κ_{HTDMA}, since the existence of the slightly soluble compounds inhibits water uptake under subsaturation conditions (Zhao et al., 2016; Pajunoja et al., 2015; Dusek et al., 2011; Petters et al., 2009; Hong et al., 2014; Hansen et al., 2015). Other factors, such as different parameters used in the CCNc and HTMDA calibration and function groups associated with the carbon chain, can lead to a gap between κ_{HTDMA} and κ_{CCN} (Rose et al., 2008; Wex et al., 2009). More future work is needed to better understand this water uptake mechanism and to improve the prediction of aerosol-cloud-climate interactions."

4. As shown in Fig. S10, the depression of surface tension is more obvious for larger particles (low SS). Is this more related to the ELVOCs? I would suggest to provide more case study, such as comparing the hygroscopicity (three methods) with different pollution condition (or OA content). For SS=0.7%, I do not suggest to adjust the surface tension, it seems more reasonable to use the sigma of water.

Reply: We thank the reviewer for this suggestion. The surfactant effect is associate with various factors, such as polarity of molecules, liquid density, vapor density, etc. (Egemen et al., 2000), while the volatility of OA is more related to functional groups, carbon number, oxidation state, and N:C ratio (Donahue et al., 2011;Donahue et al., 2012;Chuang and Donahue, 2016). Based on our current data, it is difficult to find direct evidence about the relationship between the depression of surface tension and the volatility of OA. We investigated the κ values obtained by CCNc (κ_{CCN}), HTDMA (κ_{HTDMA}), and AMS (κ_{AMS}) during polluted ($PM_{2.5}$ > 60 μg m^{-3}) and clean periods ($PM_{2.5}$ < 30 μg m^{-3}). No significant variation of κ_{CCN}, κ_{HTDMA}, and κ_{AMS} was observed between clean and pollute periods (Fig. S7), suggesting the surfactant effects might be hardly affected by pollution condition. For 0.7% SS, the overestimation of N_{CCN} based on the reduced $\sigma_{s/a}$ is due to using a fix value of κ_{OA} (0.1), while the κ_{OA} is lower than 0.1 at corresponding size range. We predicted the N_{CCN} at 0.7% SS by using the reduced $\sigma_{s/a}$ and SR κ_{OA}, and found that the overestimation could be corrected (Fig. S11).

We have added some sentences and modified the discussion in lines 409-418，

“The average κ values obtained using HTDMA fall in a range of 0.1-0.17 at 30-200 nm (Fig. S7a), which were possibly attributed to a high fraction of organic matter (Fig. S6). The κ_{AMS} is slightly higher than the κ_{HTDMA} and the differences become larger with decreasing particle sizes. This was probably due to the overestimated κ_{OA} at a small size range, which will be discussed in the next section. The hygroscopicity parameter κ values obtained by the CCNc method were 0.48, 0.47, 0.31, 0.22, 0.20, and 0.20 at the above SS, respectively, which were much higher than those measured by the HTDMA in this study. This significant discrepancy between the measured κ_{CCN} and κ_{HTDMA} values might suggest that the water uptake behavior is different under super- and sub-saturation condition, which is likely attributed to the surfactant effect.”

, and in lines 429-431,

“Meanwhile, the variation of the discrepancy between κ_{CCN} and κ_{HTDMA} is statistically insignificant during clean and polluted periods (Fig. S7b and S7c), implying that the surfactant effect was hardly affected by pollution condition.

