Supplementary Information for

CCN activity of organic aerosols observed downwind of urban emissions during CARES

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1. Measurement sequence

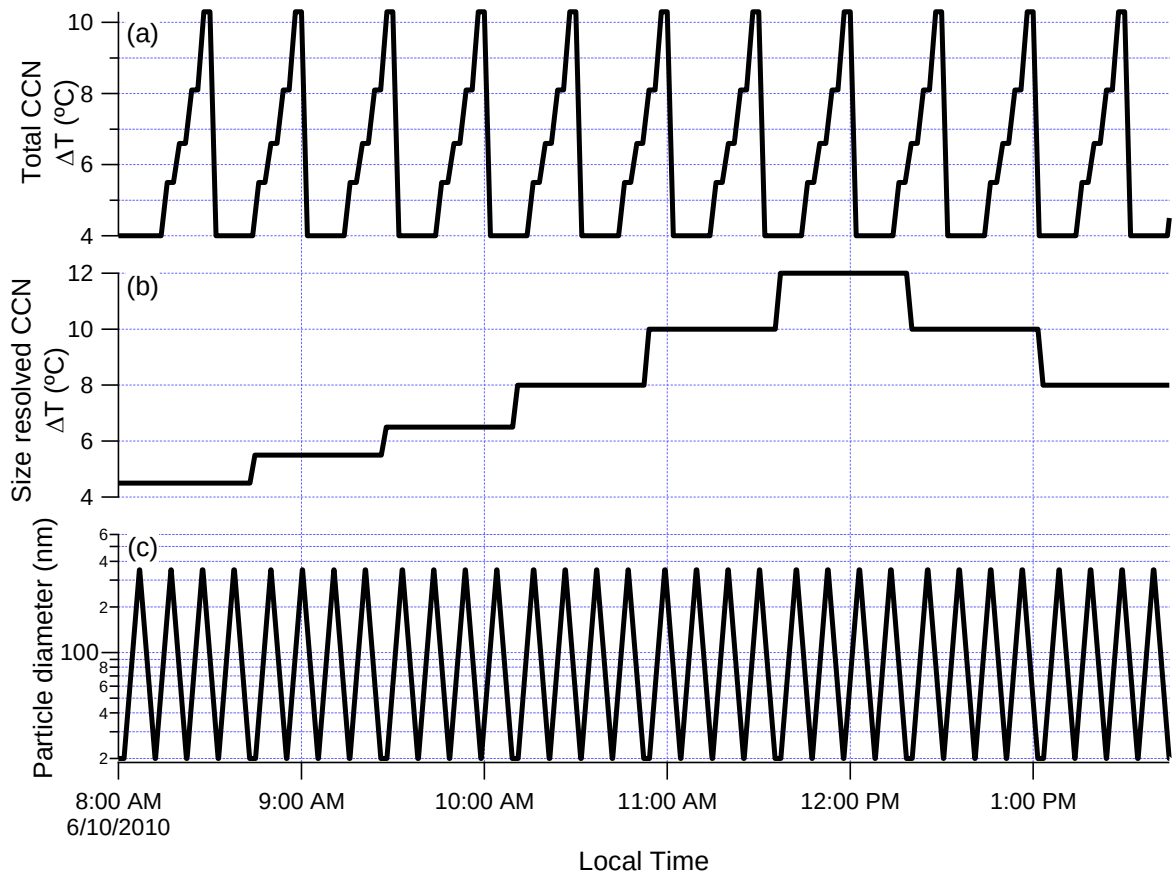

Figure S1. An example of measurement sequences for (a) the CCN counter temperature gradient for total CCN concentration measurements, (b) the CCN counter temperature gradient and (c) the particle size classified by DMA for the size resolved CCN measurements.

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., 2013):

$$R_a(S) = \frac{E}{2} \cdot \left(1 + erf\left(\frac{\ln S - \ln S^*}{\sqrt{2\sigma_S{}^2}}\right)\right) \quad \text{(S1)}$$

and (Lance, 2007;Cerully et al., 2011;Bougiatioti et al., 2011;Padro et al., 2012;Lance et al., 2013):

$$R_a(S) = \frac{E}{1+\left(\frac{S}{S^*}\right)^C} \quad \text{(S2)}$$

The fitting parameters are E, S^*, and σ_S for Eqn. (S1) and E, S^*, and C for Eqn. (S2), where σ_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:

$$p(S_c) = \frac{1}{E} \cdot \frac{dR_a(S_c)}{dS_c} \quad \text{(S3)}$$

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

$$\overline{S_c} = \int_0^\infty p(S_c) \cdot S_c \cdot dS_c \quad \text{(S4)}$$

and

$$\sigma^2(S_c) = \int_0^\infty \left(S_c - \overline{S_c}\right)^2 p(S_c) dS_c \quad \text{(S5)}$$

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

$$\frac{\sigma(S_c)}{\overline{S_c}} = \left[e^{\sigma_S^2} - 1 \right]^{1/2} \tag{S6}$$

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

$$\frac{\sigma(S_c)}{\overline{S_c}} = \left[\frac{\Gamma\left(\frac{2}{C}+1\right)\cdot\Gamma(1-2/C)}{\Gamma(2)} \Bigg/ \left(\frac{\Gamma\left(\frac{1}{C}+1\right)\cdot\Gamma(1-1/C)}{\Gamma(2)} \right)^2 - 1 \right]^{1/2} \tag{S7}$$

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., 2013):

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

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 $(NH_4)_2SO_4$ 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.

References

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