

1 **Characterization of black carbon-containing fine particles**

2 **in Beijing during wintertime**

3 Junfeng Wang¹, Dantong Liu², Xinlei Ge^{1*}, Yangzhou Wu¹, Fuzhen Shen¹, Mindong Chen¹, Jian
4 Zhao^{3,4}, Conghui Xie^{3,4}, Qingqing Wang³, Weiqi Xu^{3,4}, Jie Zhang⁵, Jianlin Hu¹, James Allan^{2,6},
5 Rutambhara Joshi², Pingqing Fu³, Hugh Coe² and Yele Sun^{3,4}

6 ¹Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, School of
7 Environmental Science and Engineering, Nanjing University of Information Science and Technology,
8 Nanjing 210044, China

9 ²School of Earth and Environmental Sciences, University of Manchester, M13 9PL, Manchester, UK

10 ³State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute
11 of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

12 ⁴University of Chinese Academy of Sciences, Beijing 100049, China

13 ⁵Atmospheric Sciences Research Center, University at Albany, State University of New York, NY,
14 12203, USA

15 ⁶National Centre for Atmospheric Science, University of Manchester, M13 9PL, Manchester, UK

16
17 *Corresponding author, Email: caxinra@163.com

18 Phone: +86-25-58731394

19
20 For *Atmospheric Chemistry & Physics*

21
22
23
24

25 **Abstract**

26 Refractory black carbon (BC) is a product from incomplete combustion of fossil fuel, biomass and
27 biofuel, etc. By mixing with other species, BC can play significant roles in climate change, visibility
28 impairment and human health. Such BC-containing particles in densely-populated megacities, like
29 Beijing, may have specific sources and properties, that are important to haze formation and air quality.
30 In this work, we characterized exclusively the BC-containing particles in urban Beijing, by using a
31 laser-only Aerodyne soot particle aerosol mass spectrometer (SP-AMS), as a part of the Air Pollution
32 and Human Health (APHH) 2016 winter campaign. The average mass ratio of coating-to-BC (R_{BC})
33 was found to be ~ 5.0 . Positive matrix factorization shows presence of significant primary fossil fuel
34 and biomass burning organics (64% of total organics). Yet secondary species, including sulfate, nitrate
35 and oxygenated organic aerosol (OA) species, could have significant impacts on the properties of BC-
36 containing particles, especially for ones with larger BC core sizes and thicker coatings. Analyses of
37 sources and diurnal cycles of organic coating reveal significant afternoon photochemical production
38 of secondary OA (SOA), as well as nighttime aqueous production of a portion of highly oxygenated
39 OA. Besides SOA, photochemical production of nitrate, not sulfate, appeared to be important. Further
40 investigations on BC-containing particles during different periods show that, on average, more
41 polluted periods would have more contributions from secondary species, and more thickly coated BC
42 tended to associate with more secondary species, indicating the important role of chemical aging to
43 the pollution of BC-containing particles in urban Beijing during wintertime. However, for individual
44 pollution events, primary species (fossil fuel, coal and biomass burning emissions) could also play a
45 dominant role, as revealed by the compositions of BC-particles in two polluted episodes during the
46 sampling period.

47

48

49 1. Introduction

50 Black carbon (BC) is generated from incomplete combustion of carbon-based fuels (Ramanathan
51 and Carmichael, 2008), and can exert significant impacts on global and regional climate, planetary
52 boundary layer height (PBLH), air quality and human health, etc. (Lee et al., 2017; Bond et al., 2013;
53 Ding et al., 2016). BC can strongly absorb solar radiation and warm up the atmosphere directly. By
54 internally or externally mix with non-BC materials (coatings, including co-emitted primary
55 organics/inorganics and secondary materials that associate with BC) (Chen et al., 2016a; Lee et al.,
56 2017; Wang et al., 2017a), the properties and morphologies of BC might be altered greatly (Liu et al.,
57 2013; Liu et al., 2017; Liu et al., 2015; Cappa et al., 2012; Peng et al., 2016; Wang et al., 2017c; Li et
58 al., 2016). Thick coating can increase the mass absorption cross section of BC, thus enhance the light
59 absorption of BC core via “lensing effect” (Jacobson, 2011; Liu et al., 2015; Pokhrel et al., 2017).
60 However, coating thickness of BC-containing particles significantly depends on sources/chemical
61 compositions and aging processes, thus there are great uncertainties on light absorption enhancement
62 (E_{abs}) of BC as well as its global radiative forcing (Cappa et al., 2012; Liu et al., 2017; Cui et al., 2016;
63 Liu et al., 2015). For instance, the mass ratio of coatings to BC core (R_{BC} , an analog of coating
64 thickness) from biomass burning is usually greater than 3 (Liu et al., 2017) and can be larger than 10
65 in remote sites (Wang et al., 2017a). Normally, when R_{BC} is less than 1.5, it is probably from traffic
66 sources, whereas secondary organic aerosol (SOA) dominated BC-containing particles is usually with
67 a R_{BC} greater than 4 (Lee et al., 2017). Moreover, the coating species can modify the hygroscopicity
68 of BC-containing particles (Liu et al., 2013) when associated with hydrophilic materials, and some of
69 them can activated into cloud condensation nuclei (CCN), therefore alter the albedo and precipitation
70 of clouds indirectly (Dusek et al., 2010; Dusek et al., 2006).

71 In the past decades, a number of field studies on BC have been conducted in the winter of Beijing,
72 and mainly focused on BC mass loadings, mixing states, optical properties, human health impacts and
73 sources (coal combustion, biomass burning and vehicles, etc.) (Wu et al., 2017; Cheng et al., 2017; Ji
74 et al., 2017; Wang et al., 2017b; Wu et al., 2016; Chen et al., 2016b; Meng et al., 2016; Wang et al.,
75 2016b; Liu et al., 2016; Yang et al., 2014; Schleicher et al., 2013a; Schleicher et al., 2013b; Song et
76 al., 2013; Zhang et al., 2017). There were real-time studies on BC, and on the chemical characteristics
77 of total fine particles (including particles with and without BC) in Beijing. However, to the best of our
78 knowledge, no study was conducted in real-time to characterize the chemical compositions exclusively

79 of BC-containing particles in Beijing despite the important effects of coating materials on BC
80 properties aforementioned. Currently, a few studies have explored BC-containing particles in other
81 locations, e.g., Toronto (Willis et al., 2016; Lee et al., 2015), California (Lee et al., 2017; Massoli et
82 al., 2015; Cappa et al., 2012), London (Liu et al., 2015) and Tibet (Wang et al., 2017a) by using the
83 Aerodyne soot-particle Aerosol Mass Spectrometer (SP-AMS) (Onasch et al., 2012; Lee et al., 2015;
84 Wang et al., 2016a; Ge et al., 2017b). The SP-AMS physically combines the 1064 nm laser vaporizer
85 of single particle soot photometer (SP2) into a high-resolution aerosol mass spectrometer (HR-AMS).
86 After removal of the AMS tungsten vaporizer and by operating the instrument with laser vaporizer
87 only, refractory BC as well as its associated coating can be evaporated since the 1064 nm laser can
88 selectively heat the BC (Massoli et al., 2015). In other words, laser-only SP-AMS can exclusively
89 measure BC cores and the species coated on BC cores. This unique technique allows us to explore in
90 details the characteristics of BC-coating species with no perturbations from other co-existing non-BC
91 containing particles in ambient air.

