Review of “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 Cai et al.

Cai et al. compile a report of findings of a comprehensive study of CCN activity for a measurement campaign in the Pearl River Delta (PRD) utilizing a complete suite of instruments to measure and understand the hygroscopicity and volatility from several differing methodologies. The work is of high quality and is complete and representative. I recommend it for publication with minor changes/corrections as listed below:

1. Line 82: “and plant” seems that some words are missing here, the intent of the sentence is unclear with the addition of plant.
Reply: We missed “wax” in this sentence. It has been revised to “… and plant wax…”.

2. Lines 87-90: Here in the summary of several previous works it isn’t mentioned where or under what conditions these varying hygroscopicities were reported.
Reply: We appreciate the reviewer for this valuable suggestion. These sentences in lines 87-91 have been revised to “Deng et al. (2018) reported a higher OA hygroscopicity ($\kappa_{OA}\approx0.22$) at about 150 nm than that ($\kappa_{OA}\approx0.19$) at sub-100 nm at a forest site. In contrast, Zhao et al. (2015) measured size-dependent hygroscopicity and chemical composition for SOA from various procedures and found that κ_{OA} of SOA from α-pinene photooxidation decreased from 0.17 at 50 nm to 0.07 at 200 nm, which was attributed to the higher oxidation degree for smaller particles.”

3. Line 174: I think that this is the line where PNSD needs to be defined, it is not defined anywhere in the paper.
Reply: It has been revised to “particle number size distribution (PNSD)”.

4. Line 226: Why not report R to one more digit at least? (8.314)
Reply: It has been revised to “…gas constant (8.314 J mol^{-1} K^{-1})”.

5. Line 228: meters not meter.
Reply: It has been revised to “meters”.

6. Line 249: Here you state the assumption relative to internally mixed particles, but the GF HTDMA data indicates that at the very least some of the mixture was externally mixed. What effect if any does this have on the analysis?
Reply: We thank the reviewer for this suggestion. We predicted the N_{CCN} using activation curve obtained by HTDMA measurement, which represented actual mixing states of the particles (Cai et al., 2018). We have modified the sentence in section 3.4 in line 578-579 and added a discussion in the supplement:
“The internal mixing assumption could slightly increase the predicted N_{CCN} by about 6-10% (Sect. S3).

Text in the supplement. Section S3 The impact of aerosol mixing state on the N_{CCN} prediction

The N_{CCN} prediction is affected by the assumed particle mixing state (Wang et al., 2010). We estimated the impact of the mixing state assumption on the N_{CCN} prediction by comparing the predicted N_{CCN} based on AMS and HTDMA measurements. For the prediction based on AMS measurement, the particles were assumed to be internally mixed. In the latter approach, the mixing state was considered. The hygroscopicity parameter $\kappa_{critical}$(Dp, SS) was defined as the point at which all particles could be activated at a specific diameter (Dp) and a specific SS. We calculated the $\kappa_{critical}$(Dp, SS) using eq. (4) for a measured diameter (Dp) and a known SS. Particles with a κ value higher than the $\kappa_{critical}$(Dp, SS) were activated. The activation ratio (AR_{HTDMA}(Dp, SS)) for a known diameter and SS was obtained by integrating the κ-PDF for $\kappa > \kappa_{critical}$(Dp, SS). Hence the predicted activation curve AR_p(Dp, SS) was determined by fitting the AR_{HTDMA}(Dp, SS) using eq. (6). Thus, the N_{CCN} can be calculated:

$$N_{CCN,p}(SS) = \int_0^{\infty} AR_p(Dp_i, SS) n_i dlogDp_i \tag{S3.1}$$

the detail of this approach could be found in Cai et al. (2018).

In general, the combination of the internal mixing assumption and fixed κ_{OA} scheme would lead to an overestimation of N_{CCN} (14%-23%, Fig. S3.1). Noting that adopting a fixed κ_{OA} value could also overpredict N_{CCN} (especially at high SS), which has been discussed in the text (section 3.4). This bias could be corrected by adopting SR κ_{OA} scheme, which showed that the N_{CCN} was overestimated by about 6%-10% (Fig. S3.1). Hence, we concluded that assuming the particle to be an internal mixture could lead to an overestimation of N_{CCN} by about 6%-10%.

