Supplementary materials:

A case study of the highly time-resolved evolution of aerosol chemical and optical properties in urban Shanghai, China

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1. Size distributions of different particle types

Biomass burning particles have been shown to have significant signals at *m*/*z* +23 (Na^+) and +39 (K^+/$C_3H_3^+$) in the positive spectra and *m*/*z* -26 (CN^-) in the negative spectra. As shown in Fig. 2a, a 0.12 μm difference (0.28 versus 0.40 μm) was observed between the maxima of the size distributions of fresh and aged biomass burning groups, which is consistent with previous studies (Reid et al., 2005). Note that in the larger size range (>0.8 μm), aged biomass burning aerosols still make up 15% of particles observed with the ATOFMS. Characterized by peaks of *m*/*z* +18 (NH_4^+), +27 ($C_2H_3^+$), +39 (K^+/$C_3H_3^+$) and +43 ($C_2H_3O^+$) in the positive spectra, organic carbon (OC) particles account for 26.6% of all particles. A peak gap (about 0.1 μm) exists between the maximum of the size distribution of fresh and aged OC types, with the peak of fresh OC type at a smaller diameter of 0.48 μm. Elemental Carbon/Organic Carbon (ECOC) particles have mass spectra containing a mixture of carbon clusters (C_n^+) and major OC peaks, and account for 8.7% of particles observed. Both fresh and aged ECOC groups have secondary markers of (NH_4^+) and ($C_2H_3O^+$). The size distribution of ECOC is bimodal. For the fresh ECOC type, the mode with higher number concentration is centered around 0.28 μm and the other is around 0.64 μm. It is the same situation for the aged type, however, the larger size mode is higher compared to the fresh (Fig.2, 0.32 and 0.68 μm, respectively). The mass spectral pattern of the ammonium group has a significant ion peak of *m*/*z* +18 (NH_4^+) in the positive spectra. Other peaks include OC fragments of *m*/*z* +27 ($C_2H_3^+$), +39 (K^+/$C_3H_3^+$), +43 ($C_2H_3O^+$) in positive spectra and -46 (NO_2^-), -62 (NO_3^-), -97 (HSO_4^-), and -125 ($H(NO_3)_2^-$) in negative spectra. The size distribution of the number fraction of the ammonium type increases with the diameter.

Other groups including EC, dust, metal-containing, and Na-K-rich groups are named after their mass spectral features, and together they account for 15.9% of all observed particles. EC particles are characterized by clusters of carbon ($C_n^{+/-}$), mainly distributed in the small size range (making up ~50% of all particle groups with diameter smaller than 0.24 μm). The particles with signals from *m*/*z* +40 (Ca^+), +57 ($CaOH^+$), -60 (SiO_2^-), -76 (SiO_3^-), and -79 (PO_3^-) were classified

as dust. They are also mixed with Na, K, nitrate and sulfate. Most dust particles have diameters of 0.8 - 1.2 μm. Particles containing typical metal elements, e.g. Na, Mg, Al, K, V, Mn, Fe, and Pb, combine to make up the metal-containing group. The Na-K-rich type has strong intensities of Na and K in the positive spectra. Metal-containing and Na-K-rich particles all have nitrate and the the nitrate cluster in the negative spectra. Most particles in these two groups have diameters larger than 0.6 μm.

2. Discussion of sulfate-, nitrate-, and ammonium- containing particle fractions

Fig. S5 shows the size distributions of the number fraction of sulfate-, nitrate- and ammonium- containing particles sampled with the ATOFMS in the three time periods. The particles were filtered by the relative intensity of each marker using a threshold (relative peak areas greater than 0.1, 0.1, and 0.05, respectively). Note that all particles containing peaks due to ammonium are included here, even if they are assigned to other particle types. Sulfate particles were typically found in the size range of 0.4 - 0.6 μm (about 80%). The increased sulfate in Period 1 likely results from the high number fraction of EC particles, as discussed in the main document. The number fraction of nitrate- containing particles stayed nearly constant at around 80% for particles with size larger than 0.4 μm. This indicates that about 60-80% of particles incorporated more nitrite as they grew. The number fraction of ammonium-containing particles also increased as the diameter grew, and the maximum number fraction got as high as 55% around 1.2 μm in Period 2.