92 Beijing, as the most comprehensive megacity with a large population in developing countries, the
93 BC-containing particles may have specific source profiles and physiochemical properties, therefore
94 elucidation of its characteristics is important to understand the haze formation and improve air quality
95 in such regions. In this work, as a part of the UK-China Air Pollution and Human Health (APHH)
96 study (Shi et al., 2018), we report for the first time the real-time measurement results on the chemical
97 composition, mass loading, size distribution, and sources/processes of BC-containing particles during
98 wintertime of 2016 in urban Beijing. Results regarding physical properties and optical properties are
99 presented in Liu et al. (2018) and Xie et al. (2018) of this special issue, respectively.

100

101 **2. Experiments**

102 **2.1 Sampling site and instrumentation**

103 As a part of the APHH winter campaign, we conducted measurements at the Tower Division of
104 Institute of Atmospheric Physics (IAP), Chinese Academy of Science (39°58'N, 116°22'E) in Beijing
105 (Figure S1 in the supplement), from 15 November to 13 December of 2016. The site was surrounded
106 by residential infrastructures and a freeway in the east (360m).

107 The SP-AMS was deployed on the rooftop of Herong Building (~8m above the ground), with a
108 PM_{2.5} cyclone (Model URG-2000-30EN) and a diffusion dryer in front of the inlet. The single particle

109 soot photometer (SP2, Droplet Measurement Technology, Inc., Boulder, CO, USA) was operated
110 simultaneously inside another container nearby (~20 m away) on the ground. The SP2 incandescence
111 signal was calibrated for BC mass by using Aquadag® black carbon standard (Aqueous Deflocculated
112 Acheson Graphite, Acheson Inc., USA) (Laborde et al., 2012). For the SP-AMS, since the filament
113 that ejects electrons can still heat the tungsten vaporizer up to ~200 °C (Willis et al., 2014) even it is
114 turned off, the tungsten vaporizer was thus physically removed to make sure only BC and its associates
115 were vaporized by the laser, and to eliminate influences from species uncoated on BC cores.

116 The tuning and calibration procedures of SP-AMS followed the procedures described previously
117 (Lee et al., 2015; Willis et al., 2016; Massoli et al., 2015; Wang et al., 2017a). During the campaign,
118 the SP-AMS was run with a 10-minutes cycle: one W mode with high chemical resolution (2.5 min)
119 and two mass sensitive V modes including one with particle time of flight (PToF) mode (2.5 min) and
120 another one (5 min) with a large mass-to-charge (m/z) range (up to 2000) (Wang et al., 2016a). The
121 filtered air measurement was performed for a day to determine the detection limits (DLs) of various
122 aerosol species and to adjust the fragmentation table. The ionization efficiency (IE) and relative
123 ionization efficiency (RIE) of sulfate and nitrate were calibrated by using pure ammonium nitrate and
124 ammonium sulfate according to Jayne et al. (2000), respectively. RIE of BC was calibrated by using
125 Regal Black (RB, REGAL 400R pigment black, Cabot Corp.) (Onasch et al., 2012), and the average
126 ratio of C_1^+ to C_3^+ was determined to be 0.53 to minimize the influence of C_1^+ from non-refractory
127 organics. However, it should be aware that laser-only SP-AMS cannot vaporize ammonium
128 nitrate/sulfate if they do not coat on BC, thus the IE and RIE calibrations were done before removal of
129 the tungsten vaporizer and the values were assumed to be unchanged after the tungsten heater's
130 removal (Willis et al., 2016). Note the RIE of BC was calibrated before the campaign and was repeated
131 in the middle and end of the campaign. RIEs of nitrate, ammonium, sulfate and BC were determined
132 to be 1.1, 3.82, 0.82, and 0.17, respectively. The default value of 1.4 was used as RIE of organics
133 (Canagaratna et al., 2007). Polystyrene latex (PSL) spheres (100-700 nm) (Duke Scientific Corp., Palo
134 Alto, CA) were used to calibrate the size before the campaign (Canagaratna et al., 2007).

135 **2.3 Data Analysis**

136 Standard AMS data analysis software (Squirrel and Pika) based on Igor Pro 6.37 (Wavemetrics,
137 Lake Oswego, OR, USA) were used to obtain the concentrations, mass spectra and size distributions
138 of BC and its coating species. All data were calculated based on high-resolution fitting results. Due to

139 different vaporization schemes between the SP-AMS and HR -AMS, mass spectra from these two
140 instruments even for the same population of particles are not entirely the same. Laser-only SP-AMS
141 can result in overall less fragmentation, therefore the mass profile may contain more large m/z
142 fragments and less small m/z fragments compared with that from HR-AMS (Massoli et al., 2015).
143 Therefore, here the elemental ratios of organics, i.e., oxygen-to-carbon, hydrogen-to-carbon and
144 nitrogen-to-carbon ratios (O/C, H/C and N/C) were determined by the Aiken approach first (Aiken et
145 al., 2008), and then O/C and H/C were corrected by using factors of 0.83 and 1.16, respectively
146 (Canagaratna et al., 2015).

147 Source apportionment for organics coated on BC was conducted by using Positive matrix
148 factorization (PMF) (Paatero and Tapper, 1994) Evaluation Tool written in Igor (Ulbrich et al., 2009).
149 In this study, high-resolution mass spectra (HR-MS) of organic (including BC) and inorganic species
150 were combined together to perform the PMF analyses (Sun et al., 2012; Wang et al., 2017a; Wang et
151 al., 2018). It should be noticed that, only fragment ions from polycyclic aromatic hydrocarbons (PAHs)
152 were included for m/z range of ~ 150 to ~ 250 in the PMF analysis because of the limited mass resolution
153 of SP-AMS. All PMF solutions were evaluated following the standard instruction (Zhang et al., 2011).
154 Finally, four types of organic aerosol (OA) associated with BC were determined eventually, including
155 a fossil fuel combustion OA (FFOA), a biomass burning OA (BBOA) and two oxygenated OA (OOA1
156 and OOA2) (a diagnostic plot was provided in Fig. S2).

157 Supporting data such as meteorological parameters including relative humidity (RH), wind speed
158 (WS), wind direction (WD) and temperature (T), as well as concentrations of gaseous species such as
159 O₃, SO₂, NO, NO₂, NO_x, NO_y, NO_z, and CO were measured in parallel simultaneously. All data
160 reported here were at local time (Beijing Time, UTC+8).

