Supplementary Information:

1. Measurement sequence

Figure S1. An example of measurement sequences for (a) the CCN counter temperature gradient for total CCN concentration measurements, (b) the CCN counter temperature gradient and (c) the particle size classified by DMA for the size resolved CCN measurements.

2. Derivation of particle hygroscopicity and mixing state

The activated fractions measured at the six supersaturations were fitted using following two different functions (Mei et al., 2012):
\[
R_a(S) = \frac{E}{2} \left( 1 + \text{erf} \left( \frac{\ln S - \ln S^*}{\sqrt{2} \sigma^2_S} \right) \right) 
\]
(S1)

and (Lance, 2007; Bougiatioti et al., 2011; Cerully et al., 2011; Lance et al., 2012; Padro et al., 2012):

\[
R_a(S) = \frac{E}{1 + \left( \frac{S}{S^*} \right)^C} 
\]
(S2)

The fitting parameters are \(E, S^*, \) and \(\sigma_S\) for Eqn. (S1) and \(E, S^*, \) and \(C\) for Eqn. (S2), where \(\sigma_S\) and \(C\) are related to the slope of the increasing \(R_a\) with \(S\) near \(S^*\). For each set of measurements, the function form that yielded the best fit (i.e. smaller least squares residue) was used for subsequent analysis.

For particles with the same size and composition (i.e., hygroscopicity), we would expect a step function for \(R_a\) as all particles would have the identical \(S_c\). Ambient aerosols show much more gradual increase in \(R_a\) (i.e., instead of a step change), suggesting heterogeneity in particle \(S_c\). The probability density function (PDF) of the critical supersaturation for size selected particles, \(p(S_c)\) is given by differentiating \(R_a(S_c)\) with respect to \(S_c\):

\[
p(S_c) = \frac{1}{E} \cdot \frac{dR_a(S_c)}{dS_c} 
\]
(S3)

The dispersion in \(S_c\) is defined as \(\sigma(S_c)/\overline{S_c}\), where \(\overline{S_c}\) is the average particle critical supersaturation:

\[
\overline{S_c} = \int_0^\infty p(S_c) \cdot S_c \cdot dS_c 
\]
(S4)
\[ \sigma^2(S_d) = \int_0^\infty \left( S_d - \overline{S_d} \right)^2 p(S_d) dS_d \]  
(S5)

When \( R_a(S) \) is fitted using Eqn. (S1), the hygroscopicity dispersion is:

\[ \frac{\sigma(S_d)}{S_d} = \left[ e^{\sigma^2} - 1 \right]^{1/2} \]  
(S6)

and for Eqn (S2), the dispersion is given by:

\[ \frac{\sigma(S_d)}{S_d} = \left[ \frac{\Gamma \left( \frac{2}{C} + 1 \right) \cdot \Gamma(1 - 2/C)}{\Gamma(2)} \right] \cdot \left[ \frac{\Gamma \left( \frac{1}{C} + 1 \right) \cdot \Gamma(1 - 1/C)}{\Gamma(2)} \right]^{2} - 1 \]  
(S7)

The dispersion in \( S_c \) is due to the combination of the width of DMA transfer function (particles classified by DMA do not have exactly the identical size) and the heterogeneity in particle composition (i.e., hygroscopicity), and can be expressed as (Lance et al., 2012):

\[ \left( \frac{\sigma(S_c)}{S_c} \right)^2 = \frac{9}{4} \left( \frac{\sigma(D_p)}{D_p} \right)^2 + \frac{1}{4} \left( \frac{\sigma(\kappa)}{\kappa} \right)^2 \]  
(S8)

Where the first term on the RHS of the equation represents the contribution due to the width of DMA transfer function, which was estimated from the dispersion in \( S_c \) measured during calibration using (NH4)2SO4 particles (i.e., the contribution of the second term was essentially zero during calibrations). The dispersion in hygroscopicity for classified ambient particles was then derived by subtracting the contribution of DMA transfer function from the total dispersion in measured critical supersaturation.
3. Uncertainty in derived $\kappa_{\text{org}}$