The size distribution trends of sulfate, nitrate, and ammonium were nearly the same in the three time periods. However, the nitrate- containing number fraction was almost 20% larger in Period 2 than in Periods 1 and 3 for particles larger than 0.4 μm. In addition, ammonium- and sulfate- containing number fractions exceeded nearly 30% and 20% in the size range of 0.8 - 1.2 μm. Periods 1 and 3 shared fairly similar size distributions of number fraction in the three periods. The shift of number fraction between different time periods could also be due to the influence of regional transport on local aerosol chemical properties. The higher fraction of nitrate and ammonium in Period 2 supports the suggestion of an input of NO_x and ammonia. Ammonia prefers partitioning from the gas phase to the particle phase when RH is high. High RH during Period 2 (average RH ~83%, see Fig. S1) promoted the partitioning of ammonia into the particles. The enhancement of particulate ammonium attracts more acid into the particle phase. To neutralize ammonium, sulfuric acid first gets exhausted. Then more nitrate acid partitions into the particle to neutralize the excess ammonium. So in the second period both the sulfate- and nitrate-containing particle number fraction was greater than in the other two periods, especially in the large size range.

References:

Reid, J. S., Koppmann, R., Eck, T. F., and Eleuterio, D. P.: A review of biomass burning emissions part II: intensive physical properties of biomass burning particles, Atmos. Chem. Phys., 5, 799-825, doi:10.5194/acp-5-799-2005, 2005.

Spencer, M. T., and Prather, K. A.: Using ATOFMS to determine OC/EC mass fractions in particles, Aerosol Sci. Tech., 40, 585-594, doi:10.1080/02786820600729138, 2006.

Table S1. Results of linear regression of the scattering, absorption, and extinction coefficients versus PM_1 mass loading in the four sub-periods.

Time Period	Scattering		Absorption		Extinction	
	Slope	R^2	Slope	R^2	Slope	R^2
Period 1a	1.41	0.86	0.63	0.85	2.04	0.90
Period 2a	4.31	0.93	0.86	0.95	5.17	0.94
Period 2b	1.54	0.88	0.76	0.82	2.29	0.88
Period 3a	2.80	0.77	2.07	0.91	4.87	0.93

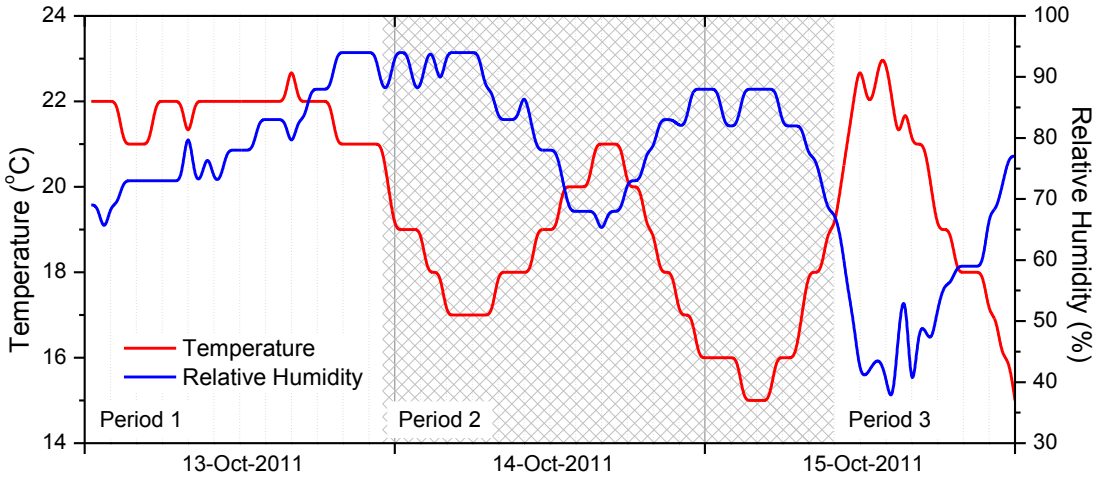

Figure S1. Temporal variation of temperature and RH over Oct 13-15, 2011 with 30-minute resolution.