161

162 **3. Results and discussion**

163 **3.1 Overview of BC-containing aerosol characteristics**

164 Figs. 1 and 2 show the temporal variations of meteorology parameters, mass loadings of gaseous
165 pollutants (CO, NO_x, SO₂ and O₃), BC and its associated coating components (sulfate, nitrate,
166 ammonium, chloride, total OA and four PMF-resolved OA factors). The campaign-averaged
167 composition of BC-containing particles and mass contributions of the four OA factors to total OA were
168 also displayed in Fig. 2. Overall, wind directions and speeds had close associations with overall mass

169 loadings of BC-containing particles. The pollution periods (characterized by concentrations of BC-
170 containing particles above $10 \mu\text{g m}^{-3}$) were accompanied by relatively low wind speeds ($<4 \text{ m s}^{-1}$) and
171 in a relatively large part from southern air masses since Beijing is at the foot of the mountains which
172 facilitate the accumulation of pollutants from southern North China Plain (NCP). The clean periods
173 (characterized by the concentrations of BC-containing particles below $10 \mu\text{g m}^{-3}$) were mainly under
174 the control of northwest strong winds ($>4 \text{ m s}^{-1}$) (Fig. S3). During the campaign, the mass loadings of
175 BC cores and BC-containing particles ranged from $0.11 \sim 26.54 \mu\text{g m}^{-3}$ and $0.71 \sim 174.40 \mu\text{g m}^{-3}$, with
176 an average of $4.9 \mu\text{g m}^{-3}$ and $29.4 \mu\text{g m}^{-3}$, respectively. We also compared BC concentrations
177 determined by the SP-AMS with those from SP2, and they correlated quite well with each other (r^2 of
178 0.93; Fig. S4), indicating the quantification of BC by the SP-AMS is reliable.

179 The coating species occupied on average about 83.4% of the mass of BC-containing particles,
180 indicating BC was generally thickly coated throughout the whole campaign, with an average mass
181 ratio of coatings to BC (R_{BC}) of ~ 5.0 . Organic aerosol (OA) was the most abundant coating component,
182 taking up to 59.4% of the total mass, followed by nitrate (8.8%), sulfate (6.5%), ammonium (4.7%)
183 and chloride (4.0%). OA correlated quite well with BC (r^2 of 0.97), suggesting that many OA species
184 were co-emitted and mixed with BC, and indeed, primary OA (POA=FFOA+BBOA) was found to
185 dominate the OA mass ($66.3\%=43.9\%+22.4\%$). Chloride (Cl^-) had a great correlation with BC (r^2 of
186 0.94), suggesting it was mainly associated with primary emissions, for example, gasoline, diesel and
187 coal combustion during wintertime in urban Beijing. Sulfate and nitrate are typically secondarily
188 formed, therefore their correlations with BC were relatively weak (r^2 of 0.64 for SO_4^{2-} vs. BC, and
189 0.60 for NO_3^- vs. BC). Their properties are discussed in details in the following sections.

190 191 **3.2 Chemically-resolved size distributions of BC-containing particles**

192 Fig. 3a shows the campaign-averaged mass-based size distributions of major BC-coating species,
193 including organics (BC-Org), sulfate (BC-Sulfate), nitrate (BC-Nitrate), chloride (BC-Chl) and BC
194 core itself. It should be noticed that the size distribution of BC was scaled from that of m/z 24 (C_2^+),
195 as other major carbon cluster ions might be significantly affected by other ions, for example, C_1^+ at
196 m/z 12 can be influenced by fragments from non-BC organics, C_3^+ at m/z 36 by HCl^+ , C_4^+ at m/z 48 by
197 SO^+ , and C_5^+ at m/z 60 by $\text{C}_2\text{H}_4\text{O}_2^+$ etc. Similarly, the size distribution of BC-Chl was scaled from Cl^-
198 signal at m/z 35. As shown in Fig. 3a, on average, size distributions of BC-Sulfate, BC-Nitrate and BC-

199 Org displayed a similar pattern with a major peak at ~550 nm (vacuum aerodynamic diameter, D_{va}),
200 suggesting that they were relatively well internally mixed. However, the BC presented a remarkably
201 different pattern with a much broader distribution and smaller peak sizes than its coating species, and
202 in particular, relatively small particles tended to have thin coatings.

203 Figs. 3b-f further present image plots of size distributions of the major aerosol components as a
204 function of R_{BC} (a surrogate of coating thickness). Different from the average data shown in Fig. 3a,
205 the coating species can be roughly classified into two modes separated by R_{BC} of ~4.5. Most sulfate
206 and nitrate concentrated at $R_{BC}>4.5$ (Figs. 3b and 3c): Sulfate peaked in a narrow R_{BC} range of 5.5~6.5,
207 while significant nitrate mass could distribute across a wider R_{BC} range (even to R_{BC} of ~8.0). Only
208 organics and chloride had a significant portion of mass distributed on relatively thinly coated BC-
209 containing particles at $R_{BC}<4.5$ (Figs. 3e and 3f). Specifically, they both showed a sub-mode locating
210 in the regime with R_{BC} of ~3.5-4.5 and D_{va} of ~200-700nm. These sub-modes suggest that organics or
211 chloride are partially from primary sources as freshly emitted BC are more likely thinly coated. This
212 is consistent with that organics included species from fossil fuel and biomass burning combustion
213 revealed by the PMF analysis. Similarly, coal burning might contribute to chloride during wintertime
214 in Beijing (Sun et al., 2016). As for sulfate and nitrate, since they are predominantly secondary species,
215 they would coat on BC cores due to chemical aging therefore mostly distributed at higher R_{BC} .

216

217 3.3 Sources of organic coating species

218 The HRMS of different factors of the organic coating resolved from PMF analyses, their relative
219 contributions and diurnal cycles of temporal variations relative to BC are shown in Fig. 4. Fig. 4a
220 illustrates the mass profile of the fossil fuel combustion OA with BC carbon clusters (FFOA + BC).
221 This factor had a low O/C ratio of 0.16. In this work, this factor might include emissions from both
222 traffic and coal combustion, as it contained a series of significant PAHs ion fragments in the mass
223 spectrum (PAHs fragments are negligible in other factors) indicative of coal burning (Sun et al., 2014;
224 Sun et al., 2016), and presented a good correlation with $C_4H_9^+$ (r^2 of 0.72) - a AMS tracer ion of vehicle
225 emissions (Zhang et al., 2005). Temporal variations of FFOA also correlated well with $C_9H_7^+$ (m/z 115,
226 r^2 of 0.92) and Cl^- (r^2 of 0.60), which have been proposed as possible coal combustion tracer species
227 (Yan et al., 2018; Sun et al., 2014). The FFOA/BC (Fig. 4f) appeared to be higher during nighttime
228 than that during daytime. Note the diurnal pattern of BC itself (Fig. 5c) was similar as that of FFOA/BC.

