Size distribution and mixing state of black carbon particles during a heavy air pollution episode in Shanghai

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Abstract: A Single Particle Aerosol Mass Spectrometer (SPAMS), a Single Particle Soot Photometer (SP2) and various meteorological instruments were employed to investigate the chemical and physical properties of black carbon (BC) aerosols during a regional air pollution episode in urban Shanghai over a five-day period in December 2013. The refractory black carbon (rBC) mass concentrations measured by SP2 averaged 3.2 μg m^{-3}, with the peak value of 12.1 μg m^{-3} at 04:26 LT on 7 December. The number of BC-containing particles captured by SPAMS in the size range 200-1200 nm agreed very well with that detected by SP2 (R^2 = 0.87). A cluster analysis of the single particle mass spectra allowed for the separation of BC-containing particles into five major classes: (1) Pure BC; (2) BC attributed to biomass burning (BBBC); (3) K-rich BC-containing (KBC); (4) BC internally-mixed with OC and ammonium sulfate (BCOC-SOx); (5) BC internally-mixed with OC and ammonium nitrate (BCOC-NOx). The size distribution of internally-mixed BC particles was bimodal. Detected by SP2, the condensation mode peaked around ~230 nm and droplet mode peaked around ~380 nm, with a clear valley in the size distribution around ~320 nm. The condensation mode mainly consisted of traffic emissions, with particles featuring a small rBC core (~60-80 nm) and a relatively thin absolute coating thickness (ACT, ~50-130 nm). The droplet mode included highly aged traffic emission particles and biomass burning particles. The highly aged traffic emissions

had a small core (~60-80 nm) and a very thick ACT (~130-300 nm), which is larger than reported in any previous literature. A fast growth rate (~20 nm h^{-1}) of rBC with small core sizes was observed during the experiment. The biomass burning particles had a larger rBC core (~80-130 nm) and a thick ACT (~110-300 nm). High concentrations pollutants like NO_2 likely accelerated the aging process and resulted in a continuous size growth of rBC-containing particles from traffic emission.

1 Introduction

Aerosols represent the largest uncertainty in estimating radiative forcing of atmospheric species, through strongly affecting the energy balance of the Earth by scattering and/or absorbing solar radiation (Pöschl, 2005), and influencing cloud formation (Jacobson, 2006). Emitted from incomplete combustion of fossil fuel and biomass (Bond et al., 2013), black carbon (BC) is a strongly light-absorbing carbonaceous material in aerosols, second to carbon dioxide as a contributor to positive radiative forcing (Ramanathan and Carmichael, 2008;Jacobson, 2001).

The physical (e.g., size distribution and morphology) and chemical (e.g., mixing state and composition) properties of ambient BC are very complex and are constantly changing in the atmosphere. For example, BC particles exposed to sub-saturated sulfuric acid vapor exhibit a marked change in morphology, characterized by a decreased mobility-based diameter but an increased fractal dimension and effective density (Zhang et al., 2008). Through using electron tomography with a transmission electron microscope and three-dimensional (3-D) imaging, Adachi et al. (2010) found that many BC particles have open, chainlike morphology even after being surrounded by organic matter, and are located in off-center positions within their host materials. China et al. (2013) analyzed the morphology of single BC particles using electron microscopy and classified them into four categories: ~50% were embedded (heavily coated), ~34% were partly coated, ~12% had inclusions and ~4% were bare. The organic coating is known to strongly affect the optical properties of the soot aggregates by acting as a lens that amplifies the absorption cross section of the BC core (Lack and Cappa, 2010;Shiraiwa et al., 2010). Schnaiter et al. (2005) observed that amplification factors of the internally-mixed BC of 1.8 to 2.1

relative to the specific absorption cross section of externally-mixed BC. Zhang et al. (2008) observed that the internally-mixed particles can increase their absorption efficiency by nearly 2-fold and scattering efficiency by approximately 10-fold at 80% relative humidity relative to fresh particles. On the other hand, Cappa et al. (2012) and Lan et al. (2013) observed a limited enhancement due to the mixing state of ambient BC, suggesting that other factors may affect their absorption properties. Through coagulation and condensation, BC can form an internal mixture, which increases its cloud nucleation activity (Khalizov et al., 2009;Moffet and Prather, 2009). Most BC is removed from the troposphere via wet deposition with a short lifetime of 5 to 10 days (Kanakidou et al., 2005;Chung and Seinfeld, 2002).

Many measurement methods for refractory BC (rBC) particles have been developed and used in recent years (Petzold et al., 2013). Among them, the Single Particle Soot Photometer (SP2) has become increasingly recognized as a valuable tool for characterizing rBC-containing particles (Stephens et al., 2003;Schwarz et al., 2006). SP2 can quantitatively measure the mass and determine the mixing state of an individual rBC-containing particle (Schwarz et al., 2010). Taylor et al. (2014) evaluated the capability of the SP2 to determine the particle mixing state through using the concentric core/shell model. Liu et al. (2014) analyzed the size distribution and mixing state of rBC aerosols in London during winter time based on the same technique. Furthermore, Moteki et al. (2014) identified two morphological types of the mixed rBC-containing particles as attached and coated, an important finding for understanding the climate impact of rBC particles. Recently, a soot particle aerosol mass spectrometer (SP-AMS) was developed to characterize rBC and non-refractory particulate matter simultaneously (Cross et al., 2010;Onasch et al., 2012;Corbin et al., 2014). SP-AMS was previously used to quantify rBC mass concentration, mixing state and chemical composition in urban environment and biomass burning influenced air (Lee et al., 2015a;Lee et al., 2015b;Willis et al., 2015).

As a highly complementary instrument, single particle aerosol mass spectrometer (SPAMS, not to be confused with the SP-AMS instrument mentioned above) can detect

88 the chemical properties of BC particles. Moffet and Prather (2009) observed a rapid
89 coating process of organic carbon and sulfate on the BC core and assessed the related
90 absorption enhancement during an air pollution episode of the Mexico City. Healy et al.
91 (2012b) found that the mass size distribution for BC-containing particles was bimodal at
92 an urban background site in Paris. The smaller mode was attributed to local emission,
93 mostly externally-mixed BC particles, while the larger mode was dominated by aged
94 particles associated with continental transport events. Zhang et al. (2014) found that an
95 active photochemical formation of secondary organic aerosol (SOA) led to a distinct
96 diurnal pattern of mixing state of BC with SOA in the condensation mode, while the
97 photochemical aging had limited or negligible influence on the mixing state and growth
98 of BC in the droplet mode. The size ranges of condensation mode (Vacuum Aerodynamic
99 Diameter (D_{va})= ~100-300 nm) and droplet mode (D_{va}= ~300- 1000 nm) were defined by
100 John et al. (1990) and Seinfeld and Pandis (2012).

101 Depending on the experimental method, different terms are used in the literature for the
102 most refractory and light-absorbing components of carbonaceous aerosols: black carbon
103 (BC), refractory black carbon (rBC) and elemental carbon (EC). The definitions of BC,
104 rBC and EC have been discussed in details elsewhere (Bond and Bergstrom,
105 2006;Almeida et al., 2013;Petzold et al., 2013). In this paper, we use rBC and BC to
106 illustrate the SP2 and SPAMS data, respectively.