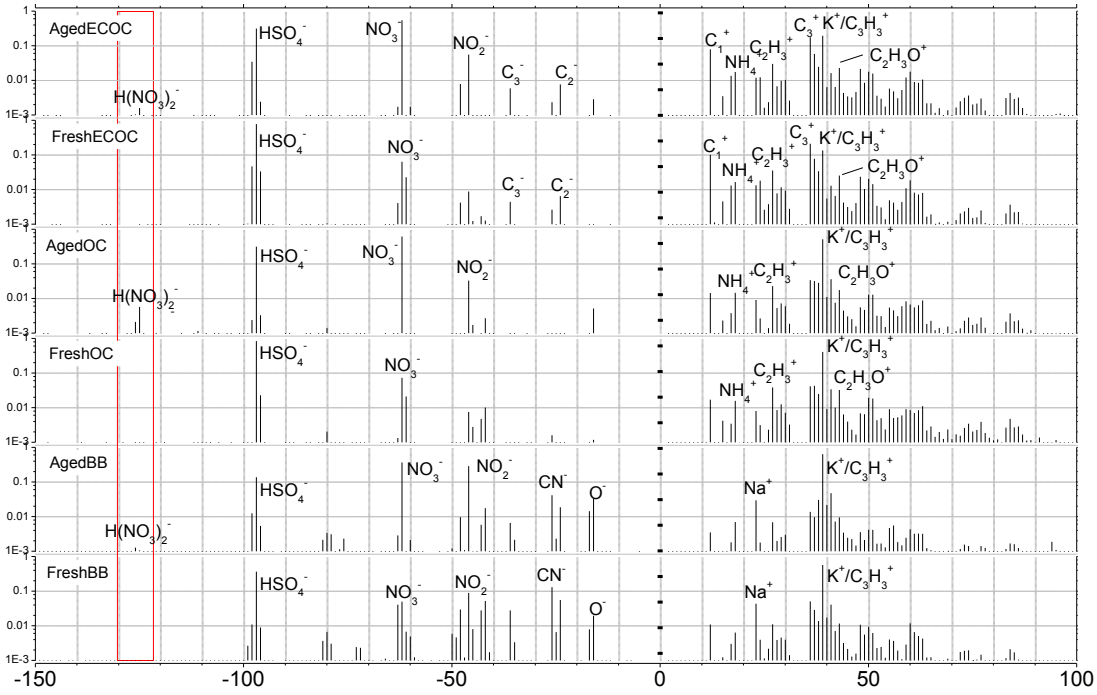

Figure S2. ATOFMS spectra for fresh and aged biomass burning (BB), organic carbon (OC) and elemental/organic carbon (ECOC) particle types. The red box highlights the nitrate cluster ion $H(NO_3)_2^-$, a marker for aging.

