Supplementary information

Instrument and operation

HTDMA: Briefly, the custom-built HTDMA consists of two long DMAs (3081L, TSI Inc.), a humidifier (PD-50T-12MSS, Perma Pure Inc.), and a condensation particle counter (CPC, model 3771, TSI Inc.). Particles were dried to ～20% RH using a diffusion drier, and then size-selected by first DMA, and humidified to ～85% RH. The resulting humidified size distribution was scanned using the second DMA connected to a water based condensation particle counter (water-CPC, TSI 3782). The DMAs were operated with recirculating sheath flows and a sheath-to-sample flow rate of 10:1. The housing that hosts the DMAs was temperature controlled and kept at 20 ºC. With this setup, the GF of a particle can be calculated from the following equation: $GF=D_{RH}/D_0$, where D_{RH} and D_0 are the humidified and dried particle mobility diameter measured by the second and first DMA, respectively. Aerosol flow was set at 0.43 L/min (the sum of the CPC (0.4 L/min) and the SP2 (0.03 L/min)). With this flow rate, the aerosol residence time in the humidifier was about 25s (Chan and Chan, 2005). Hygroscopicity was calibrated using $(NH_4)_2SO_4$ particles.

SP2: SP2 detects incandescence and scattering signals of BC-containing particles induced by a 1064 nm Nd: YAG intracavity laser. If a particle was detected by the avalanche photodiode (APD) sensor but with no thermal radiation observed, the mass of rBC in the particle was below the SP2 incandescence detection limit. These particles were classified as purely scattering and assigned a size using the intensity of the APD detector signal and the PSL calibration response. The mass of rBC is proportional to the intensity of the laser-induced incandescence signal. Any measured particle with a detectable incandescence signal is treated as a BC-containing particle. The SP2 uses the maximum detected emission of thermal radiation (“incandescence”) to determine the rBC mass for individual BC-containing particles. For the BC-containing particles with core–shell structures, the coating thickness can be semi-qualitatively represented by the delay time of the LII peak (Δt), which is defined as the elapsed time between the occurrence of the peak of the scattering signal and the peak of the incandescence signal; a positive value of this quantity indicates that the peak of the incandescence signal occurs after the peak of the scattering signal. In principle, the larger the Δt value is, the more likely the rBC core has thicker coating. Therefore, the SP2 measurement is capable of examining whether a single particle contains rBC or not by detecting the ambient incandescence signal.

SPAMS: Particles in the size range of 0.2–2.0 μm are first drawn into the vacuum through an aerodynamic focusing lens. Each particle is accelerated to a size-dependent aerodynamic velocity, which is calculated based on two continuous lasers (Nd: YAG; 532 nm). The two lasers are fixed at a 6 cm distance and the scatter light is collected by two photomultiplier tubes (PMTs). When a particle arrives at the ion source region, a pulsed desorption–ionization laser (Qswitched Nd: YAG; 266 nm) is triggered. And a bipolar time-of-flight spectrometer records both positive and negative mass spectra for each single particle. In this work, the power of the desorption–ionization laser was set to ～0.6 mJ per pulse. The vacuum aerodynamic diameter measurement is calibrated with monodisperse polystyrene latex spheres (Nanosphere Size Standards; Duke Scientific Corp.) with known diameters (0.2–2.0 μm).

All single-particle mass spectra acquired were converted to a list of peaks at each m/z by setting a minimum signal threshold of 20 arbitrary units above the baseline with TSI MS-Analyze software. The resulting peak lists together with other SPAMS data were imported into YAADA (version 2.11; www.yaada.org), a software toolkit for single-particle data analysis written in MATLAB (version R2012b).

