Supplement of

Measurement report: Distinct size dependence and diurnal variation in organic aerosol hygroscopicity, volatility, and cloud condensation nuclei activity at a rural site in the Pearl River Delta (PRD) region, China

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Section S1. Supersaturation calibration of the CCNc

Before and after the measurement, the CCNc was calibrated with ammonium sulfate ((NH₄)₂SO₄) particles. The critical supersaturation ($Sc$) was calculated by using Köhler theory:

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

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), $\rho_w$ 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 (NH₄)₂SO₄, $n_s = \frac{\pi \rho_s D_{50}^5}{6M_s}$, $D_{50}$ is the critical diameter, $\rho_s$ 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).
Section S2. Estimation of the uncertainty caused by the decomposition

During the heating process, ammonium sulfate \((\text{NH}_4)_2\text{SO}_4\) would decompose to ammonium bisulfate \((\text{NH}_4\text{HSO}_4)\) or triammonium hydrogen sulfate \((\text{NH}_3)_3\text{H(SO}_4)_2)\, and ammonia \((\text{NH}_3)\). 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 \((\text{NH}_4)_2\text{SO}_4\) would decompose to \((\text{NH}_4)_3\text{H(SO}_4)_2\) 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 \((\text{NH}_4)_2\text{SO}_4\) would decompose to \((\text{NH}_4)_3\text{H(SO}_4)_2\) and sublimation at 150°C, and all of EVLOA would decompose to SVOA at 100°C.

The results show that the decomposition of \((\text{NH}_4)_2\text{SO}_4\) plays a minor role in the simulation if the decomposition of organics was ignored (Case 1, Fig. S6). It is probably owing to the fact that \((\text{NH}_4)_2\text{SO}_4\) 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 \((\Delta H_{\text{vap}}=80 \text{ kJ mol}^{-1} \text{ and } \alpha=0.09)\). Thus, the results in case 2 and 3 are highly uncertain. In short summary, the decomposition of \((\text{NH}_4)_2\text{SO}_4\) 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.
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 \(\kappa\) 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 \(\kappa\)-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:

\[
N_{CCN,p}(SS) = \int_{0}^{\infty} AR_{p}(Dp, SS)n_idlogDp_i
\]

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

In general, the combination of the internal mixing assumption and fixed \(\kappa_{OA}\) scheme would lead to an overestimation of \(N_{CCN}\) (14%-23%, Fig. S11). Noting that adopting a fixed \(\kappa_{OA}\) 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 \(\kappa_{OA}\) scheme, which showed that the \(N_{CCN}\) was overestimated by about 6%-10% (Fig. S11). 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 S1. Schematic diagram of the experimental setup
Figure S2. The average mass distribution of each species measured by the AMS, along with bimodal lognormal fitted modes (grey dash line).
Figure S3. The transmission efficiency ($\eta$) of NaCl between DMA$_1$ and DMA$_2$ at different sizes and temperatures.
Figure S4. SSR values of different fitness of the campaign averaged MFR. The color code represents the value of SSR. The distribution of each species is solved based on different combinations of $\Delta H_{vap}$ of OA and $\alpha$. The $\Delta H_{vap}$ is assumed to be as a function of $C_i(T_{ref})$, $\Delta H_{vap} = -a \cdot \log_{10} C_i(T_{ref}) + b$, e.g., “0, 50” on the x axis suggests $a=0$ and $b=50$. A lower SSR suggests a better fit. The orange square represents the best fitting results.
Figure S5. Measured (blue lines) and modeled (red lines) campaign average MFRs at six measured diameters (30, 50, 80, 100, 150, and 200 nm). The error bar of measured MFRs represents \( \pm 1 \) standard deviation. \( \Delta H_{\text{vap}} = 80 \text{ kJ mol}^{-1} \) and \( \alpha = 0.09 \) are adopted in the simulation.
Figure S6. The mass fraction distribution of SVOA, LVOA, and ELVOA of the campaign averaged MFR based on different assumptions.
Figure S7. The average mass fraction of the size-resolved composition based on the lognormal fit (a) and measurement (b).
Figure S8. The mean and standard deviation values of $\kappa_{\text{CCN}}$, $\kappa_{\text{HTDMA}}$, and $\kappa_{\text{AMS}}$ during the campaign (a), clean (b) and pollute periods (c). The $\kappa$ values were pointed against their corresponding mean $D_{50}$ ($\kappa_{\text{CCN}}$) or selected diameter ($\kappa_{\text{HTDMA}}$ and $\kappa_{\text{AMS}}$). 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$_{2.5}$ ($< 30 \mu g m^{-3}$ and $> 60 \mu g m^{-3}$, respectively).
Figure S9. The campaign average size-resolved f44 with the upper and lower error bars.
Figure S10. $\kappa_{\text{CCN}}$ and $\kappa_{\text{HTDMA}}$ at different assumed $\sigma_{sa}$. $\kappa_{\text{HTDMA}}$ at 50, 80, 100 and 150 nm is adopted to compared with $\kappa_{\text{CCN}}$ at 0.7%, 0.9%, and 1.0% SS, 0.4% SS, 0.2% SS, and 0.1% SS, respectively. Red dot represents the intersection point of $\kappa_{\text{CCN}}$ and $\kappa_{\text{HTDMA}}$. 
Figure S11. 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 $\kappa_{OA}$ scheme (blue dots) and SR $\kappa_{OA}$ scheme (yellow dots) were adopted in the prediction based on the internal mixing assumption.
Figure S12. The measured and predicted $N_{\text{CCN}}$ at 0.1%, 0.2%, 0.4%, and 0.7% SS based on the $\sigma_{\text{s/a}}$ value (0.0728 N m$^{-1}$) for pure water (blue dots) and reduced $\sigma_{\text{s/a}}$ values (purple dots). The reduced $\sigma_{\text{s/a}}$ values were set to be 0.049 N m$^{-1}$ at 0.1% SS, 0.047 N m$^{-1}$ at 0.2% SS, 0.053 N m$^{-1}$ at 0.4% SS, and 0.059 N m$^{-1}$ at 0.7% SS, respectively. The $N_{\text{CCN}}$ at four SS was predicted based on fixed $\kappa_{\text{OA}}$ scheme.
Figure S13. The predicted and measured $N_{\text{CCN}}$ at 0.7% SS based on the $\sigma_{s/a}$ value (0.0728 N m$^{-1}$) for pure water and fixed $\kappa_{\text{OA}}$ (blue dots), reduced $\sigma_{s/a}$ value (0.059 N m$^{-1}$) and fixed $\kappa_{\text{OA}}$ (purple dots), and reduced $\sigma_{s/a}$ value (0.059 N m$^{-1}$) and SR $\kappa_{\text{OA}}$ (red dots).
Reference:

