<u>**Supplemental information**</u>

<u>**for**</u>

"Direct links between hygroscopicity and mixing state of ambient aerosols: Estimating particle hygroscopicity from their single particle mass spectra"

1. Particle numbers detected by ATOFMS and concurrent CPC number concentrations during the HTDMA-ATOFMS characterization.

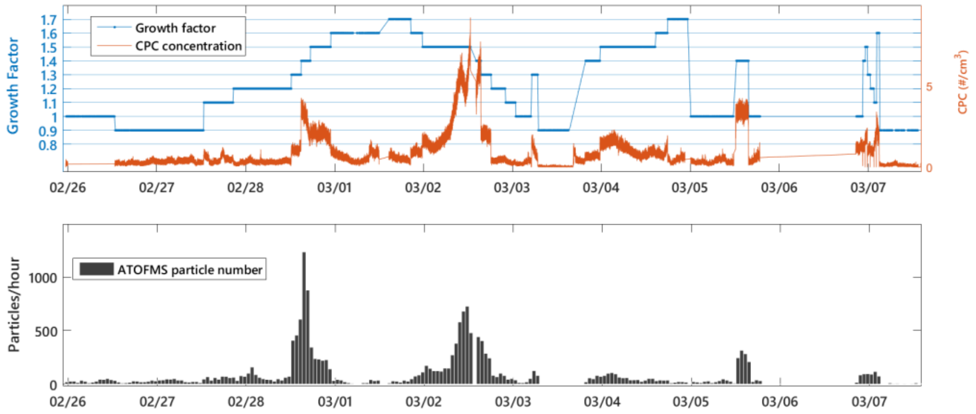

Figure S1. Particle number concentrations in the outflow of HTDMA as measured by CPC and the prescribed GFs in HTDMA-ATOFMS characterization (upper). The concurrent ATOFMS particle numbers (hour resolution) are shown in the lower panel.

2. Peak intensity variations of EC particles as a function of GF

The nitrate and sulfate were internally mixed in most of the EC particles. Secondary nitrate and sulfate are the major contributor to the hygroscopic growth due to their high hydrophilicity [1, 2]. The signal intensities of nitrate, sulfate and ammonium in EC particle spectra are summarized in Figure S2. Noted that ATOFMS is not a quantitative method and the area of mass peaks cannot be used directly to infer chemical quantity in single particles. However the variations of peak intensities based on statistics of many particles can be used to demonstrate their relative trends [3-5]. In Figure S2 we present secondary peak intensities of nitrate (-62 NO_3^-), sulfate (-97 SO_4^-), ammonium (+18 NH_4^+) and EC related peaks of -24C_2^- -25C_2H^-, -36C_3^- as a function of hygroscopicity. As shown in the figure, nitrate intensity increases within the GF <1.2 range, and then a roughly stable level was reached in the GF>1.2 range (MH mode). This feature is also present in sulfate and ammonium peaks. The signal intensity trends demonstrate the aging process of fresh EC particles with the formation of secondary nitrate, sulfate and ammonium. The signal intensity trends obtained here are comparable with the previous study, although some differences were noticed [6, 7]. Herich et al. similarly found the nitrate intensity increased with GF in GF <1.3 range before a plateau was reached [6]. However, in that study the sulfate intensity did not show clear trend with GF, which is not consistent with the present data. The aging process of EC particles is indicated by the intensity variations of other peaks in the negative spectra. As shown in the right panels in Figure S2, the negative peaks at -24C_2^- -25C_2H^-, -36C_3^-, which are stronger in spectra of fresh EC particles [8], gradually decrease as the GF increase, suggesting their potential application to indicate the degree of aging of EC particles.

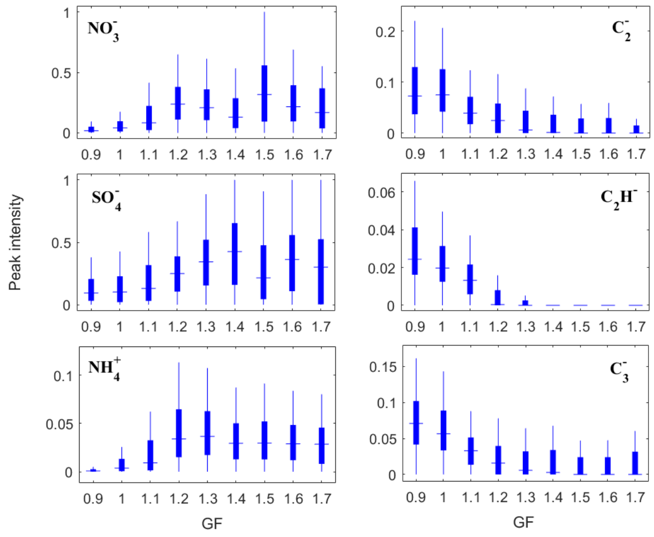

Figure S2. Statistics of relevant peak intensities in EC particle spectra as a function of GF. The statistics from bottom to top for each GF: minimum, 25th percentile, median, 75th percentile, maximum.