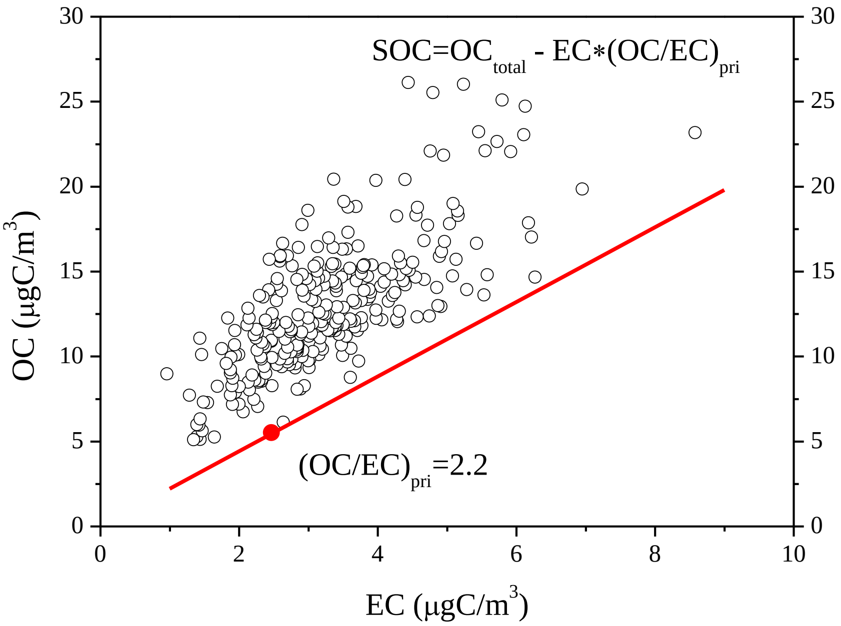
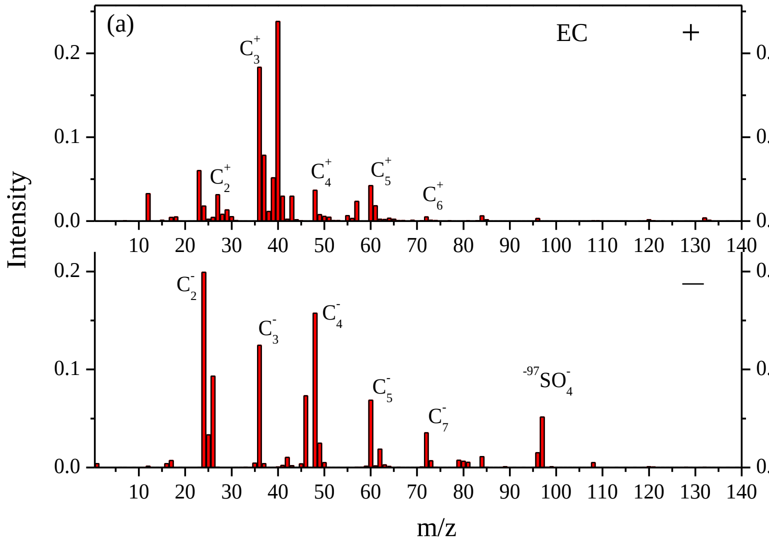
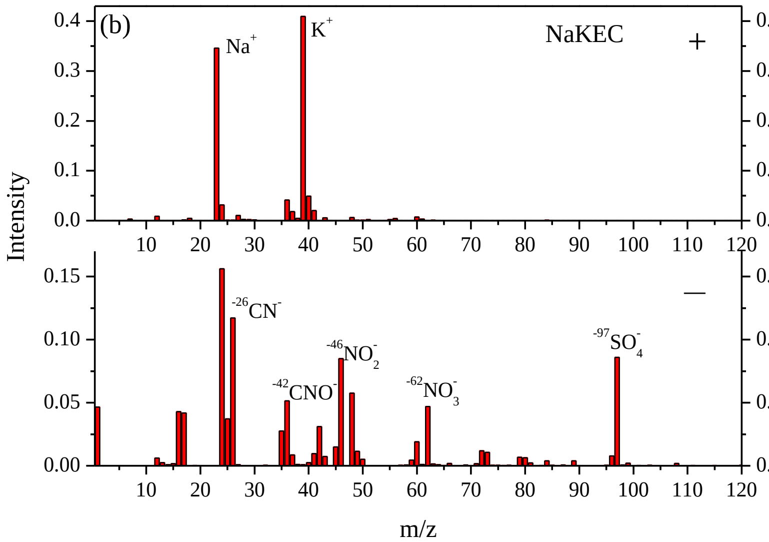
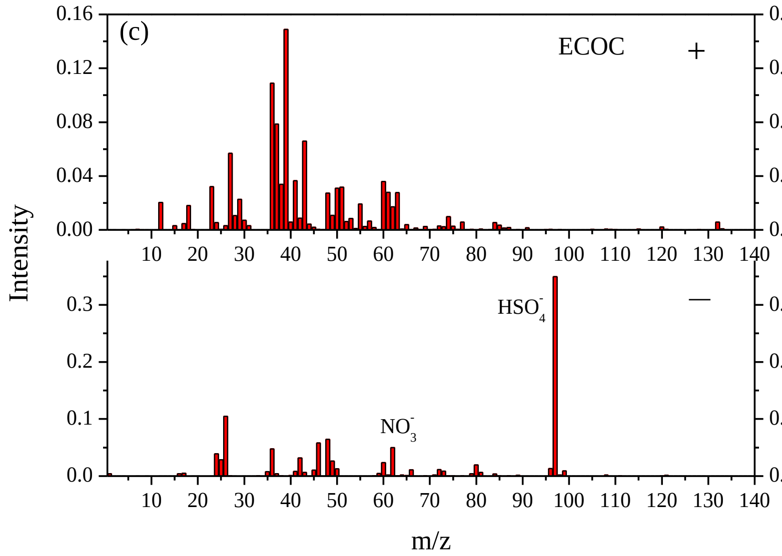