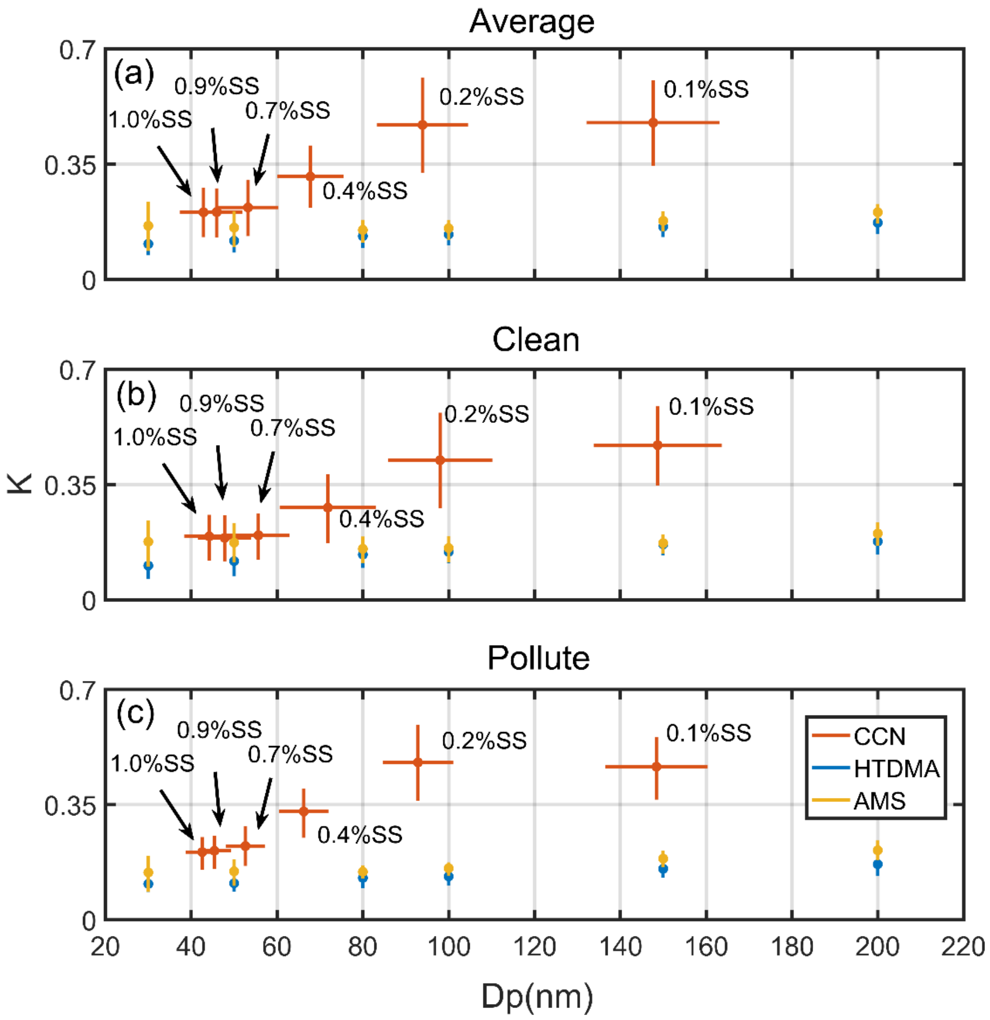

Figure. S7 The mean and standard deviation values of κ_{CCN}, κ_{HTDMA}, and κ_{AMS} during the campaign (a), clean (b) and pollute periods (c). The κ values were pointed against their corresponding mean D_{50} (κ_{CCN}) or selected diameter (κ_{HTDMA} and κ_{AMS}). The dots represent the mean values, and the bars represent the one standard deviation. The relative clean and polluted periods were classified by the mass concentration of $PM_{2.5}$ ($<$ 30 μg m^{-3} and $>$ 60 μg m^{-3}).

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, and in lines 588-590,

“The N_{CCN} was slightly overestimated by using reduced $\sigma_{s/a}$ values, which was probably due to using a fixed κ_{OA} values. This bias could be corrected by adopting SR κ_{OA} scheme (Fig. S11).

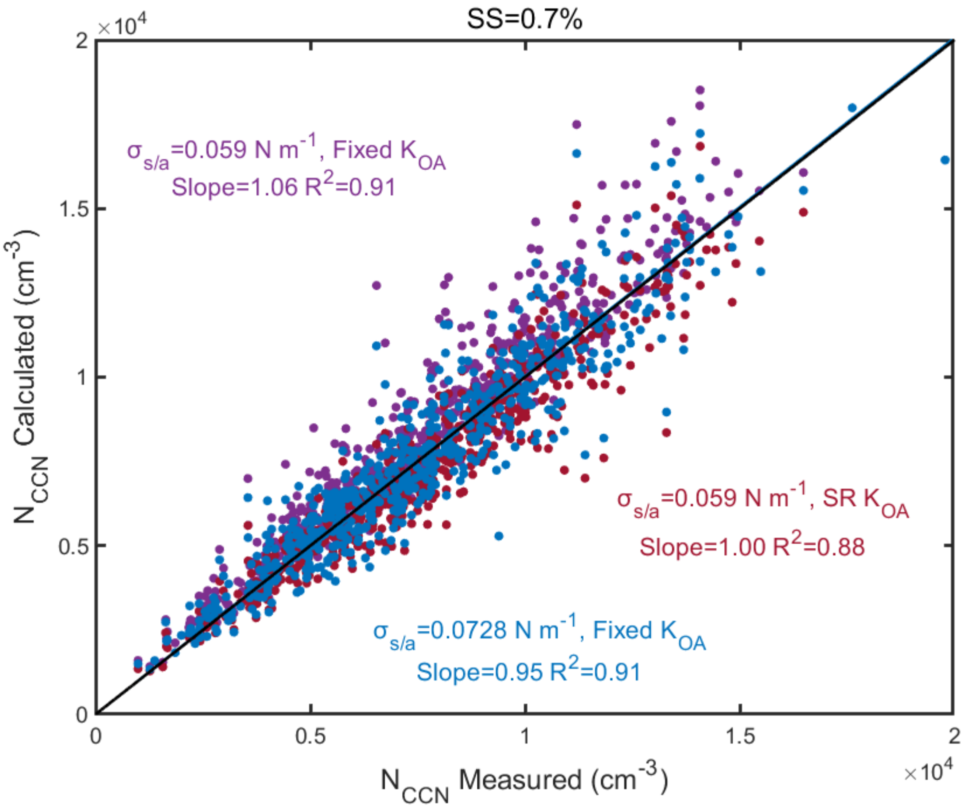

Figure S11. The predicted and measured N_{CCN} at 0.7% SS based on the $\sigma_{s/a}$ value (0.0728 N m^{-1}) for pure water and fixed κ_{OA} (blue dots), reduced $\sigma_{s/a}$ value (0.059 N m^{-1}) and fixed κ_{OA} (purple dots), and reduced $\sigma_{s/a}$ value (0.059 N m^{-1}) and SR κ_{OA} (red dots).

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5. Line 491: If there is a paper about the hygroscopicity of OA in the same study, please clarify the similarities and differences

Reply: We have modified the corresponding sentences in lines 512-515,

"For the same campaign, Kuang et al. (2021) reported the bulk κ_{OA} of PM_1 based on aerosol optical hygroscopicity measurements, which could provide high time resolution data of κ_{OA}. The relationship between κ_{OA} and different OA factors was investigated, which showed a negative correlation (R=-0.25) between LOOA and κ_{OA}, while a positive correlation (R=0.35) between aBBOA and κ_{OA}."

Reference:

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