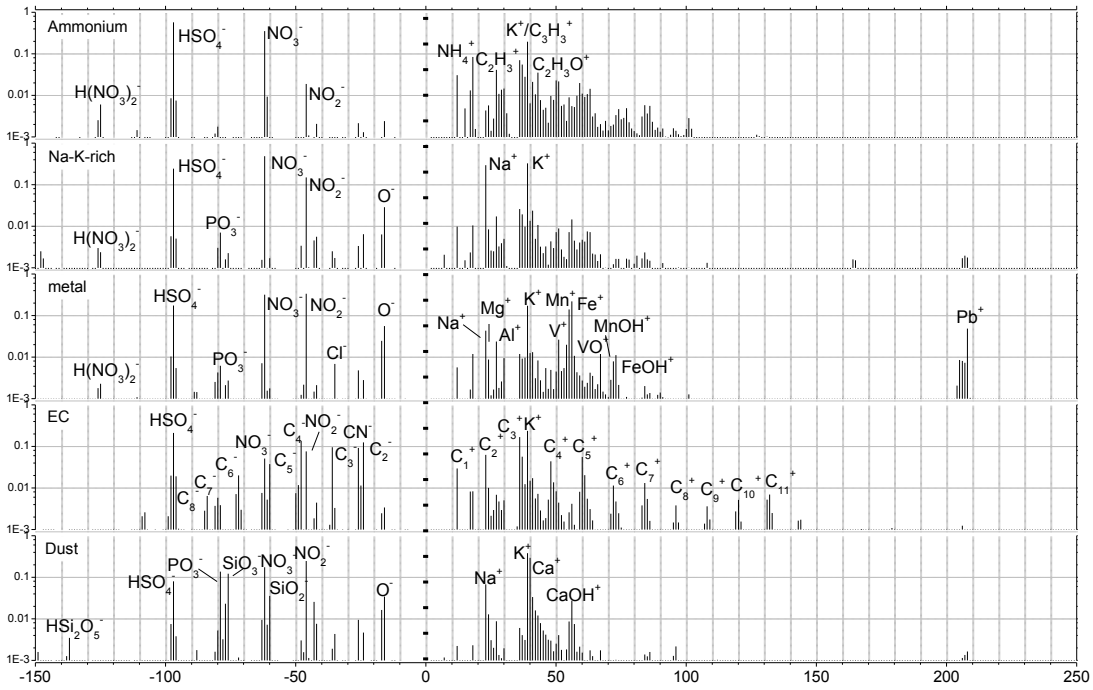

Figure S3. ATOFMS spectra for ammonium, Na-K-rich, metal, elemental carbon (EC) and dust-containing particle types.