Figure S1. The scattering plot for the measured OC and EC concentration. The red line represents the minimum value of OC/EC ratio.

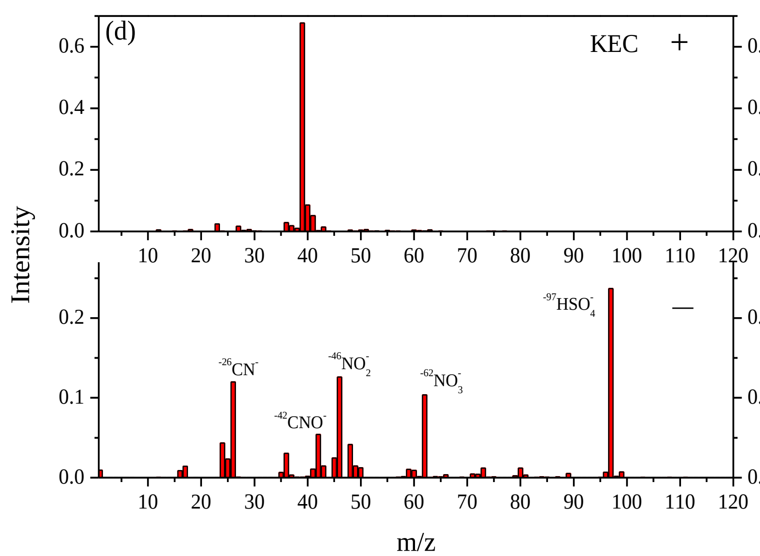

(a)
EC
+
Intensity
m/z
—


(b)
NaKEC
+
Na+
K+
Intensity
m/z
—



(c)
ECOC
+
—
HSO$_4^-$
NO$_3^-$
Intensity
m/z

67



(d)
KEC
+
—
-97HSO$_4^-$
-26CN-
-46NO$_2^-$
-62NO$_3^-$
-42CNO-
Intensity
m/z

68

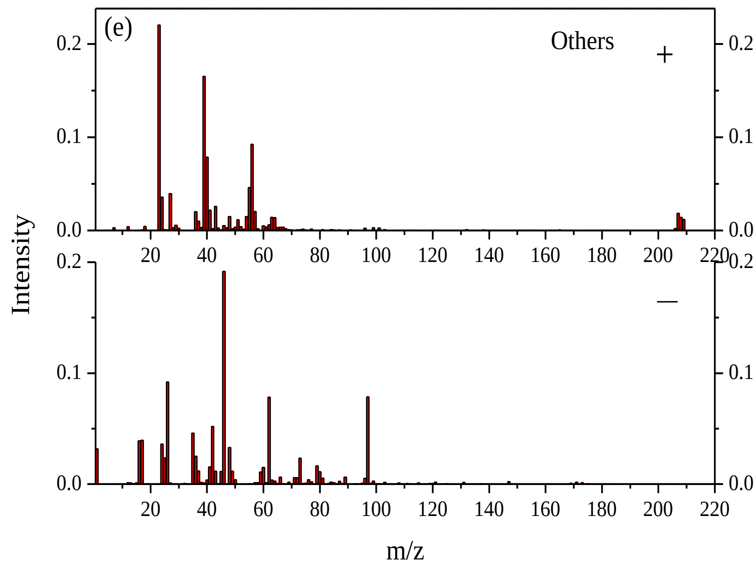


Figure S2. Averaged mass spectra of different types of BC-containing particles: (a) EC; (b) NaKEC; (c) ECOC; (d) KEC; (e) Others (the unit for the intensity is arbitrary).