229 The diurnal variations of BC might be influenced by both fossil fuel combustion activities and
230 relatively low PBLH during nighttime. The fossil fuel combustion included coal burning and vehicle
231 emissions (gasoline cars, and the heavy-duty diesel vehicles that are only allowed to enter the city
232 during later night). The mass ratios of different factors to BC shall have less influences from PBLH,
233 therefore high levels of FFOA/BC strongly indicate that co-emitted organic species with BC from
234 fossil fuel combustion were enhanced during nighttime.

235 Figure 4b shows the mass spectrum of BBOA and related BC clusters. One feature of this factor
236 is that it had relatively high fractional contributions of $C_2H_4O_2^+$ (1.47% of total) and $C_3H_5O_2^+$ (0.95%),
237 which are often regarded as AMS marker ions from biomass burning emitted levoglucosan (Cubison
238 et al., 2011; Mohr et al., 2009). Note the FFOA also contained appreciable $C_2H_4O_2^+$ and $C_3H_5O_2^+$
239 signals, partially due to that coal burning (such as lignite) can emit some levoglucosan as well (Yan et
240 al., 2018). Nevertheless, mass fractions of $C_2H_4O_2^+$ and $C_3H_5O_2^+$ in FFOA were less than those in
241 BBOA, and they correlated much better with BBOA than those with FFOA (for examples, r^2 of 0.90
242 for BBOA vs. $C_2H_4O_2^+$, and 0.72 for FFOA vs. $C_2H_4O_2^+$). The BBOA correlated very well with another
243 biomass burning tracer - K^+ (r^2 of 0.90). In addition, BBOA had negligible PAHs ion fragments while
244 the FFOA contained remarkably high PAHs signals. Such characteristics are generally in agreement
245 with previous AMS findings in the same location during wintertime in Beijing (Sun et al., 2016). For
246 these reasons, the second factor was identified as BBOA. The diurnal pattern of BBOA/BC reached
247 minimum during afternoon and was overall high during nighttime, similar as FFOA/BC, indicating the
248 nighttime enhancement of BB-related organics emissions in wintertime Beijing.

249 Besides the two POA factors, we also identified two secondary OA factors (OOA1 and OOA2),
250 whose O/C ratios were 0.45 and 0.28, respectively. OOA1 was the most oxidized OA factor that had a
251 higher $CO_2^+/C_2H_3O^+$ ratio than that of OOA2. The correlation between OOA1 and sulfate was better
252 than it with nitrate (r^2 of 0.99 vs. 0.86). As a comparison, the less oxygenated OOA2 correlated better
253 with nitrate than it with sulfate (r^2 of 0.59 vs. 0.34). These characteristics are consistent with previous
254 AMS-PMF results (Zhang et al., 2011). Opposite to the diurnal cycles of FFOA and BBOA, the
255 OOA2/BC ratio arose significantly from early morning and peaked in the afternoon (~3pm). The
256 diurnal pattern of OOA1/BC presented a similar peak at ~3pm. This result demonstrates a clear
257 evidence and important role of afternoon photochemical reactions to the formation of secondary
258 organic species. However, the precursors leading to the formations of OOA1 and OOA2 remain to be

259 elucidated. Interestingly, for OOA1/BC, in addition to the peak during afternoon, it increased during
260 early evening and remained at high levels until early morning. This result indicates that nighttime
261 aqueous-phase processing (high levels of RH during nighttime shown in Fig. 5a) can also contribute
262 to OOA1 production. As such behavior was not observed for OOA2/BC, it agrees with previous field
263 and laboratory findings that aqueous-phase reactions tend to produce more highly oxygenated species
264 (Ervens et al., 2011; Ge et al., 2012; Herrmann et al., 2015; Xu et al., 2017).

265 Overall, the mass fractions of BC cores that were associated with fossil fuel combustion, biomass
266 burning, less and more oxygenated secondary processes were 32.7%, 31.8%, 18.7% and 16.9%,
267 respectively (Fig. 4e). The organic coating of BC was predominantly primary species.

268

269 **3.4. Diurnal patterns of BC and coating species**

270 Fig. 5 presents the diurnal cycles of meteorological parameters (T, RH, WS and WD), BC
271 concentrations and R_{BC} , mass ratios of major species to BC, gaseous species (CO, SO₂ and NO_x), O/C
272 and OS_c (oxidation state, defined as $2 \cdot O/C - H/C$) (Kroll et al., 2011). Note BC did not present a peak
273 at 8:00 am, yet R_{BC} , Org/BC, SO₄²⁻/BC, NO₃⁻/BC and Cl⁻/BC were all low at ~8:00 am. This was likely
274 attributed to increase of the mass fractions of fresh and barely coated BC-containing particles (rather
275 than the increase of absolute concentrations of fresh BC-containing particles) emitted during morning
276 rush hours from traffic emissions, etc. This was consistent with the decreases of O/C and OS_c and
277 increases of CO and NO₂ at 8:00 am of the day. On the contrary, the R_{BC} drop at ~4:00 pm was unlikely
278 due to influences of afternoon rush hours, as there were no increases of CO, NO₂, and both O/C and
279 OS_c were at high levels. In fact, the 4:00pm R_{BC} drop was mainly caused by the large decrease of
280 Org/BC (as SO₄²⁻/BC, NO₃⁻/BC and Cl⁻/BC did not decrease at 4:00pm, Fig. 5d) - mainly the portions
281 of fossil fuel and biomass burning OA (Fig. 4f).

282 The diurnal variation of NO₃⁻/BC peaked at ~3-4 pm, consistent with the variation of T, and similar
283 as those in the previous reports during wintertime in Beijing (Ge et al., 2017a; Sun et al., 2016),
284 reflecting the dominated contribution of photochemical formation of nitrate. SO₄²⁻/BC showed a
285 relatively small afternoon increase, indicating partial sulfate was produced from photochemical
286 activities; it also presented a nighttime enhancement, similar as OOA1/BC, suggesting the sulfate
287 formation in aqueous-phase, consistent with the nighttime increase of RH and decrease of temperature
288 (Fig. 5a). Due to increases of FFOA/BC, BBOA/BC and OOA1/BC (the portion likely from aqueous-

289 phase production), Org/BC remained at high levels during nighttime. All these increases added together,
290 leading to the high R_{BC} during nighttime. In addition, Cl/BC varied generally similar to those of
291 FFOA/BC and BBOA/BC, again indicating its strong association with primary emissions.