107 All of the studies mentioned above relied on either an SP2 instrument or a single particle
108 mass spectrometer to characterize BC particles. Combining these two methods would
109 provide the chemical and physical prosperities of individual BC particles simultaneously
110 and greatly enhance our understanding of their sources and evolution processes.
111 Furthermore, most previous SP2 studies focused on the BC particles during relatively
112 clean days. Quantitative analysis on the mixing state of BC particles during heavy
113 pollution episodes is still lacking. In this study, we deployed two complementary
114 techniques, with single particle resolution and high time resolution, to detect the
115 evolution of the urban BC aerosols in Shanghai during an extreme pollution period. We
116 used an SP2 instrument to measure the mass and size distribution, and the mixing state of

individual rBC particles. A SPAMS instrument was used in parallel to record chemical characteristics and mixing state of individual BC particles.

2 Experimental

2.1 Single Particle Soot Photometer

2.1.1 Description

The number and mass size distribution, as well as the mixing state of individual rBC particles were characterized using a single particle soot photometer (SP2, Droplet Measurement Technologies, Inc., Boulder, CO) (Stephens et al., 2003;Baumgardner et al., 2004). In brief, SP2 detects incandescence and scattering signals of rBC-containing particles induced by a 1064 nm Nd: YAG intra-cavity laser. 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 an rBC particle; whereas a particle that only exhibits scattering signal is considered as a non-rBC particle. The total rBC mass loading is reported as the sum of all detected single rBC masses. The SP2 instrument samples at low flow (30 cm^3 min^{-1}) in order to avoid multiple particles crossing the laser at the same time. We only saved data for every 50^{th} particle in order to extend the sampling time without generating excessively large data sets.

2.1.2 Calibration and detection efficiency

The SP2 incandescence signal was calibrated using Aquadag® black carbon particles (Aqueous Deflocculated Acheson Graphite, manufactured by Acheson Inc., USA). The Aquadag® black carbon particles were selected by mobility diameter using a differential mobility analyzer (DMA) and the corresponding particle masses were calculated using the effective density data provided in Gysel et al. (2011) (Fig. S1). The scattering signal was calibrated using mono-disperse polystyrene latex spheres (Nanosphere Size Standards, Duke Scientific Corp., Palo Alto, CA, USA) with known diameters (80–350 nm). More details about the SP2 calibration can be found in Gysel et al. (2011),

Baumgardner et al. (2012) and Laborde et al. (2012). A diagram of the calibration system is shown in the supplement (Fig. S2).

The detection efficiency was measured using Aquadag® black carbon particles, and the results are shown in Fig. S3. The details of the measurement method were described in Schwarz et al. (2010). SP2 detection efficiency was nearly unity for larger rBC particles. The minimum rBC mass that could be observed with near-unity detection efficiency was ~ 0.7 fg rBC, corresponding to 90 nm mass-equivalent diameter; the detection efficiency declined rapidly at lower sizes (Fig. S3). The total ambient mass concentrations of rBC were underestimated because of the low detection efficiency of the smaller rBC particles, likely by ~20 % (Schwarz et al., 2006;McMeeking et al., 2010). During the calibration and sampling time, the SP2 was operated at a stable temperature 20 ℃ and pressure ~1013 hPa. The SP2 laser current was at 1750 mA through the whole experiment.

2.1.3 Data analysis

The rBC mass in each individual particle was determined from the peak intensity of the incandescence signal according to the Aquadag® black carbon calibration (Sect. 2.1.2). The measured ambient rBC mass was converted to the mass equivalent diameter, assuming a density of 1.8 g cm^{-3} (Bond and Bergstrom, 2006). In addition to the rBC mass, the measurement of the scattering signal of a rBC-containing particle allows for the determination of its scattering cross section. However, the scattering properties of externally- and internally-mixed rBC particles, as detected by the SP2, may be distorted, because the mass of each particle is reduced by the laser heating. Thus, scattered light from a sampled rBC particle does not yield a full Gaussian waveform. The Gaussian scattering function was reconstructed from the leading edge of the scattering signal (before the particle is perturbed by the laser), which was measured with a two-element avalanche photodiode (APD). This method allows SP2 to determine the scattering properties of individual rBC particles as well as the rBC mass and to distinguish the mixing state of a single rBC particle (so called, LEO-fit method (Gao et al., 2007)). The optical diameter of a rBC particle or the coated rBC size (D_p) was derived by inputting the LEO fitted scattering signal and rBC core size (D_c) into Mie calculations, and using a

core refractive index m = 2.26-1.26i (Moteki et al., 2010;Liu et al., 2014;Laborde et al., 2013) and a coating refractive index m = 1.5 + 0i (Laborde et al., 2013). The absolute coating thickness (ACT) of a rBC particle was calculated as $(D_p - D_c)/2$, based on the assumption of a concentric core-shell morphology. However, rBC aging processes in the real atmosphere may result in aerosols with particles that have a morphology that deviates from the core-shell model (Matsui et al., 2013). For example, when a small rBC particle coagulates with a relatively large rBC-free particle, the small rBC particle may stay at the surface and lead to an effective negative coating thickness if determined by the methods used here. In this study, the negative coating thickness was observed for less than 2% of all rBC-containing particles; we did not take those particles into account when we calculated the average ACT. More details of data analysis and uncertainties are discussed in supplement, as well as in Liu et al. (2014) and Laborde et al. (2013).

2.2 Single Particle Aerosol Mass Spectrometer

A SPAMS instrument (Hexin Analytical Instrument Co., Ltd., Guangdong, China) was deployed simultaneously with SP2 to detect chemical composition of BC-containing particles. The technical details of SPAMS have been described elsewhere (Li et al., 2011). Briefly, aerosols in the size range of 0.2–2.0 μm are introduced into the focus lens through a 0.1 mm critical orifice at a flow of 80 mL min^{-1} due to the pressure drop from ~760 to ~2.2 Torr. Then particles are accelerated to a terminal size-dependent aerodynamic velocity, which is measured by two orthogonally-oriented continuous lasers (532 nm) separated by a fixed 6.0 cm distance. A pulsed desorption/ionization laser (Q-switched Nd: YAG laser, 266 nm) is triggered when a particle arrives at the ion source region. Both positive and negative ions are detected simultaneously by the time-of-flight mass spectrometer. In this work, the power of the desorption/ionization laser was kept at ~0.6 mJ per pulse. The particle size was calculated from the measured speed using a calibration curve generated by mono-disperse polystyrene latex spheres (Nanosphere Size Standards, Duke Scientific Corp., Palo Alto, CA, USA) with known diameters (0.22–2.00 μm).

All single particle mass spectra were converted into a list of peaks at each *m/z* using TSI MS-Analyze software with a minimum signal threshold of 30 arbitrary units above the baseline. The resulting peak lists were then imported into YAADA (www.yaada.org), a software toolkit in Matlab (version R2012b) for further analysis of particle sizes and chemical components. A total of 385 683 particles were chemically analyzed with both positive and negative ion spectra, accounting for about 56 % of all sized particles. Based on the similarities of the mass-to-charge ratio and peak intensity, particles were clustered by using the ART-2a (adaptive resonance theory) method (Song et al., 1999) with a vigilance factor of 0.85, a learning rate of 0.05 and 20 iterations. Then BC-containing particles, with D_{va} in the size range of 200-1200 nm, were chosen from the clusters, since this size range was consistent with the dominant fraction of BC-containing mass in the atmosphere (Zhang et al., 2014;Healy et al., 2012b). Finally, a total of 86 057 BC-containing particles were grouped into six general particle types according to mass spectral patterns.

2.3 Monitor for AeRosols and GAses (MARGA)

A MARGA instrument (ADI 2080, Applikon Analytical B. B. Corp., Netherlands) was used to measure water-soluble inorganic ions in particles. The details of MARGA have been described previously (Jongejan et al., 1995;Du et al., 2011). Briefly, air to be analyzed enters into sample boxes via a PM_1 cyclone. The air flow is maintained at 1 m^3 h^{-1} by a mass flow controlled air pump. In the sample box, water-soluble gases (HCl, HONO, SO_2, HNO_3, NH_3) are completely absorbed in a dilute solution of hydrogen peroxide by using a wet rotating denuder (WRD). Aerosols pass through the WRD and are subsequently collected in a steam-jet aerosol collector (SJAC). The two liquid samples with absorbed gases and particles are accumulated in syringes in the analytical box. After filling the syringes for one hour, the samples are then injected into an ion chromatograph (IC). The IC is continuously controlled by an internal calibration method using a standard LiBr solution. In this study, the water-soluble inorganic ions (i.e., K^+, SO_4^{2-}, NO_3^-) in bulk particles were analyzed.

2.4 Sampling period and site

The sampling lasted for almost 5 days, from 5 to 10 December, 2013. The instruments were operated in the building of the Department of Environmental Science and Engineering, Fudan University (FDU, 31° 14' N, 121° 29' E) in urban Shanghai, close to both residential and traffic emissions sources. Aerosols were sampled with a $PM_{2.5}$ cyclone positioned 2 m above the roof of the building and transferred to the instruments through a 6 m long stainless steel pipe (45 mm inner diameter). A pump was used to pull air through the sampling system at 30 L min^{-1}, minimizing the particle residence time in the sampling line. Aerosols were dried by diffusion drying tubes before they reached the SP2 and SPAMS inlets, which were connected in parallel. The measurement system is presented in Fig. S2. Because of the extremely high particle mass loading, the inlets of SP2 and SPAMS were clogged two times during the sampling period.

3 Result and discussion

3.1 Overview of the meteorology and air quality

Temporal variations of measured relative humidity, temperature, CO, O_3, NO, NO_2, SO_2, $PM_{2.5}$ and PM_{10} in Shanghai from 12:00 LT on 5 December to 14:00 LT on 10 December are shown in Fig. 1. The meteorology and air quality information were provided by the Shanghai Environmental Monitoring Center, Hongkou Station (http://www.semc.com.cn/aqi/home/Index.aspx). The station is 3.3 km north from the sampling site. The temperature and relative humidity varied between 2-19℃ and 30-100%, with an average of 19℃ and 73%, respectively, during the study. The O_3 concentration was relatively low from 18:00 LT on 5 December to 8:00 LT on 7 December. The CO concentration showed two peaks during this period, and its peak value reached 4.1 mg m^{-3} at 14:00 LT on 6 December. The NO_2 concentration increased quickly at the beginning, reached 202.5 μg m^{-3} at 21:00 LT on 5 December, and then decreased slowly until 12:00 LT on 7 December. After 12:00 LT on 7 December, the concentrations of O_3, CO, NO_2 and SO_2 fluctuated without an obvious pattern. The concentrations of O_3 and NO_2 showed the expected anti-correlation, because NO was oxidized to NO_2 by O_3. The CO concentration was found to correlate reasonably well with rBC mass concentration (R^2= 0.59, slope=0.33), as shown in Fig. S4.

The mass loading of $PM_{2.5}$ was extremely high during this period. Its maximum value reached 636 μg m^{-3} at 12:00 LT on 6 December, which was a record-breaking hourly concentration for Shanghai. The daily average concentration was 221 μg m^{-3}. Meanwhile, PM_{10} varied from 47 to 691 μg m^{-3}, with an average of 252 μg m^{-3}. Concentrations of CO, O_3, NO, NO_2, SO_2, PM_{10} and $PM_{2.5}$ during 5-10 December all exceeded the Chinese national ambient air quality standards.

3.2 BC size distributions and concentration measurement by SP2

We fitted a log-normal distribution to the rBC core number and mass size measurements during the entire sampling period, as shown in Fig. 2. The number size ranged from ~60 to ~400 nm and the peak was around ~60 nm. The measured number concentrations dropped below 60 nm because the SP2 detection efficiency greatly decreases (Sect. 2.1.2) below this particle size. Using the same method, Schwarz et al. (2008) also found that the peak concentration was around 60 nm in boundary layer. The rBC core mass size distribution had a peak around 200 nm, and the most rBC mass was distributed between 70-500 nm.

As shown in Fig. 1, the rBC mass concentration varied from 0.6 μg m^{-3} at 00:02 LT on 10 December to 12.1 μg m^{-3} at 04:26 LT on 7 December, with an average of 3.2 μg m^{-3}. The rBC mass concentration observed in Shanghai was similar to other cities in China, e.g., ~4.1 μg m^{-3} in Shenzhen (Huang et al., 2012) and ~3.3 μg m^{-3} in Kaiping (Huang et al., 2011). However, it was much higher than in other mega-cities around the world, e.g., ~0.9 μg m^{-3} in Paris (Laborde et al., 2013) and ~1.3 μg m^{-3} in London (Liu et al., 2014). All of the values quoted above were based on SP2 measurement. The rBC mass accounted for 1.45% of $PM_{2.5}$ mass on average in our measurements.

3.3 BC particles classification by SPAMS

Classification of particles analyzed by the SPAMS can help elucidate the sources, degree of aging, and mixing state of BC particles. We classified BC-containing particles into six groups according to their mass spectral characteristics. The names of these groups and their number fractions are shown in Table 1. The average mass spectral patterns of each

group are shown in Fig. S5.

Pure BC particles only presented strong signals for black carbon fragment ions (C_n^- and C_n^+) in both positive and negative ion mass spectra without any signal of secondary species like sulfate or nitrate, suggesting they were fresh BC particles that had not undergone any aging process.

Biomass burning BC-containing (BBBC) particles were characterized by an intense K^+ signal for +39 (the charge and *m/z* of the observed ion), +113 (K_2Cl^+) and +213 ($K_3SO_4^+$) in the positive ion mass spectra and a strong signal for -26 (CN^-) and -42 (CNO^-) in the negative ion mass spectra. A significant fragment of levoglucosan, -71 ($C_3H_3O_2^-$), was also observed. Typical black carbon fragments (C_n^-) appeared in the negative ion mass spectra. A high signal at -46 (NO_2^-), -62 (NO_3^-) and a relatively low signal at -97 (HSO_4^-) were also observed, suggesting a significant accumulation of nitrate ions on BC particles throughout the air pollution period. Potassium-containing soot is a well-established tracer for biomass combustion (Andreae, 1983;Soto-Garcia et al., 2011). Water-soluble K^+ in ambient particles measured by an online MARGA method correlated reasonably well with the BBBC particles number (R^2=0.64). Particles with similar mass spectral patterns were previously observed in several urban field studies and assigned to biomass burning sources (Moffet et al., 2008;Healy et al., 2012b;Bi et al., 2011).

BC internally-mixed with organic carbon and ammonium sulfate (BCOC-SOx) particles exhibited signals for ammonium +17 (NH_3^+), +18 (NH_4^+), organic carbon +37 (C_3H^+), +43 (CH_3CO^+), +50 ($C_4H_2^+$), +51 ($C_4H_3^+$), +61 ($CH_3C(OH)=OH^+$), +62 ($(CH_3)_2NHOH^+$), and a small signal for sodium +23 (Na^+) in the positive ion mass spectra, along with black carbon fragment ions (C_n^+). There was a high signal for sulfate -97 (HSO_4^-) and a relatively low signal for nitrate -46 (NO_3^-), -62 (NO_3^-) in the negative ion spectra. BC internally-mixed with organic carbon and ammonium nitrate (BCOC-NOx) particles are characterized by very similar positive ion mass spectra to BCOC-SOx, but exhibit lower signals for sulfate and higher signals for nitrate in the negative ion spectra, i.e., -46 (NO_3^-), -62 (NO_3^-). BC particles with various intensities for organic carbon, nitrate and sulfate were commonly detected in urban ATOFMS field studies (Moffet et al.,

2008;Ault et al., 2009;Dall'Osto and Harrison, 2006) and were assigned to traffic emissions (Healy et al., 2012b).

K-rich BC-containing (KBC) particles exhibited strong signals for black carbon fraction in both positive and negative ion mass spectra. This class also had signals for potassium +39 (K^+), sodium +23 (Na^+) and ammonium +17 (NH_3^+), +18 (NH_4^+) in positive ion mass spectra and nitrate -46 (NO_2^-), -62 (NO_3^-), sulfate -97 (HSO_4^-) in the negative ion mass spectra. This class was detected from diesel vehicle emissions in a previous study by (Li et al., 2013). The KBC exhibited pronounced diurnal variation, with two major peaks during early morning (4:00- 7:00 LT) and night hours (20:00- 22:00 LT) (Fig. S7). Shanghai municipal government regulates that the heavily loaded diesel trucks cannot go into downtown area from 7:00- 20:00 LT. The diurnal variation of KBC is consistent with the traffic flow of diesel trucks based on our results.

NOx can be used as a tracer of local traffic emissions in urban areas. In this study, the NOx concentrations agreed well with the sum of KBC, BCOC-NOx and BCOC-SOx particles numbers (R^2=0.65) (Fig. S8). Based on the above analysis, we believed that the BBBC came from biomass burning, KBC, BCOC-NOx and BCOC-SOx came from traffic emissions.

We should note that SPAMS preferentially detected internally-mixed BC particles, and had reduced detection efficiency for pure BC particles. The particles detected and chemically analyzed by SPAMS range from 200 to 2000 nm in size, and the detection efficiency decreases rapidly below 400 nm and above 1200 nm (Li et al., 2011). The majority of the pure BC particles diameter are smaller than 200 nm in diameter (Kondo et al., 2006), and therefore, they are missed by SPAMS.

3.4 Mixing state and size distribution of internally-mixed BC particles

3.4.1 Temporal variations of internally-mixed BC particles

A comparison of the internally-mixed BC particles number concentration between SP2 and SPAMS is given in Fig. 3. The agreement observed is reasonably good (R^2 = 0.87,

slope = 0.65) considering the combined experimental uncertainties of the methods. Detected by SP2, the internally-mixed rBC particles accounted for approximately 70% number fraction of BC-containing particles during the whole period. Moteki et al. (2007) also found the internally-mixed rBC particles accounted for 63% number fraction of BC-containing particles in the aged urban plume. The high correlation coefficient indicates that we can use the two complementary techniques to analyze the mixing state and chemical composition of internally-mixed BC particles with single particle resolution at the same time (although not for the same particle since both methods are destructive).

The temporal variation of number size distribution and particle types changed rapidly and intricately, as shown in Fig. 4. From 12:00 LT on 5 December to 00:00 LT on 7 December, the $PM_{2.5}$ and rBC mass increased slowly to an extremely polluted state. The number fraction of BBBC particles also increased during this period (Fig. 4(b)) and the D_p of rBC showed two distinct modes (Fig. 4(a)). Then, the BC-containing particles number increased rapidly at 02:00 LT on 7 December. Presumably, boundary layer compression during the night led the fast change of BC-containing particles. After that, the number concentration of BC-containing particles exhibited diurnal variation, with two major peaks at the rush hours, i.e., from 8:00-12:00 LT or from 16:00-20:00 LT.

3.4.2 Size distribution and source apportionments of internally-mixed BC particles

Fig. 5(a) shows the entire diameter (D_p) number size distribution histogram of internally-mixed rBC particles detected by SP2 during the entire sampling period. The BC-containing particles were detected in both the condensation and droplet modes in this study. The condensation mode peak was centered around ~230 nm and droplet mode peak was centered around ~380 nm, with a boundary D_p around ~320 nm. The presence of condensation mode (D_{va}= ~200-500 nm) and droplet mode (D_{va}= ~550-1200 nm) was confirmed by the SPAMS data (Fig. 5(b)). Here the SPAMS size distribution was based on the number fraction of BC-containing particles in all detected particles. Similar particle size distributions were also found in other studies in China (Huang and Yu, 2008;Zhang et al., 2014).

The specific composition in condensation and droplet modes were quite different (Fig.5 (b)). BBBC particles exhibited a higher number fraction in the droplet mode than in the condensation mode. Ammonium nitrate can condense on particle surfaces during atmospheric transport if sulfate is fully neutralized and excess ammonia is available (Riemer et al., 2004). The sulfate condensation on BC surfaces occurs soon after the BC emission , while ammonium nitrate condensation occurs over longer timescales during transport (Healy et al., 2012a). In this work, most KBC and BBBC particles and all the BCOC-NOx particles showed stronger NO_3^- signals than SO_4^- signals (as shown in Fig. S5), suggesting that most BC-containing were deeply aged. Based on the particle classification and source apportionment analysis, the internally-mixed BC particles from traffic emissions accounted for almost all of the particles observed in the condensation mode. However, the particle sources in the droplet mode were more diverse, including traffic emissions and biomass burning.

Previous studies revealed that different sources emit different core diameters for rBC-containing particles (Liu et al., 2014;Takahama et al., 2014;Reddington et al., 2013;Schwarz et al., 2008) and the aging processes affect the coating thickness (Laborde et al., 2013;Liu et al., 2014). We identified the sources and estimated aging process of rBC-containing particles by using 2-D image plot "fingerprint" of D_c and absolute coating thickness (ACT) information. Fig. 5(c) shows the dependence of ACT on D_c, weighed by the number concentration. In the condensation mode, the particles were characterized by small D_c values (~60-80 nm) with thin ACT (~50-130 nm). In combination with the SPAMS information, these particles with small D_c and thin ACT should be mainly from the traffic sources (Fig. 5(b)).