The hygroscopicity of organic component can be derived from the CCN hygroscopicity as (Eq. 5 in the main text):

$$\kappa_{\text{org}} = \frac{1}{x_{\text{org}}} \left( \kappa_{\text{CCN}} - \kappa_{\text{NH}_4\text{NO}_3} x_{\text{NH}_4\text{NO}_3} - \kappa_{\text{(NH}_4\text{)}_2\text{SO}_4} x_{\text{(NH}_4\text{)}_2\text{SO}_4} \right) \quad (S9)$$

Given the similar hygroscopicities for (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$, we will combine both species and refer to as the inorganic component of the CCN. The hygroscopicity and volume fraction of the inorganic component are given by:

$$\kappa_{\text{inorg}} = \frac{\kappa_{\text{NH}_4\text{NO}_3} x_{\text{NH}_4\text{NO}_3} + \kappa_{\text{(NH}_4\text{)}_2\text{SO}_4} x_{\text{(NH}_4\text{)}_2\text{SO}_4}}{x_{\text{NH}_4\text{NO}_3} + x_{\text{(NH}_4\text{)}_2\text{SO}_4}} \quad (S10)$$

$$x_{\text{inorg}} = x_{\text{NH}_4\text{NO}_3} + x_{\text{(NH}_4\text{)}_2\text{SO}_4} \quad (S11)$$

Because (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ have very similar $\kappa$ values (0.67 and 0.61, respectively), for the derivation of the uncertainty in $\kappa_{\text{org}}$, a constant value of 0.64 was used for $\kappa_{\text{inorg}}$. Combining Eqn. (S9-S11) we have:

$$\kappa_{\text{org}} = \frac{1}{x_{\text{org}}} \left( \kappa_{\text{CCN}} - \kappa_{\text{inorg}} \cdot x_{\text{inorg}} \right) \quad (S12)$$

The total volume concentration at the classified size is calculated as:

$$v_{\text{total}} = v_{\text{org}} + v_{\text{inorg}} \quad (S13)$$

where $v_i$ is the volume concentration of species $i$. The volume fractions of organics and inorganics are given by:
\[ x_{\text{org}} = \frac{v_{\text{org}}}{v_{\text{total}}} = \frac{v_{\text{org}}}{v_{\text{org}} + v_{\text{inorg}}}, \]  
\[ x_{\text{inorg}} = 1 - x_{\text{org}} = \frac{v_{\text{inorg}}}{v_{\text{total}}} = \frac{v_{\text{inorg}}}{v_{\text{org}} + v_{\text{inorg}}}, \]  
\[ (S14) \]

2. Inserting Eq. (S14) into Eq. (S12), we can write the uncertainty in derived \( \kappa_{\text{org}} \) as:

\[ \sigma_{\kappa_{\text{org}}}^2 = \left( \frac{\partial \kappa_{\text{org}}}{\partial \kappa_{\text{CCN}}} \right)^2 \sigma_{\kappa_{\text{CCN}}}^2 + \left( \frac{\partial \kappa_{\text{org}}}{\partial v_{\text{org}}} \right)^2 \sigma_{v_{\text{org}}}^2 + \left( \frac{\partial \kappa_{\text{org}}}{\partial v_{\text{inorg}}} \right)^2 \sigma_{v_{\text{inorg}}}^2, \]
\[ (S15) \]

where

\[ \frac{\partial \kappa_{\text{org}}}{\partial \kappa_{\text{CCN}}} = \frac{1}{x_{\text{org}}} \]
\[ \frac{\partial \kappa_{\text{org}}}{\partial v_{\text{org}}} = \frac{\kappa_{\text{CCN}} - \kappa_{\text{org}}}{v_{\text{org}}} \]
\[ \frac{\partial \kappa_{\text{org}}}{\partial v_{\text{inorg}}} = \frac{(\kappa_{\text{CCN}} - \kappa_{\text{inorg}})}{v_{\text{org}}} = \frac{(K_{\text{CCN}} - K_{\text{inorg}}) x_{\text{inorg}}}{v_{\text{inorg}}}, \]
\[ (S16) \]