292

293 **3.5 Characteristics of coating species during different periods**

294 **3.5.1 Coating compositions during clean and pollution periods**

295 Fig. 6 shows the variations of BC-coating compositions as a function of R_{BC} during clean (CP)
296 and pollution periods (PP) (divided by the concentration of $10 \mu\text{g}/\text{m}^3$), respectively. Contrasting
297 difference of the coating composition during these two cases was observed: primary OA (especially
298 FFOA) appeared to be the most abundant component during CP while mass contributions of secondary
299 organic and inorganic species were remarkably high during PP (Figs. 6a and b), and the average R_{BC}
300 during PP (~ 5.1) was also higher than that during CP (~ 4.5) (Fig. 6f). These results again reinforce the
301 importance of secondarily formed species to the heavy haze pollution in urban Beijing (Huang et al.,
302 2014). Furthermore, the BC coating composition as well as OS_c during CP were both relatively stable
303 against R_{BC} (Fig. 6c). On the contrary, during PP, with the increase of R_{BC} , the mass fractions of
304 secondary species (OOA1, nitrate and sulfate) increased clearly, especially at $R_{BC} > 5$; consistently, OS_c
305 of organic coating increased from ~ -0.85 to > -0.70 . Such behavior again highlights the contribution of
306 chemical aging process to the heavy haze pollution.

307 Relative to other observations (Wang et al., 2017a; Massoli et al., 2015; Cappa et al., 2012), the
308 levels of R_{BC} during both CP and PP are much smaller than those for highly aged BC, which might
309 have $R_{BC} > 10$. As BC-containing particle in urban Beijing were influenced by multiple local/regional
310 primary sources, relative amount of secondarily formed coating species would be less than those of
311 highly aged BC, therefore this lower R_{BC} is expected. On the other hand, the R_{BC} levels are generally
312 higher than those found for the BC-containing particles in Los Angeles where the average R_{BC} was
313 typically smaller than 4 due to direct and prominent influence of vehicle emissions (Lee et al., 2017).
314 Regarding the variations of coating composition vs. R_{BC} , the behavior during PP is in fact consistent
315 with a few previous field measurement results in American or European urban locations (Massoli et
316 al., 2015; Liu et al., 2017; Lee et al., 2017; Cappa et al., 2012; Collier et al., 2018), indicating a general
317 behavior for BC-containing particles in urban area that more aged BC tends to have thicker coating.
318 Yet this property can be altered if significant POA emissions exist, such as the case during CP in this

319 work, and a case with heavy BBOA influences observed in Tibet Plateau (Wang et al., 2017a).

320

321 **3.5.2 Coating compositions during two different episodes**

322 Although we demonstrated in Section 3.5.1, the heavy pollution of BC-containing particles was
323 on average associated with more secondary species, the underlying governing factors of individual
324 pollution events might vary from each other. Here we investigated the characteristics of BC-containing
325 particles in two most polluted episodes occurring during the campaign. The first episode (FE) was
326 accompanied with relatively high RH (from 6:00 pm of 3 Dec. to 8:00 am of 4 Dec., 2016), while the
327 second episode (SE) was dominated by primary emissions (from 0:00 am to 6:00 am of 11 Dec., 2016).
328 The average mass loadings of BC cores and BC-containing particles were $18.1 \mu\text{g m}^{-3}$ and $123.1 \mu\text{g}$
329 m^{-3} during FE, $14.4 \mu\text{g m}^{-3}$ and $80.0 \mu\text{g m}^{-3}$ during SE, respectively - both were much higher than the
330 campaign-averaged BC of $4.9 \mu\text{g m}^{-3}$ and BC-containing particles of $29.4 \mu\text{g m}^{-3}$. Back trajectories,
331 wind rose plots and distributions of the wind speeds/directions of these two episodes were provide in
332 Fig. S5, showing that these two episodes had remarkably different air mass origins and sources.

333 For FE, the average T and RH were $\sim 4.2 \text{ }^\circ\text{C}$ and $\sim 78\%$, respectively. The average T was close to
334 the campaign-average value of 4.8°C , but the air was more humid than the campaign-average RH of
335 $\sim 50\%$. Correspondingly, we observed remarkable elevations of the mass contributions of sulfate from
336 6.5% to 10.3% , nitrate from 8.8% to 10.2% , OOA1 from 7.5% to 11.5% (Figs. 7a and 7c). Such
337 enhancements were very likely linked with the aqueous-phase processing as this episode occurred
338 during nighttime and was characterized with high RH conditions. During FE, nitrate and sulfate also
339 correlated very well (r^2 of 0.94; Fig. S6), therefore formation of nitrate would also relate with aqueous-
340 phase processing in this episode. Consistently, nitrate and sulfate formations driven by high RH in
341 North China Plain have been proved previously (Kuang et al., 2016; Sun et al., 2018; Wu et al., 2018).
342 As a comparison, the mass fraction of photochemical-relevant OOA2 decreased significantly from
343 campaign-average 13.3% to 9.8% . In addition, mass fraction of Cl^- also increased from campaign-
344 average 4.0% to 5.3% ; meanwhile, we found that relative to the campaign-average values, the KCl^+/BC
345 ratio decreased 14% , the $\text{K}_3\text{SO}_4^+/\text{BC}$ ratio increased 28% , possibly indicating that the heterogeneous
346 replacement reactions of coal-burning related Cl^- by SO_4^{2-} during FE (Fig. S6). Overall, due to mainly
347 the aqueous-phase production of secondary coating components, comparing to campaign-average
348 values, the average R_{BC} during FE became larger (5.5 vs. 5.0), OA became more oxygenated (O/C of

349 0.18 vs. 0.15), and size distributions of OA, sulfate and nitrate all shifted to larger peak sizes (Fig. S7a).

350 On the other hand, for SE, even though it also occurred during nighttime, the average RH was
351 significantly low (~47%), and it was overwhelmingly dominated by primary species (50.6% of FFOA,
352 15.2% of BBOA and 18% of BC). Secondary sulfate and nitrate only took up 2.5% and 2.2% of the
353 total mass of BC-containing particles. Nighttime aqueous-phase related OOA1 contribution was nearly
354 negligible (only 0.8%), which in another way, manifests that during nighttime OOA1 production was
355 strongly associated with high RH conditions. Due to the contribution of fresh primary emissions, the
356 coating OA was less oxygenated than that of campaign-averaged OA (O/C of 0.12 vs. 0.15), and the
357 average R_{BC} during SE was consistently smaller (4.5 vs. 5.0). Mass spectrum of BC-Org (Fig. 7b) also
358 contained significant PAHs fragments, in line with the large contribution from FFOA (mainly coal
359 combustion). Average size distribution of OA during SE was broader and peaked in a smaller diameter
360 (<500 nm D_{va}) (Fig. S7b), in response to the dominance of POA. Occurrence of the highly polluted SE
361 demonstrates that even though the pollutions of BC-containing particles in urban Beijing during winter
362 are on average governed by secondary species, local primary emissions sometimes can lead to serious
363 and short-term pollution events as well.