However, the droplet mode was very different from the condensation mode and showed a diversity of sources. In the droplet mode, the "fingerprint" showed two peaks. The first peak had small D_c values (~60-80 nm) and thick ACT (~130-300 nm). We assume that the rBC-containing particles in the first peak were from traffic emissions. In previous studies, the particles associated with traffic emissions had small core sizes and thin coating thickness (Laborde et al., 2013;Liu et al., 2014). However, in this study, we

found that the rBC-containing particles from traffic could be highly-aged, resulting in a much thicker coating than previously observed. This could be because polluted air masses promote faster rBC aging processes (Matsui et al., 2013). The second peak showed larger D_c (~80-130 nm) and thick ACT (~110-300 nm). These particles were presumably from biomass burning. It has been reported using SP2 measurements that fresh biomass burning rBC particles are thickly coated (Schwarz et al., 2008;Sahu et al., 2012;Liu et al., 2014).

Since there was no clear-cut separation between traffic emissions and biomass burning rBC-containing particle in droplet mode, it was hard to distinguish them when we just used the core and shell information from SP2 (Liu et al., 2014). We selected those larger core (80-130 nm) with thicker coating (120-300 nm) particles as biomass burning particles and compared with the biomass burning particles number concentration from SPAMS, as shown in Fig. S9. The good correlation (R^2 = 0.71) verified the conclusion that the rBC-containing particles with bigger core and thicker coating were from biomass burning. Even though these larger rBC-containing particles only accounted for less than 20% number fraction, they are likely to be more hygroscopic (Liu et al., 2013;Wang et al., 2014) and be scavenged by wet deposition (Moteki et al., 2012). Besides, those particles will also have greater potential to enhance the semi-direct effect (Koch and Del Genio, 2010) through interaction with cloud processes.

The diversity of sources of the droplet mode BC-containing particles was also detected in SPAMS, as we discussed before. SPAMS data showed that, in the droplet mode, the internally-mixed BC particles from traffic emissions were more abundant than those form biomass burning (Fig. 5(b)). However, the SP2 data showed that particles with a small core and thick ACT (major traffic emission) were less abundant than particles with a larger core with thick ACT (major biomass burning) (Fig. 5(c)). As we discussed in part 2.1.2, rBC-containing particle with smaller cores are not efficiently detected by SP2, which may result in an underestimation of the fraction of traffic emission rBC-containing particles in the droplet mode.

The aging of traffic-emitted rBC-containing particles during the heavy air pollution episode (12:00 LT, 5 December 2013 – 12:00 LT, 7 December 2013) was elucidated using the temporal variation of relative coating thickness (RCT, entire particle diameter/rBC core diameter, D_p/D_c) of rBC-containing particles (D_c = 60-80 nm), as shown in Fig. 6a. Note that we could only obtain optical sizing information from sufficiently coated particles because of the SP2 obtained minimal detectable optical diameter of ~170 nm. From 16:00 LT to 22:00 LT on 5 December, the RCT of rBC-containing particles and $PM_{2.5}$ concentration grew rapidly. Even though the SP2's inlet was blocked from 23:00 LT on 5 December to 10:00 LT on 6 December due to the extremely high PM mass loading, the data collected around that time suggest the rBC-containing particles growth was continuous until 13:00 LT on 6 December. The absolute coating growth rate was around 20 nm/hour during this period (16:00 LT, 5 December – 13:00 LT, 6 December).

Variations of the major chemical species in the vehicle-emitted BC-containing particles (selected by SPAMS) were also analyzed. The relative peak areas of nitrate -63 (NO_3^-) and organic carbon (i.e., +27 ($C_2H_3^+$), +43 (CH_3CO^+)) showed a relatively high level during 16:00 LT on 5 December- 13:00 LT on 6 December (Fig. 6(b)). Guo et al. (2014) observed that gaseous emissions of volatile organic compounds, nitrogen oxides from urban transportation and sulfur dioxide from region industry were responsible for large secondary particle matter formation in Beijing. Fig. S10 shows the mass concentrations of SO_2, NO_2, the mass ratio of NO_2/SO_2, MARGA-measured mass concentrations of particulate sulfate and nitrate, and the mass ratio of NO_3^-/SO_4^{2-} in PM_1 during the whole sampling period. The average mass ratios of NO_2/SO_2 in gas phase and NO_3^-/SO_4^{2-} in particles phase were 2.8 and 1.4 respectively. During the heavy air pollution episode (12:00 LT, 5 December 2013 – 13:00 LT, 6 December 2013), both NO_2 and particulate nitrate increased dramatically along with the traffic emitted BC particle growth (as shown Fig. 6), while SO_2 and sulfate remained at a relatively low level. Apparently, the gas to particle conversion of NO_2 to nitrate played a more important role in the particle growth during this pollution episode. In the previous field studies (Huebert et al., 1988;Yao et al., 2002), the high mass ratio of NO_3^-/SO_4^{2-} (>1.0) was regarded as a sign of dominant traffic

emission. Wang et al. (2015) found that the high mass ratio of NO_2/SO_2 resulting from traffic emissions was a major reason in triggering the heavy haze in Shanghai. In this work, the evaluation of BC-containing particles also suggested that high concentrations of NO_2 and possibly volatile organics and their transformations play a vital role for particle growth and the increase of PM loading in urban area especially during a heavy pollution episode. Reductions in the emissions of gaseous precursors are critical for remediation of the severe urban haze pollution in China.

4 Conclusions

In this study, we characterized BC-containing particles during a heavy air pollution episode in Shanghai. The rBC mass loading in Shanghai was similar to other cities in China but much higher than in other mega-cities around the world, with an average of 3.2 μg m^{-3} and the peak value of 12.1 μg m^{-3} at 04:26 LT on 7 December 2013. The rBC mass accounted for 1.45% of $PM_{2.5}$ mass on average. The number- and mass-weighted BC core size distributions were around ~60-400 and 70-500 nm, with peaks around ~60 and ~200 nm, respectively.

Through SPAMS, we classified the BC-containing particles into 6 groups, according to their mass spectral patterns. The pure BC particles accounted for 0.62% number fraction of BC-containing particles (although this number could be underestimated because of the low detection efficiency for pure BC in SPAMS). The BBBC particles from biomass burning accounted for 25.57%. The KBC, BCOC-NOx and BCOC-SOx from traffic emissions accounted for 70.18%. The remaining unidentified particles accounted for 3.63%.

The size distribution of internally-mixed rBC particles was bimodal. The condensation mode mainly consisted of traffic emissions, which had a small core (~60-80 nm) with thin ACT (~50-130 nm). The droplet mode included biomass burning and deeply aged traffic-emitted rBC-containing particles. The biomass burning particles had larger core sizes (~80-130 nm) with thick ACT (~110-300 nm) and the highly aged traffic emissions had small core sizes (~60-80 nm) with thick ACT (~130-300 nm). It is rare to see the

traffic-emitted rBC growing so quickly to the droplet mode. The high concentration of NO_2 and its rapid conversion to particulate nitrate accelerated the growth of BC-containing particles and contributed to the high particle mass concentration during this heavy air pollution episode.

The quantitative number and mass information provided by SP2 supplemented the SPAMS chemical analysis in the entire experiment. The two complementary techniques can detect the physical and chemical properties of BC aerosol with single particle resolution. The combined use of SP2 and SPAMS would have potential of wider applications for future projects.

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800 **Table 1.** Names, numbers and fractions of six types of BC-containing particles detected
801 by the SPAMS instrument.