5. Substituting Eq. (S16) into (S15) gives:

\[ \sigma_{\kappa_{\text{org}}}^2 = \left( \frac{\kappa_{\text{CCN}}}{x_{\text{org}}} \right)^2 \left( \frac{\sigma_{\kappa_{\text{CCN}}}}{\kappa_{\text{CCN}}} \right)^2 + \left( \frac{\kappa_{\text{CCN}} - \kappa_{\text{org}}}{v_{\text{org}}} \right)^2 \left( \frac{\sigma_{v_{\text{org}}}}{v_{\text{org}}} \right)^2 + \left( \frac{\kappa_{\text{CCN}} - \kappa_{\text{inorg}}}{x_{\text{org}}} \right)^2 \left( \frac{\sigma_{v_{\text{inorg}}}}{v_{\text{inorg}}} \right)^2, \]
\[ (S17) \]

6. From Eqn. (S12), we have:

\[ \kappa_{\text{CCN}} - \kappa_{\text{org}} = \kappa_{\text{inorg}} x_{\text{inorg}} + \kappa_{\text{org}} x_{\text{org}} - \kappa_{\text{org}} = \kappa_{\text{inorg}} x_{\text{inorg}} - \kappa_{\text{org}} (1 - x_{\text{org}}) = \kappa_{\text{inorg}} x_{\text{inorg}} - \kappa_{\text{org}} x_{\text{inorg}} = (\kappa_{\text{inorg}} - \kappa_{\text{org}}) x_{\text{inorg}}, \]
\[ (S18) \]

7. Similarly we have:
\[ \kappa_{CCN} - \kappa_{inorg} = \kappa_{org} x_{org} - \kappa_{inorg} \left(1 - x_{inorg}\right) \]
\[ = \kappa_{org} x_{org} - \kappa_{inorg} x_{org} \]
\[ = - \left(\kappa_{inorg} - \kappa_{org}\right) x_{org} \]  
(S19)

Equation (S17) can be simplified by inserting Eqn (S18) and (S19):

\[ \sigma_{\kappa_{org}}^2 = \left(\frac{\kappa_{CCN}}{x_{org}}\right)^2 \left(\frac{\sigma_{\kappa_{CCN}}}{\kappa_{CCN}}\right)^2 + \left(\kappa_{inorg} - \kappa_{org}\right)^2 \left(\frac{\sigma_{x_{inorg}}}{x_{inorg}}\right)^2 + \left(\kappa_{inorg} - \kappa_{org}\right)^2 \left(\frac{\sigma_{\kappa_{inorg}}}{\kappa_{inorg}}\right)^2 \]
\[ = \left(\frac{\kappa_{CCN}}{x_{org}}\right)^2 \left(\frac{\sigma_{\kappa_{CCN}}}{\kappa_{CCN}}\right)^2 + \left(\kappa_{inorg} - \kappa_{org}\right)^2 \left(\frac{\sigma_{x_{inorg}}}{x_{inorg}}\right)^2 + \left(\kappa_{inorg} - \kappa_{org}\right)^2 \left(\frac{\sigma_{\kappa_{inorg}}}{\kappa_{inorg}}\right)^2 \]  
(S20)