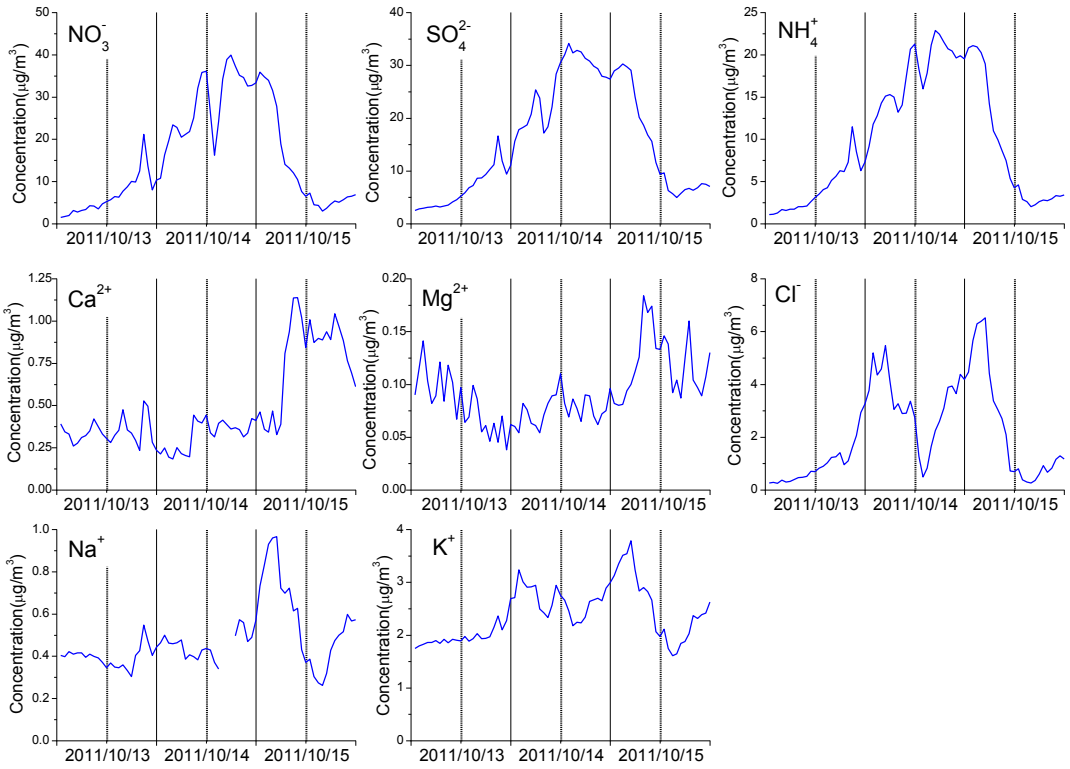

Figure S4. Temporal profiles of eight water-soluble ion mass concentrations measured by MARGA.

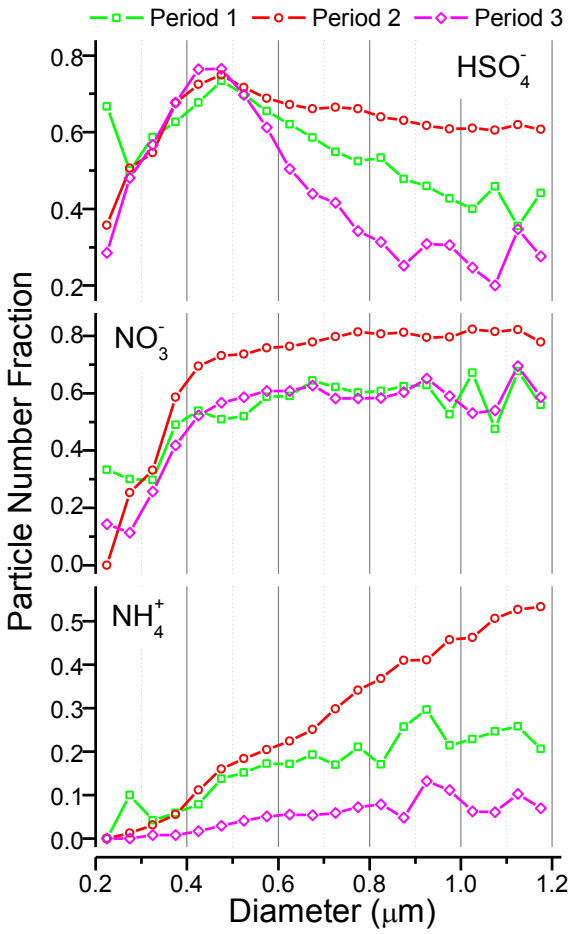

Figure S5. Size distributions of number fractions of particles sampled with the ATOFMS containing HSO_4^- (*m*/*z* -97), NO_3^- (*m*/*z* -62) and NH_4^+ (*m*/*z* +18) in the three time-periods.