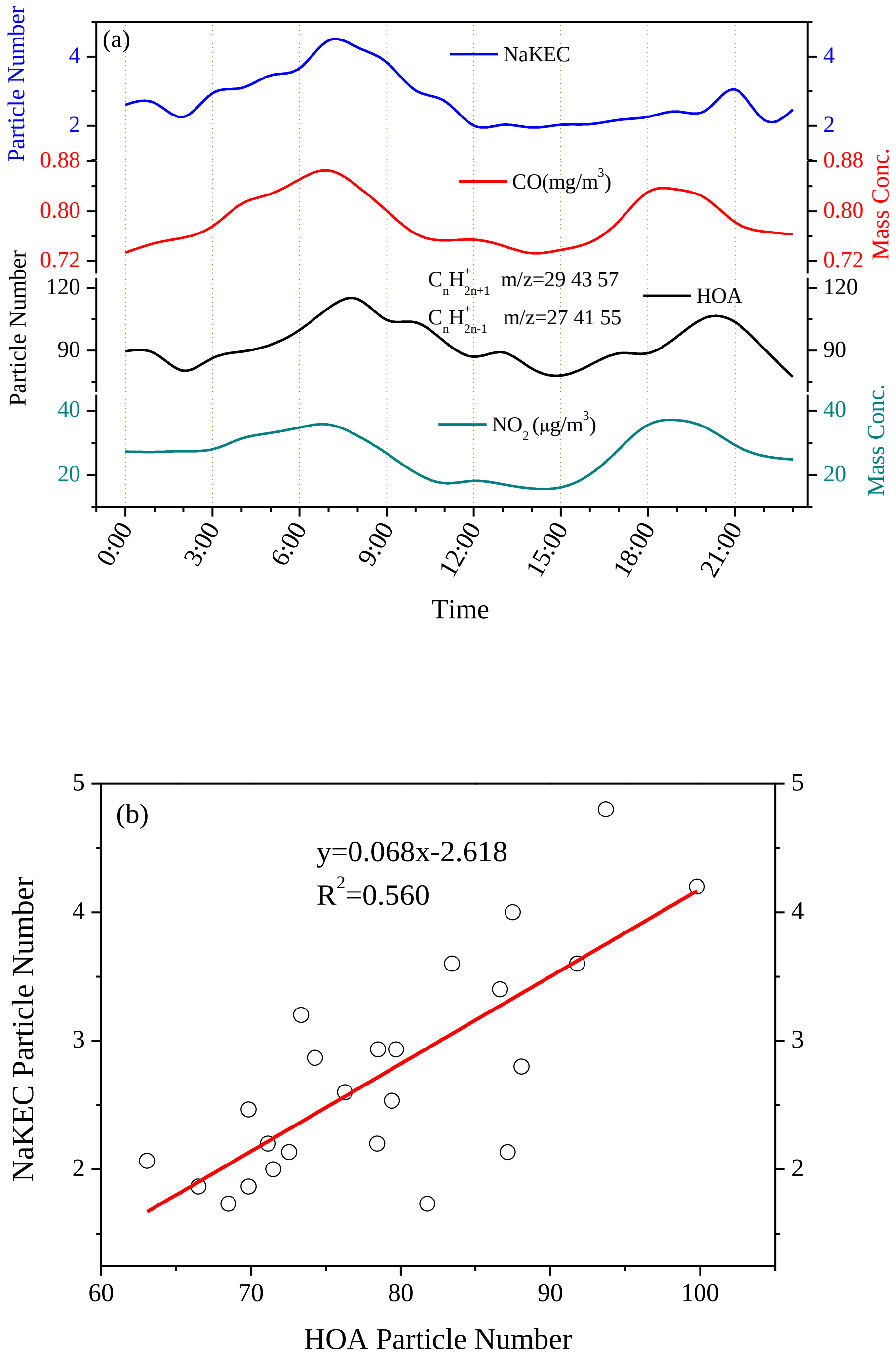


Figure S3. (a) Diurnal variation of NaKEC and HOA particle number sampled by SPAMS, as well as CO and NO_2 concentrations; (b) Correlation between NaKEC and HOA particles.