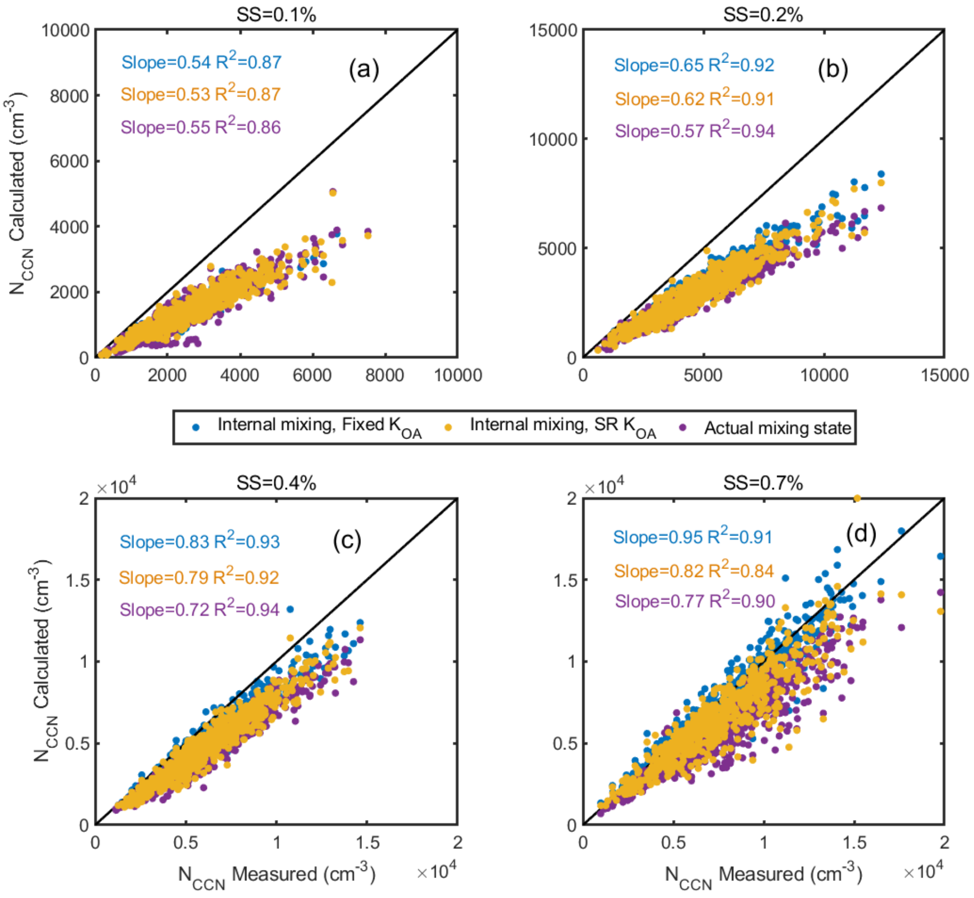

Figure S3.1. The predicted and measured N_{CCN} at 0.1%, 0.2%, 0.4%, and 0.7% SS based on internal mixing assumption (blue and yellow dots) and actual mixing state (purple dots). The fixed κ_{OA} scheme (blue dots) and SR κ_{OA} scheme (yellow dots) were adopted in the prediction based on the internal mixing assumption.”

7. Line 368: Hong Kong (two words).

Reply: It has been revised.

8. Line 376: Replace “It” with “This”.

Reply: It has been revised.

9. Line 411: replace organics with organic.

Reply: It has been revised.

10. Line 418: This paragraph appears to make an argument that CCN measurements report kappa values that would be considered incorrect. If this is used to measure actual CCN activity and predict them, wouldn’t a CCN instrument be the more appropriate measurement instead of an HTDMA, where the hygroscopicity of the HTDMA instrument would be the biased one? Understanding that

the kappa values are different, which is more appropriate for estimating modeled Nccn? (this is again brought up on line 560).

Reply: We appreciate the reviewer for this suggestion. The κ values can be obtained at sub- and super-saturated conditions. The discrepancy between κ_{CCN} and κ_{HTDMA} does not suggest that the κ_{CCN} or κ_{HTDMA} is incorrect. It rather implies that water uptake ability of particles could be different under sub- and super-saturated conditions. Noting that the discrepancy between κ_{HTDMA} and κ_{CCN} 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 CCNc measurement is the most accurate method in the CCN activity measurement and prediction. However, the long-term CCNc measurement is expensive and requires human effort. The availability of CCNc measurement in field campaigns is still limited. Alternatively, the combination of PNSD measurement and chemical composition or hygroscopicity measurement can provide the estimation of N_{CCN}. On the other hand, the estimation of N_{CCN} in the model is usually based on particle size distribution, composition, and supersaturation (Luo and Yu, 2011; Yu and Luo, 2009; Rastak et al., 2017; Abdul-Razzak and Ghan, 2002). The hygroscopicity of particles is calculated based on their chemical composition under sub-saturated conditions. However, the surfactant effect was found to increase the CCN activity relative to predictions derived for subsaturated condition, which would lead to uncertainty in the N_{CCN} and climate simulation. Using different methods in predicting N_{CCN} will help us to investigate this water uptake mechanism and improve the prediction of aerosol-cloud-climate interactions.