364

365 **4. Conclusions**

366 As part of the UK-China 2016 APHH winter campaign, for the first time, an Aerodyne SP-AMS
367 was introduced to exclusively determine the chemical compositions of BC-containing particles in
368 urban Beijing. We found the average concentrations of BC and its coating species were 4.9 and 24.5
369 $\mu\text{g m}^{-3}$, therefore the R_{BC} (mass ratio of coating to BC) was ~5.0. The coating was dominated by
370 organics (59.4% of total mass of BC-containing particles), followed by nitrate and sulfate (15.3%
371 together). Size distribution data demonstrates that larger BC-containing particles tend to have thicker
372 coating, more secondary species and more internally mixed coating components. PMF analyses of
373 organic coating further identified two POA factors relevant with fossil fuel and biomass burning,
374 respectively, which dominated the total OA mass. Two SOA factors were also separated, and both of
375 them were found to be mainly contributed by photochemical activities, besides a fraction of the highly
376 oxidized OA factor could be produced by nighttime aqueous-phase reactions. In addition, significant
377 photochemical formation of nitrate rather than sulfate in the afternoon was observed.

378 Comparisons of the coating compositions between clean and pollution periods shows the critically

379 important role of chemical aging for the pollution of BC-containing particles in urban Beijing. We also
380 found that in one case, aqueous-phase production might lead to serious pollution under high RH
381 conditions, while in another case, fossil fuel combustion could cause extreme and short-term heavy
382 pollution. Comparisons between the BC-containing particles and the total submicron aerosol particles
383 during this campaign will be presented in details in near future.

384

385 **Acknowledgements**

386 This work was supported by the National Key R&D program of China (2016YFC0203501), the
387 Natural Science Foundation of China (21777073, 91544220, 21577065, and 41571130034), the
388 International ST Cooperation Program of China (2014DFA90780), and the UK Natural Environment
389 Research Council (grant ref. NE/N00695X/1).

390

391 **References**

- 392 Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel,
393 J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B.,
394 Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and
395 OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass
396 spectrometry, *Environ. Sci. Tech.*, 42, 4478-4485, 2008.
- 397 Bond, T. C., Doherty, S. J., Fahey, D. W., Forster, P. M., Berntsen, T., DeAngelo, B. J., Flanner, M. G., Ghan, S., Kärcher,
398 B., Koch, D., Kinne, S., Kondo, Y., Quinn, P. K., Sarofim, M. C., Schultz, M. G., Schulz, M., Venkataraman, C.,
399 Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S. K., Hopke, P. K., Jacobson, M. Z., Kaiser, J. W., Klimont, Z.,
400 Lohmann, U., Schwarz, J. P., Shindell, D., Storelvmo, T., Warren, S. G., and Zender, C. S.: Bounding the role of black
401 carbon in the climate system: A scientific assessment, *J. Geophys. Res.-Atmos.*, 118, 5380-5552, 2013.
- 402 Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T. B., Drewnick, F., Coe,
403 H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J., DeCarlo, P. F., Kolb, C. E.,
404 Davidovits, P., and Worsnop, D. R.: Chemical and microphysical characterization of ambient aerosols with the
405 aerodyne aerosol mass spectrometer, *Mass Spectrom. Rev.*, 26, 185-222, 2007.
- 406 Canagaratna, M. R., Massoli, P., Browne, E. C., Franklin, J. P., Wilson, K. R., Onasch, T. B., Kirchstetter, T. W., Fortner,
407 E. C., Kolb, C. E., Jayne, J. T., Kroll, J. H., and Worsnop, D. R.: Chemical compositions of black carbon particle cores
408 and coatings via soot particle aerosol mass spectrometry with photoionization and electron ionization, *J. Phys. Chem.*
409 *A*, 119, 4589-4599, 2015.
- 410 Cappa, C. D., Onasch, T. B., Massoli, P., Worsnop, D. R., Bates, T. S., Cross, E. S., Davidovits, P., Hakala, J., Hayden, K.
411 L., Jobson, B. T., Kolesar, K. R., Lack, D. A., Lerner, B. M., Li, S.-M., Mellon, D., Nuaaman, I., Olfert, J. S., Petäjä,
412 T., Quinn, P. K., Song, C., Subramanian, R., Williams, E. J., and Zaveri, R. A.: Radiative absorption enhancements
413 due to the mixing state of atmospheric black carbon, *Science*, 337, 1078-1081, 2012.
- 414 Chen, C., Fan, X., Shaltout, T., Qiu, C., Ma, Y., Goldman, A., and Khalizov, A. F.: An unexpected restructuring of
415 combustion soot aggregates by subnanometer coatings of polycyclic aromatic hydrocarbons, *Geophys. Res. Lett.*, 43,
416 11080-11088, 2016a.

417 Chen, Y., Schleicher, N., Fricker, M., Cen, K., Liu, X.-l., Kaminski, U., Yu, Y., Wu, X., and Norra, S.: Long-term variation
418 of black carbon and PM_{2.5} in Beijing, China with respect to meteorological conditions and governmental measures,
419 *Environ. Pollut.*, 212, 269-278, 2016b.

420 Cheng, Y., He, K.-b., Engling, G., Weber, R., Liu, J., Du, Z.-y., and Dong, S.-p.: Brown and black carbon in Beijing aerosol:
421 Implications for the effects of brown coating on light absorption by black carbon, *Sci. Total. Environ.*, 599-600, 1047-
422 1055, 2017.

423 Collier, S., Williams, L. R., Onasch, T. B., Cappa, C. D., Zhang, X., Russell, L. M., Chen, C.-L., Sanchez, K. J., Worsnop,
424 D. R., and Zhang, Q.: Influence of emissions and aqueous processing on particles containing black carbon in a polluted
425 urban environment: insights from a soot particle-aerosol mass spectrometer, *J. Geophys. Res.-Atmos.*, 123, 6648-
426 6666, 2018.

427 Cubison, M. J., Ortega, A. M., Hayes, P. L., Farmer, D. K., Day, D., Lechner, M. J., Brune, W. H., Apel, E., Diskin, G. S.,
428 Fisher, J. A., Fuelberg, H. E., Hecobian, A., Knapp, D. J., Mikoviny, T., Riemer, D., Sachse, G. W., Sessions, W.,
429 Weber, R. J., Weinheimer, A. J., Wisthaler, A., and Jimenez, J. L.: Effects of aging on organic aerosol from open
430 biomass burning smoke in aircraft and laboratory studies, *Atmos. Chem. Phys.*, 11, 12049-12064, 2011.

431 Cui, X., Wang, X., Yang, L., Chen, B., Chen, J., Andersson, A., and Gustafsson, Ö.: Radiative absorption enhancement
432 from coatings on black carbon aerosols, *Sci. Total Environ.*, 551-552, 51-56, 2016.

433 Ding, A. J., Huang, X., Nie, W., Sun, J. N., Kerminen, V. M., Petäjä, T., Su, H., Cheng, Y. F., Yang, X. Q., Wang, M. H.,
434 Chi, X. G., Wang, J. P., Virkkula, A., Guo, W. D., Yuan, J., Wang, S. Y., Zhang, R. J., Wu, Y. F., Song, Y., Zhu, T.,
435 Zilitinkevich, S., Kulmala, M., and Fu, C. B.: Enhanced haze pollution by black carbon in megacities in China,
436 *Geophys. Res. Lett.*, 43, 2873-2879, 2016.