Group	Number of particles	Fraction of particles
Pure BC	535	0.62%
Biomass Burning BC-containing (BBBC)	22 007	25.57%
K-rich BC-containing (KBC)	11 343	13.18%
BC internally-mixed with OC and ammonium nitrate (BCOC-NOx)	33 760	39.23%
BC internally-mixed with OC and ammonium sulfate (BCOC-SOx)	15 291	17.77%
Unidentified	3121	3.63%
Total BC-containing	86 057	100%

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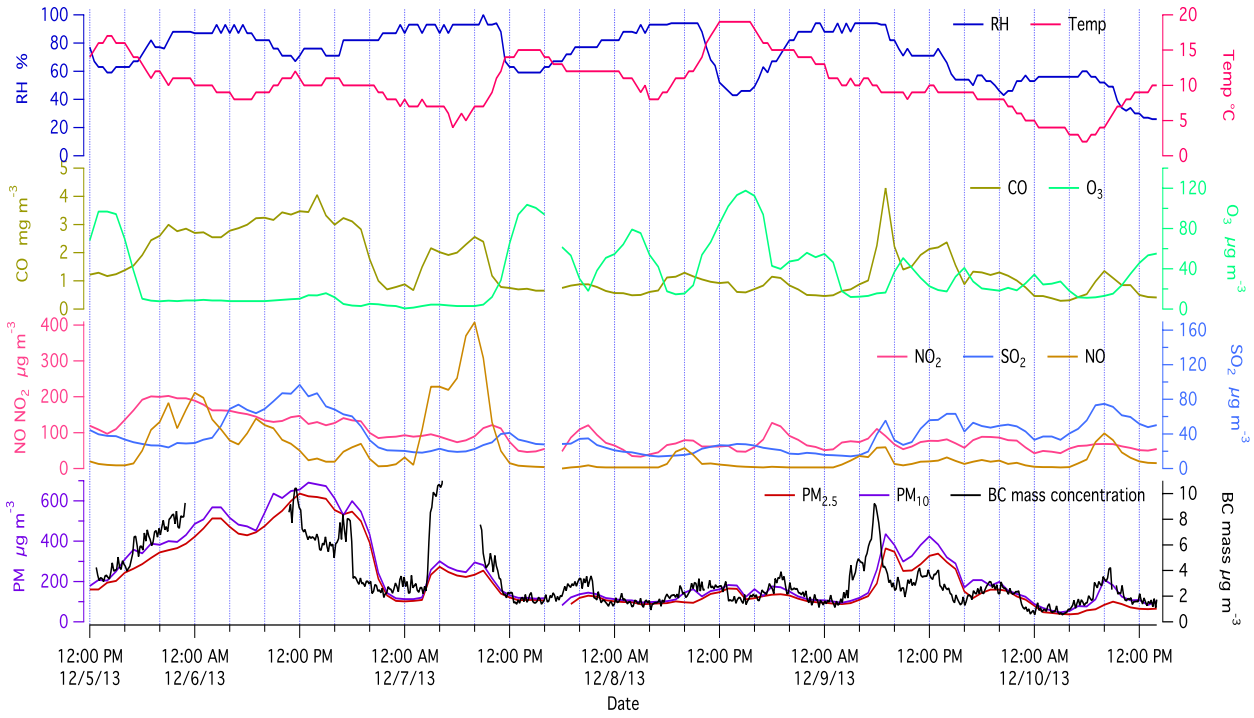

805

806 **Figure 1.** Temporal profiles of selected meteorological parameters (temperature,
807 relative humidity) with 30 min resolution, gaseous pollutants (CO, O_3, SO_2, NO and NO_2),
808 $PM_{2.5}$ and PM_{10} mass concentrations with 60 min resolution. The concentration of rBC
809 mass (black trace in the bottom panel, 10 min resolution) was continuously measured by
810 SP2.

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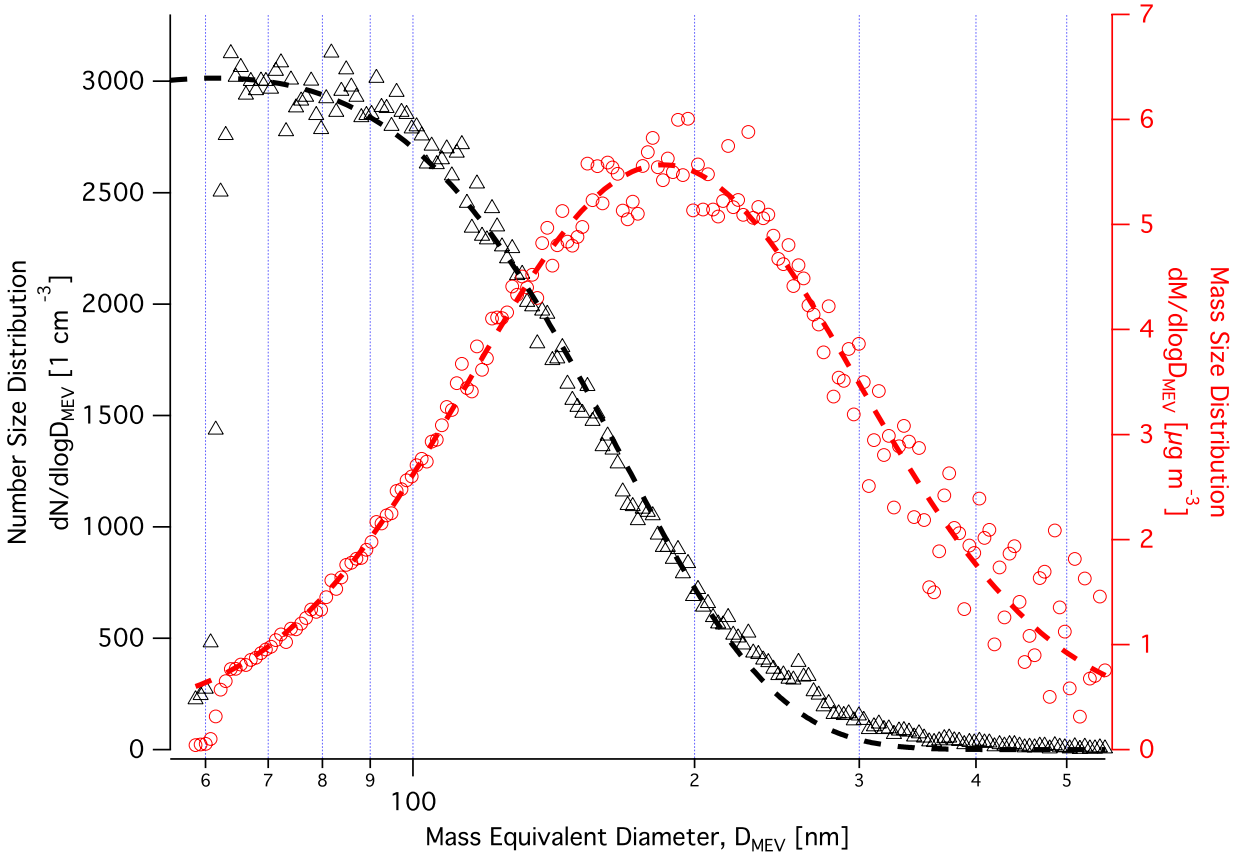
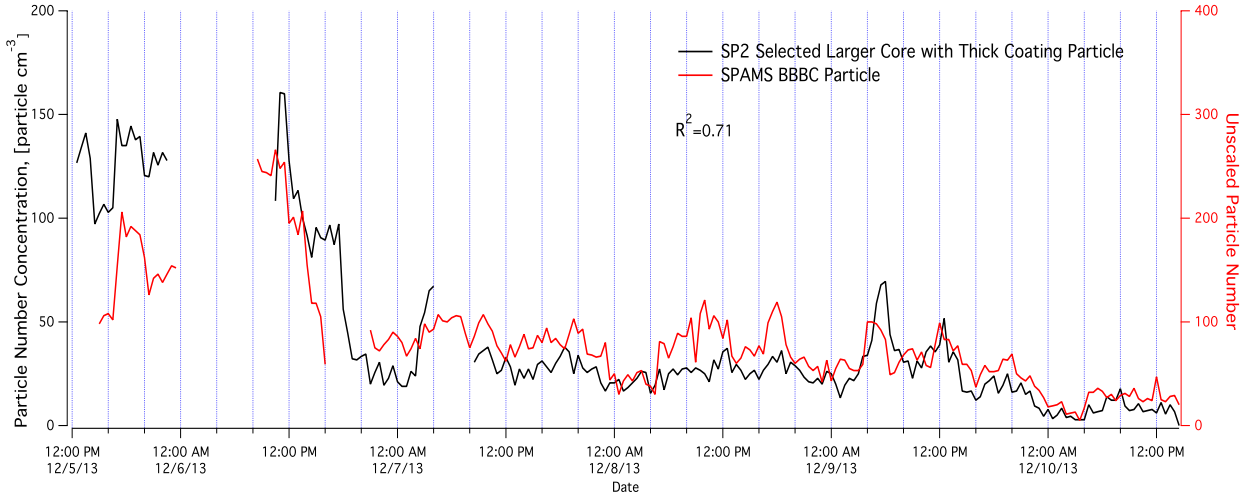