The first term on the right hand side of Eqn. (S20) is associated with the uncertainty in derived \( \kappa_{CCN} \). Based on Eq. (4) in the main text, the uncertainty in \( \kappa_{CCN} \) is given by:

\[ \sigma_{\kappa_{CCN}}^2 = \left(\frac{\partial \kappa_{CCN}}{\partial D_p}\right)^2 \sigma_{D_p}^2 + \left(\frac{\partial \kappa_{CCN}}{\partial S^*}\right)^2 \left(\sigma_{S^*}^\ast\right)^2 \]
\[ = \left(\frac{3\kappa_{CCN}}{D_p}\right)^2 \sigma_{D_p}^2 + \left(\frac{2\kappa_{CCN}}{S^*}\right)^2 \left(\sigma_{S^*}^\ast\right)^2 \]  
(S21)

Therefore we can write the relative uncertainty in \( \kappa_{CCN} \) as:

\[ \left(\frac{\sigma_{\kappa_{CCN}}}{\kappa_{CCN}}\right)^2 = 9 \left(\frac{\sigma_{D_p}}{D_p}\right)^2 + 4 \left(\frac{\sigma_{S^*}}{S^*}\right)^2 \]  
(S22)

\( \frac{\sigma_{D_p}}{D_p} \) represents the accuracy of the dry size of particles classified by the DMA, which is mainly determined by the accuracy of DMA sheath flow rate and classifying voltage, and is typically less than 2% (Wang et al., 2003). As \( S^* \) was derived from data collected during periods ranging from 7.6 to 14 hours, the uncertainty of \( S^* \) can be attributed to the accuracy in instrument
supersaturation (i.e., uncertainty in calibrated instrument supersaturation), counting statistics, and the potential variation due to minor changes in particle composition during the periods. The uncertainty in calibrated instrument supersaturation was estimated from the uncertainty of the dry size of pure ammonium sulfate particles classified by DMA during calibration and the standard deviation of the repeated calibrations performed before and after the field study, and this uncertainty was generally less than 2% (relative uncertainty). The uncertainty due to counting statistics and potential variations in particle composition during the periods combined was estimated from the standard error (standard deviation divided by the square root of the sample number) of $S^*$ derived from multiple measurements during the periods, and ranged from 2% to 5%, which dominated the uncertainty in derived $S^*$ and the overall uncertainty in $\kappa_{CCN}$. The overall uncertainty in derived $\kappa_{CCN}$ ranged from 5% to 12%.

The second term on the right hand side of Eqn. (S20) represents contributions due to the uncertainties in volume fractions of organics and inorganics (i.e. particle composition). The volume fractions were derived from the average mass concentrations measured during the periods, and densities of the species. For sulfate and nitrate, the uncertainty in their densities should be negligible. The organic density estimated from O:C (ranged from 0.29 to 0.46) and H:C (ranged from 1.49 to 1.28) ratios ranged from 1150 to 1350 kg m$^{-3}$ (Kuwata et al., 2012). The assumed organic density of 1250 kg m$^{-3}$ represented an uncertainty less than 8%, which was significantly smaller than the uncertainty in measured organics mass concentration. As shown later, only periods that showed minimum variation in particle composition were selected for the analysis, therefore, the minor variation of particle composition during these periods was neglected, and the uncertainty in volume fractions for these periods were estimated from the uncertainty of mass concentration measurements measured by AMS. The uncertainties in mass
concentrations measured by AMS were generally ~30% (Middlebrook et al., 2012). However, it is worth noting that not all uncertainties in measured mass concentrations translate into uncertainty in derived species volume fractions. For example, one major uncertainty in mass concentrations measured by AMS originates from the uncertainty in collection efficiency (i.e., particle bounce). However, for internally mixed particles observed at T1 site, the collection efficiency influenced measured mass concentrations of both non-refractory inorganic and organic components to the same degree, and therefore had little impact on the derived volume fractions of the components. For the purpose of estimating uncertainty in species volume fraction, an uncertainty of 10% was estimated for measured inorganics and organics mass concentrations, which were mainly due to the uncertainties in relative ionization efficiencies.

References


Lance, S.: Quantifying compositional impacts of ambient aerosol on cloud droplet formation, Ph.D., Georgia Institute of Technology, Atlanta, 2007.