437 Dusek, U., Reischl, G. P., and Hitzenberger, R.: CCN activation of pure and coated carbon black particles, *Environ. Sci.*
438 *Tech.*, 40, 1223-1230, 2006.

439 Dusek, U., Frank, G. P., Curtius, J., Drewnick, F., Schneider, J., Kurten, A., Rose, D., Andreae, M. O., Borrmann, S., and
440 Poschl, U.: Enhanced organic mass fraction and decreased hygroscopicity of cloud condensation nuclei (CCN) during
441 new particle formation events, *Geophys. Res. Lett.*, 37 (3) :174-180, 2010.

442 Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles
443 (aqSOA): a review of laboratory, field and model studies, *Atmos. Chem. Phys.*, 11, 22301-22383, 2011.

444 Ge, X., Zhang, Q., Sun, Y., Ruehl, C. R., and Setyan, A.: Effect of aqueous-phase processing on aerosol chemistry and size
445 distributions in Fresno, California, during wintertime, *Environ. Chem.*, 9, 221-235, 2012.

446 Ge, X., He, Y., Sun, Y., Xu, J., Wang, J., Shen, Y., and Chen, M.: Characteristics and formation mechanisms of fine
447 particulate nitrate in typical urban areas in china, *Atmosphere*, 8, 62, 2017a.

448 Ge, X., Li, L., Chen, Y., Chen, H., Wu, D., Wang, J., Xie, X., Ge, S., Ye, Z., Xu, J., and Chen, M.: Aerosol characteristics
449 and sources in Yangzhou, China resolved by offline aerosol mass spectrometry and other techniques, *Environ. Pollut.*,
450 225, 74-85, 2017b.

451 Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M., and Otto, T.: Tropospheric aqueous-phase
452 chemistry: kinetics, mechanisms, and its coupling to a changing gas phase, *Chem. Rev.*, 115, 4259, 2015.

453 Huang, R.-J., Zhang, Y., Bozzetti, C., Ho, K.-F., Cao, J.-J., Han, Y., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco,
454 F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M.,
455 Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., Haddad, I. E., and Prévôt,
456 A. S. H.: High secondary aerosol contribution to particulate pollution during haze events in China, *Nature*, 514, 218-
457 222, 2014.

458 Jacobson, M. Z.: Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature*, 409,
459 695-697, 2001.

460 Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., and Worsnop, D. R.: Development of an

461 aerosol mass spectrometer for size and composition analysis of submicron particles, *Aerosol Sci. Tech.*, 33, 49 - 70,
462 2000.

463 Ji, D., Li, L., Pang, B., Xue, P., Wang, L., Wu, Y., Zhang, H., and Wang, Y.: Characterization of black carbon in an urban-
464 rural fringe area of Beijing, *Environ. Pollut.*, 223, 524-534, 2017.

465 Kroll, J.H., Donahue, N.M., Jimenez, J.L., Kessler, S.H., Canagaratna, M.R., Wilson, K.R., Altieri, K.E., Mazzoleni, L.R.,
466 Wozniak, A.S., Bluhm, H., Mysak, E.R., Smith, J.D., Kolb, C.E., Worsnop, D.R.: Carbon oxidation state as a metric
467 for describing the chemistry of atmospheric organic aerosol. *Nat. Chem.* 3, 133-139, 2011.

468 Kuang, Y., Zhao, C. S., Ma, N., Liu, H. J., Bian, Y. X., Tao, J. C., and Hu, M.: Deliquescent phenomena of ambient aerosols
469 on the North China Plain, *Geophys. Res. Lett.*, 43, 8744-8750, 2016.

470 Laborde, M., Schnaiter, M., Linke, C., Saathoff, H., Naumann, K., Möhler, O., Berlenz, S., Wagner, U., Taylor, J., and Liu,
471 D.: Single particle soot photometer intercomparison at the AIDA chamber, *Atmos. Meas. Tech.*, 5, 3077-3097, 2012.

472 Lee, A. K. Y., Willis, M. D., Healy, R. M., Onasch, T. B., and Abbatt, J. P. D.: Mixing state of carbonaceous aerosol in an
473 urban environment: single particle characterization using the soot particle aerosol mass spectrometer (SP-AMS),
474 *Atmos. Chem. Phys.*, 15, 1823-1841, 2015.

475 Lee, A. K. Y., Chen, C. L., Liu, J., Price, D. J., Betha, R., Russell, L. M., Zhang, X., and Cappa, C. D.: Formation of
476 secondary organic aerosol coating on black carbon particles near vehicular emissions, *Atmos. Chem. Phys.*, 2017, 1-
477 20, 2017.

478 Li, W., Sun, J., Xu, L., Shi, Z., Riemer, N., Sun, Y., Fu, P., Zhang, J., Lin, Y., Wang, X., Shao, L., Chen, J., Zhang, X., Wang,
479 Z., and Wang, W.: A conceptual framework for mixing structures in individual aerosol particles, *J. Geophys. Res. -*
480 *Atmos.*, 121, 13784-13798, 2016.

481 Liu, D., Allan, J., Whitehead, J., Young, D., Flynn, M., Coe, H., McFiggans, G., Fleming, Z. L., and Bandy, B.: Ambient
482 black carbon particle hygroscopic properties controlled by mixing state and composition, *Atmos. Chem. Phys.*, 13,
483 2015-2029, 2013.

484 Liu, D., Whitehead, J., Alfarra, M. R., Reyes-Villegas, E., Spracklen, D. V., Reddington, C. L., Kong, S., Williams, P. I.,
485 Ting, Y.-C., Haslett, S., Taylor, J. W., Flynn, M. J., Morgan, W. T., McFiggans, G., Coe, H., and Allan, J. D.: Black-
486 carbon absorption enhancement in the atmosphere determined by particle mixing state, *Nat. Geosci.*, 10, 184-188,
487 2017.

488 Liu, D., Joshi, R., Wang, J., Yu, C., Allan, J. D., Coe, H., Flynn, M. J., Xie, C., Lee, J., Squires, F., Kotthaus, S., Grimmond,
489 S., Ge, X., Sun, Y., and Fu, P.: Contrasting physical properties of black carbon in urban Beijing between winter and
490 summer, *Atmos. Chem. Phys. Discuss.*, 2018, 1-30, 10.5194/acp-2018-1142, 2018.

491 Liu, Q., Ma, T., Olson, M. R., Liu, Y., Zhang, T., Wu, Y., and Schauer, J. J.: Temporal variations of black carbon during
492 haze and non-haze days in Beijing, *Sci. Rep.*, 6, 33331, 2016.