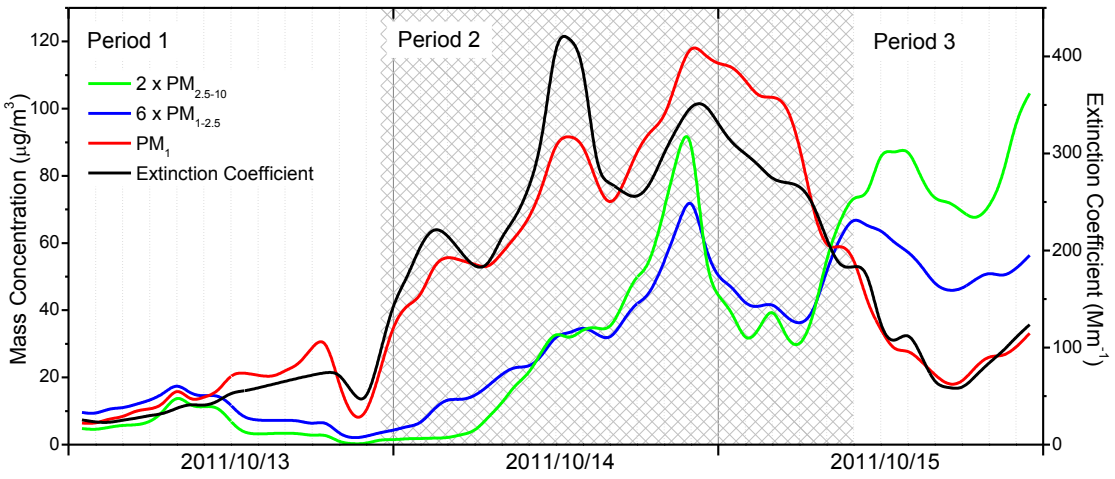

Figure S6. Temporal variations of size segregated PM mass concentrations (PM_1, $PM_{1\text{-}2.5}$, $PM_{2.5\text{-}10}$) and extinction coefficient.

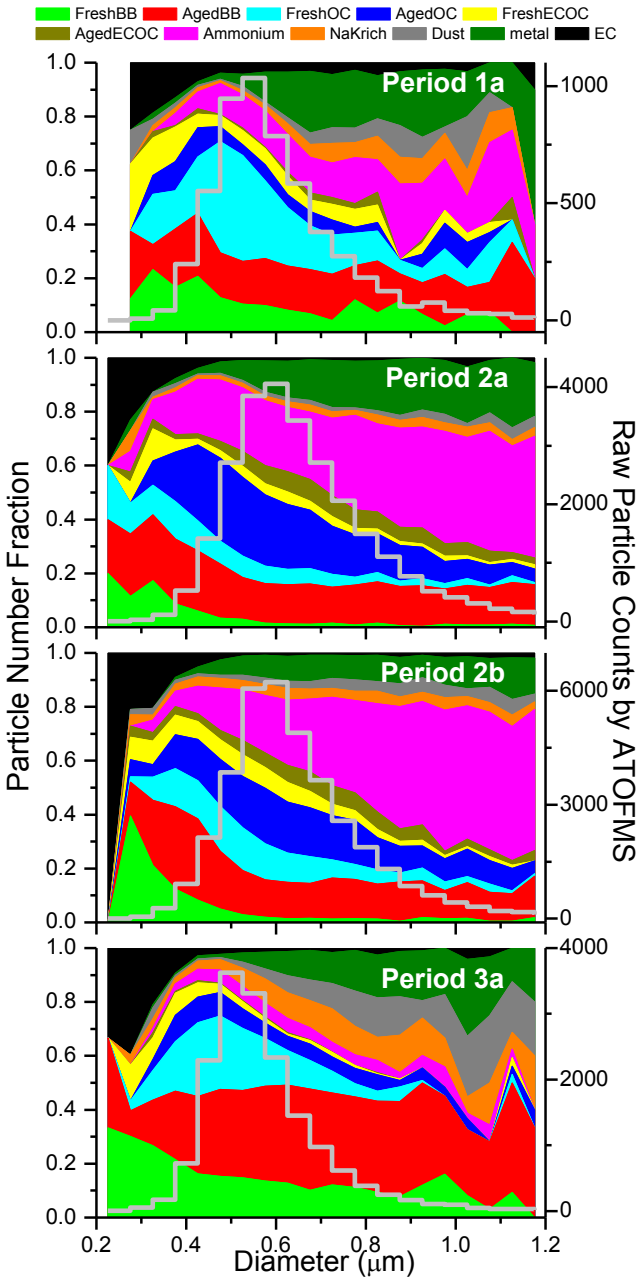

Figure S7. Chemically resolved size distributions of different particle type number fractions and raw particle counts by ATOFMS in the four sub-periods.