812

813 **Figure 2.** The measured rBC core mass size distribution and number size distribution are
814 shown in open red and black markers, respectively. The log-normal fits to the observed
815 distributions are shown by the dashed lines.



816

817 **Figure 3.** Comparison of the SPMAS-detected BC-containing particles and SP2-detected
818 internally-mixed rBC-containing particles.

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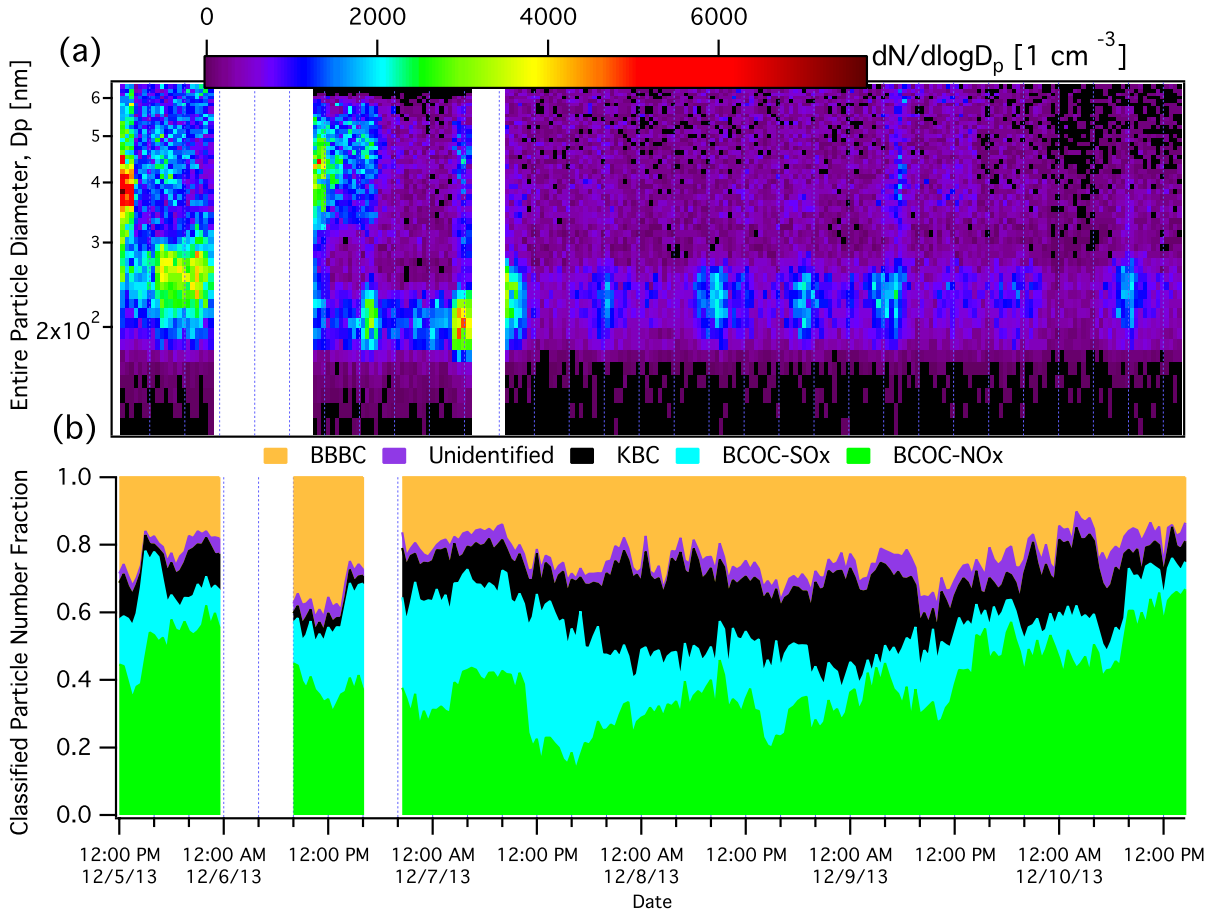