3. Hygroscopic pattern of Al-Si particles

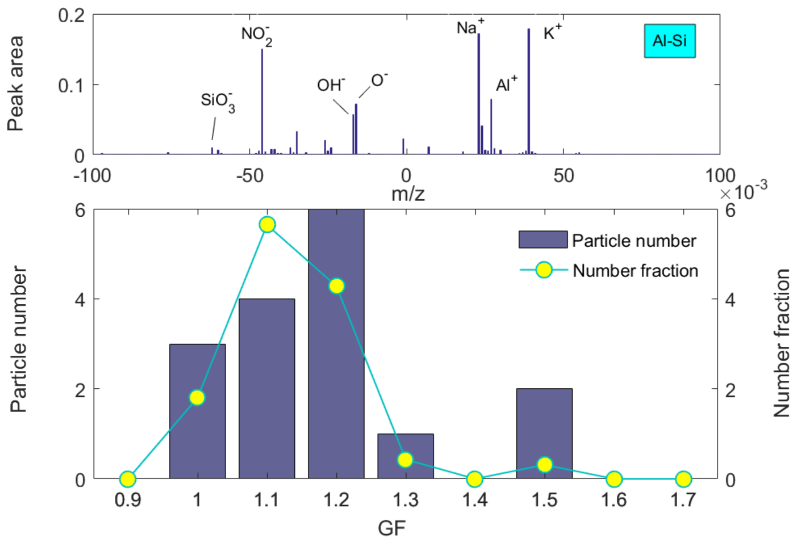

Figure S3. Average mass spectra and hygroscopicity distribution of Al-Si particles.

4. Average mass spectra of GF=1.6 mode particles.

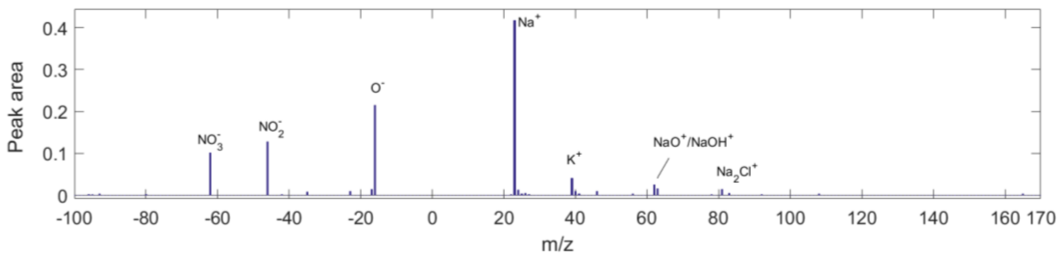

Figure S4. The average mass spectra of particles in GF 1.6 mode

5. Comparison of atmospheric visibility at Hongqiao and Pudong airport in Shanghai.

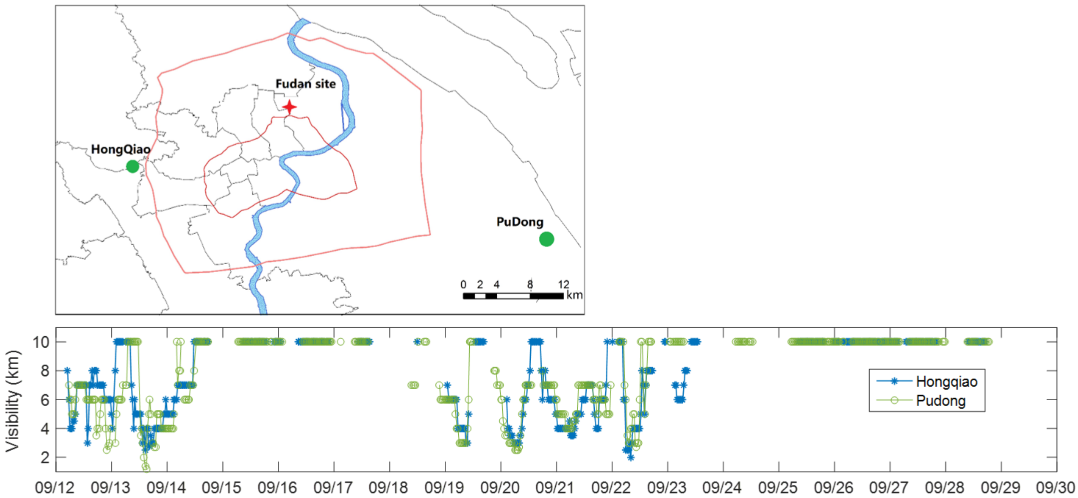

Figure S5. Temporal variations of visibility at Hongqiao and Pudong airport from Sep-12 to Sep-28,2012. The map shows the positions of Hongqiao, Pudong airport and the Fudan site.

References

1. Gysel, M., et al., Closure study between chemical composition and hygroscopic growth of aerosol particles during TORCH2. Atmospheric Chemistry and Physics, 2007. 7(24): p. 6131-6144.
2. Aggarwal, S.G., et al., Chemical closure study on hygroscopic properties of urban aerosol particles in Sapporo, Japan. Environmental Science & Technology, 2007. 41(20): p. 6920-6925.
3. Gross, D.S., et al., Relative sensitivity factors for alkali metal and ammonium cations in single particle aerosol time-of-flight mass spectra. Analytical Chemistry, 2000. 72(2): p. 416-422.
4. Hatch, L.E., et al., Impacts of Aerosol Aging on Laser Desorption/Ionization in Single-Particle Mass Spectrometers. Aerosol Science and Technology, 2014. 48(10): p. 1050-1058.
5. Pratt, K.A., L.E. Hatch, and K.A. Prather, Seasonal Volatility Dependence of Ambient Particle Phase Amines. Environmental Science & Technology, 2009. 43(14): p. 5276-5281.
6. Herich, H., et al., In situ determination of atmospheric aerosol composition as a function of hygroscopic growth. Journal of Geophysical Research-Atmospheres, 2008. 113(D16).
7. Wang, X.N., et al., Online hygroscopicity and chemical measurement of urban aerosol in Shanghai, China. Atmospheric Environment, 2014. 95: p. 318-326.
8. Suess, D.T., Single particle mass spectrometry combustion source characterization and atmospheric apportionment of vehicular, coal and biofuel exhaust emissions, 2002, University of California, Riverside: United States -- California. p. 377-377 p.