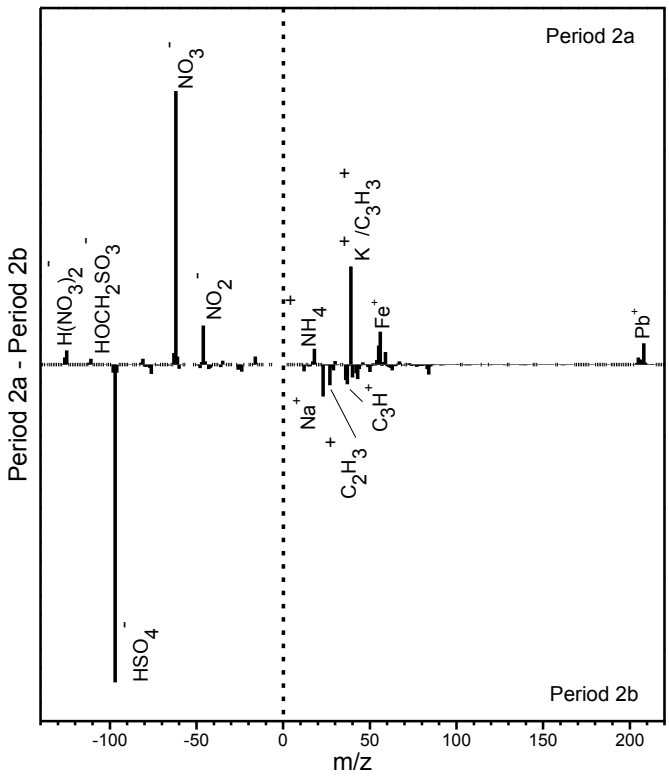

Figure S8. Difference of the average mass spectra (relative peak area) of particles in Period 2a and Period 2b.

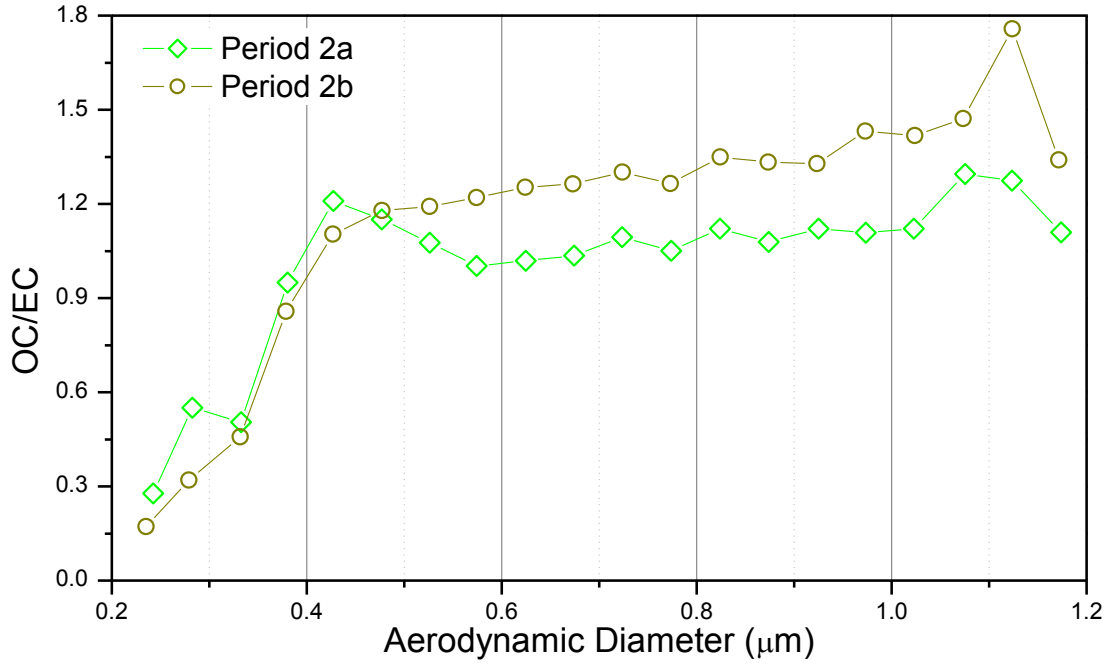

Figure S9. Sized resolved distributions of the OC/EC ion ratio in carbonaceous particles in Period 2a and Period 2b.