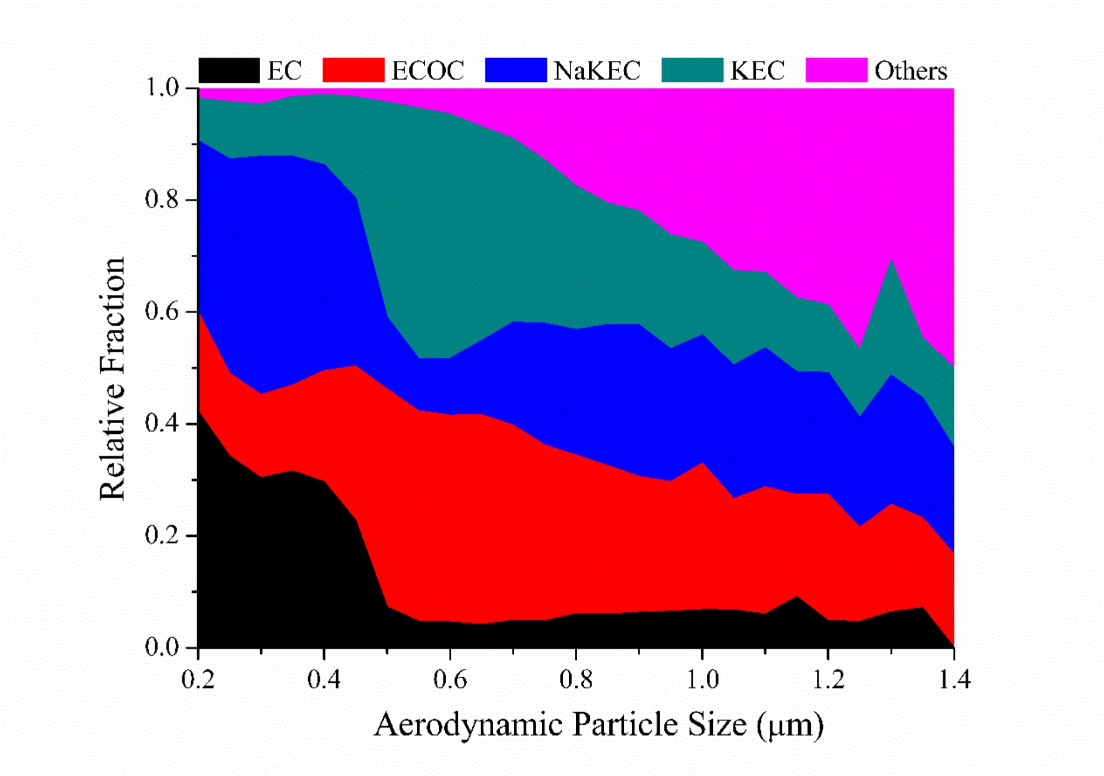
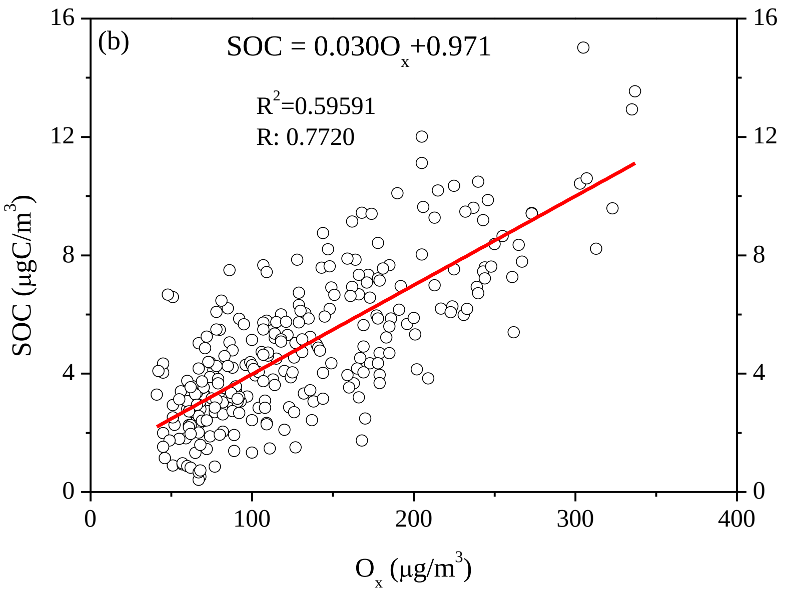


Figure S4. Relative fractions of five particle types as a function of particle size measured by SPAMS.



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92 **Figure S5.** Linear correlation between SOC and O_x concentration.

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