In order to avoid confusion, we have modified the sentences 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."

11. Line 602/603: This sentence needs to be reworked, it is unclear which statements and values correspond.

Reply: It has been revised to "For Aitken mode particles (30-100 nm), the κ_{OA} values reached minimal (0.02-0.07) during daytime. Meanwhile, a daytime peak was observed for the κ_{OA} value (~0.09) in the accumulation mode (150 and 200 nm), suggesting that the aging processes of preexisting particles were more dominant at accumulation mode particles."

12. Figure 4: In panel, A consider different colors (red/green color-blind issues).

Reply: We have revised the figure to improve the contrast as follows.

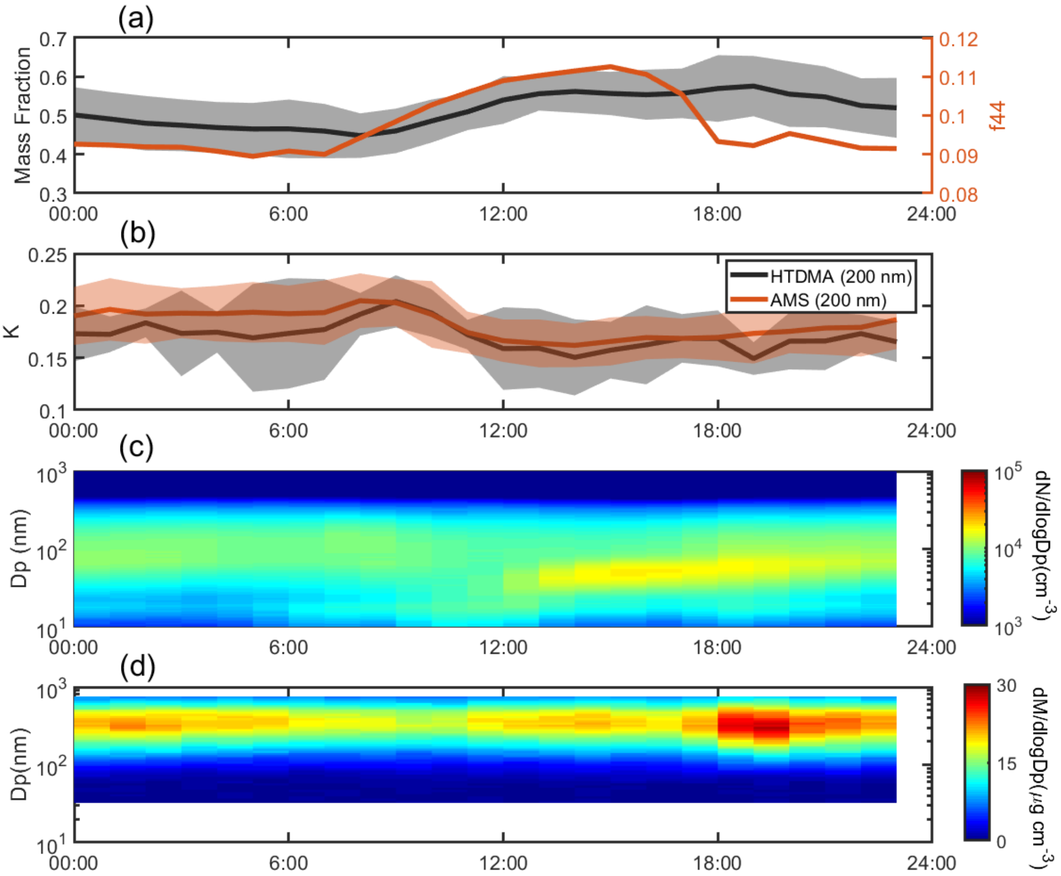

Figure 4. The campaign average diurnal variation of mass fraction of organics and f44 in bulk PM_1 (a), the κ values at 200 nm obtained by HTDMA (κ_{HTDMA}) and AMS (κ_{AMS}) measurements (b), the PNSD (c) and mass distribution of organics (d). The shaded area represents standard deviation.

Reference:

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