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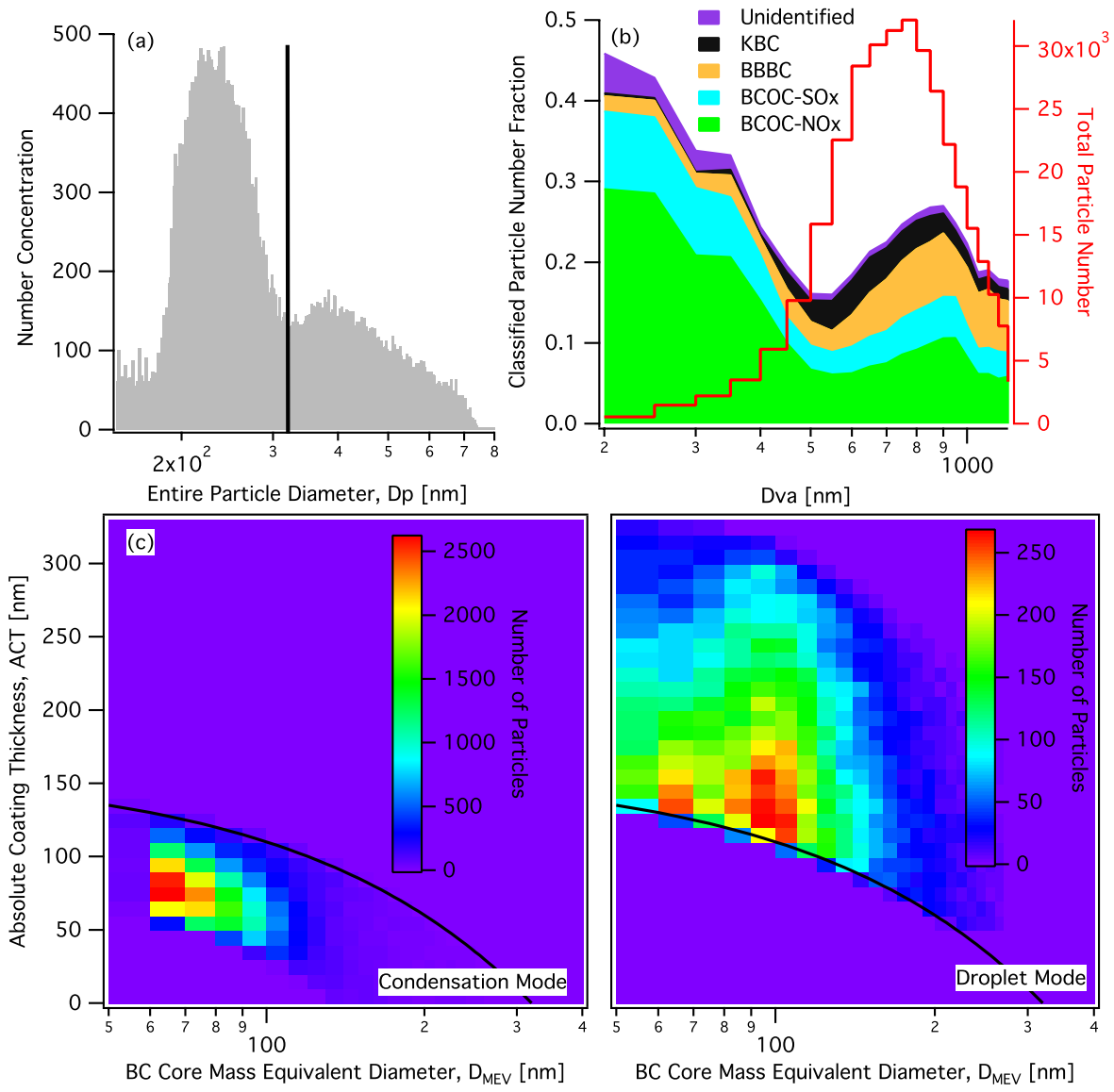
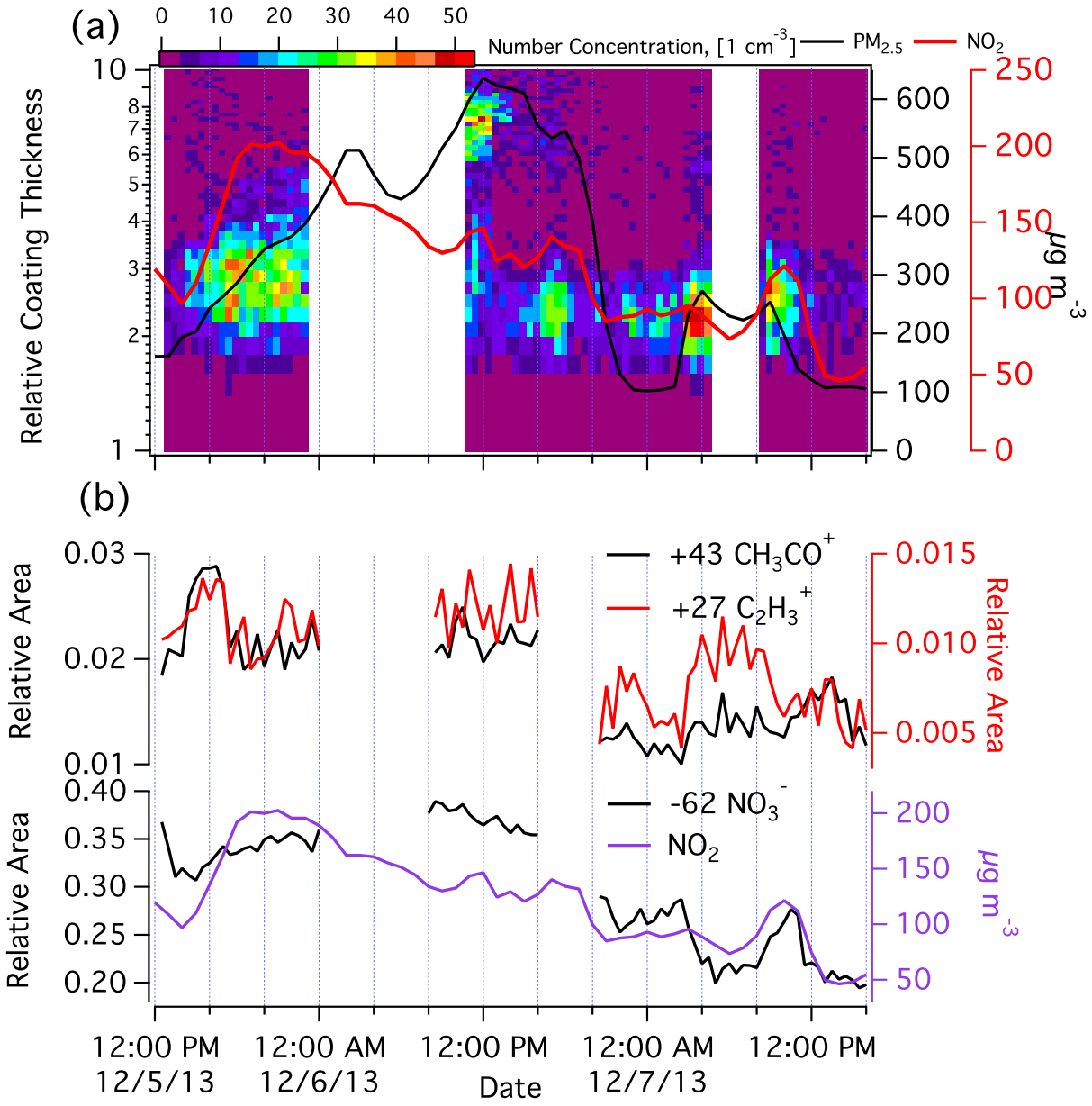
822 **Figure 4.** (a) Temporal variations of number and size distributions for rBC-containing
823 particles detected by SP2 with 30 min resolution. (b) Temporal variation of number
824 fractions of different BC-containing particle types with 10 min time resolution (detected
825 by SPAMS).



826

827 **Figure 5.** **(a)** D_p number size distribution histogram for the SP2-detected rBC-containing
828 particles. **(b)** D_{va} number fraction distribution of SPAMS-detected BC-containing
829 particles color-coded by the particle type. **(c)** D_c and ACT with number size distribution
830 in the condensation and droplet modes.



831

832 **Figure 6.** (a) Temporal variation of the relative coating thickness distribution of
833 traffic-emitted rBC-containing particles (SP2) with resolutions of 0.2 RCT and 30 min
834 and the temporal profile of NO_2 and $PM_{2.5}$ concentrations with 60 min resolution. (b)
835 Temporal variation of relative peak areas of +27 ($C_2H_3^+$), +43 (CH_3CO^+) and -62 (NO_3^-)
836 of traffic-emitted BC-containing particles (SPAMS) and NO_2 concentration with 30 min
837 resolution.