493 Liu, S., Aiken, A. C., Gorkowski, K., Dubey, M. K., Cappa, C. D., Williams, L. R., Herndon, S. C., Massoli, P., Fortner, E.
494 C., Chhabra, P. S., Brooks, W. A., Onasch, T. B., Jayne, J. T., Worsnop, D. R., China, S., Sharma, N., Mazzoleni, C.,
495 Xu, L., Ng, N. L., Liu, D., Allan, J. D., Lee, J. D., Fleming, Z. L., Mohr, C., Zotter, P., Szidat, S., and Prevot, A. S. H.:
496 Enhanced light absorption by mixed source black and brown carbon particles in UK winter, *Nat. Commun.*, 6: 8435,
497 2015.

498 Massoli, P., Onasch, T. B., Cappa, C. D., Nuamaan, I., Hakala, J., Hayden, K., Li, S.-M., Sueper, D. T., Bates, T. S., Quinn,
499 P. K., Jayne, J. T., and Worsnop, D. R.: Characterization of black carbon-containing particles from soot particle aerosol
500 mass spectrometer measurements on the R/V Atlantis during CalNex 2010, *J. Geophys. Res.-Atmos.*, 120,
501 2014JD022834, 2015.

502 Meng, J., Liu, J., Guo, S., Li, J., Li, Z., and Tao, S.: Trend and driving forces of Beijing's black carbon emissions from
503 sectoral perspectives, *J. Clean. Prod.*, 112, 1272-1281, 2016.

504 Mohr, C., Huffman, J. A., Cubison, M. J., Aiken, A. C., Docherty, K. S., Kimmel, J. R., Ulbrich, I. M., Hannigan, M., and

505 Jimenez, J. L.: Characterization of primary organic aerosol emissions from meat cooking, trash burning, and motor
506 vehicles with high-resolution aerosol mass spectrometry and comparison with ambient and chamber observations,
507 *Environ. Sci. Tech.*, 43, 2443-2449, 2009.

508 Onasch, T. B., Trimborn, A., Fortner, E. C., Jayne, J. T., Kok, G. L., Williams, L. R., Davidovits, P., and Worsnop, D. R.:
509 Soot particle aerosol mass spectrometer: development, validation, and initial application, *Aerosol Sci. Tech.*, 46, 804-
510 817, 2012.

511 Paatero, P., and Tapper, U.: Positive matrix factorization: A non-negative factor model with optimal utilization of error
512 estimates of data values, *Environmetrics*, 5, 111-126, 1994.

513 Peng, J., Hu, M., Guo, S., Du, Z., Zheng, J., Shang, D., Levy, Z. M., Zeng, L., Shao, M., and Wu, Y. S.: Markedly enhanced
514 absorption and direct radiative forcing of black carbon under polluted urban environments, *P Natl. Acad. Sci. USA*,
515 113, 4266, 2016.

516 Pokhrel, R. P., Beamesderfer, E. R., Wagner, N. L., Langridge, J. M., Lack, D. A., Jayarathne, T., Stone, E. A., Stockwell,
517 C. E., Yokelson, R. J., and Murphy, S. M.: Relative importance of black carbon, brown carbon, and absorption
518 enhancement from clear coatings in biomass burning emissions, *Atmos. Chem. Phys.*, 17, 5063-5078, 2017.

519 Ramanathan, V., and Carmichael, G.: Global and regional climate changes due to black carbon, *Nat. Geosci*, 1, 221-227,
520 2008.

521 Schleicher, N., Cen, K., and Norra, S.: Daily variations of black carbon and element concentrations of atmospheric particles
522 in the Beijing megacity – Part 1: general temporal course and source identification, *Chem Erde Geochem.*, 73, 51-60,
523 2013a.

524 Schleicher, N., Norra, S., Fricker, M., Kaminski, U., Chen, Y., Chai, F., Wang, S., Yu, Y., and Cen, K.: Spatio-temporal
525 variations of black carbon concentrations in the Megacity Beijing, *Environ. Pollut.*, 182, 392-401, 2013b.

526 Shi, Z., Vu, T., Kotthaus, S., Grimmond, S., Harrison, R. M., Yue, S., Zhu, T., Lee, J., Han, Y., Demuzere, M., Dunmore,
527 R. E., Ren, L., Liu, D., Wang, Y., Wild, O., Allan, J., Barlow, J., Beddows, D., Bloss, W. J., Carruthers, D., Carslaw,
528 D. C., Chatzidiakou, L., Crilley, L., Coe, H., Dai, T., Doherty, R., Duan, F., Fu, P., Ge, B., Ge, M., Guan, D., Hamilton,
529 J. F., He, K., Heal, M., Heard, D., Hewitt, C. N., Hu, M., Ji, D., Jiang, X., Jones, R., Kalberer, M., Kelly, F. J., Kramer,
530 L., Langford, B., Lin, C., Lewis, A. C., Li, J., Li, W., Liu, H., Loh, M., Lu, K., Mann, G., McFiggans, G., Miller, M.,
531 Mills, G., Monk, P., Nemitz, E., O'Connor, F., Ouyang, B., Palmer, P. I., Percival, C., Popoola, O., Reeves, C., Rickard,
532 A. R., Shao, L., Shi, G., Spracklen, D., Stevenson, D., Sun, Y., Sun, Z., Tao, S., Tong, S., Wang, Q., Wang, W., Wang,
533 X., Wang, Z., Whalley, L., Wu, X., Wu, Z., Xie, P., Yang, F., Zhang, Q., Zhang, Y., Zhang, Y., and Zheng, M.:
534 Introduction to Special Issue – In-depth study of air pollution sources and processes within Beijing and its surrounding
535 region (APHH-Beijing), *Atmos. Chem. Phys. Discuss.*, 2018, 1-62, 10.5194/acp-2018-922, 2018.

536 Song, S., Wu, Y., Xu, J., Ohara, T., Hasegawa, S., Li, J., Yang, L., and Hao, J.: Black carbon at a roadside site in Beijing:
537 Temporal variations and relationships with carbon monoxide and particle number size distribution, *Atmos. Environ.*,
538 77, 213-221, 2013.

539 Sun, J., Liu, L., Xu, L., Wang, Y., Wu, Z., Hu, M., Shi, Z., Li, Y., Zhang, X., Chen, J., and Li, W.: Key Role of Nitrate in
540 Phase Transitions of Urban Particles: Implications of Important Reactive Surfaces for Secondary Aerosol Formation,
541 *J. Geophys. Res.-Atmos.*, 123, 1234-1243, 2018.

542 Sun, Y., Jiang, Q., Wang, Z., Fu, P., Li, J., Yang, T., and Yin, Y.: Investigation of the sources and evolution processes of
543 severe haze pollution in Beijing in January 2013, *J Geophys. Res.-Atmos.*, 119, 4380-4398, 2014.

544 Sun, Y., Du, W., Fu, P., Wang, Q., Li, J., Ge, X., Zhang, Q., Zhu, C., Ren, L., Xu, W., Zhao, J., Han, T., Worsnop, D. R.,
545 and Wang, Z.: Primary and secondary aerosols in Beijing in winter: sources, variations and processes, *Atmos. Chem.*
546 *Phys.*, 16, 8309-8329, 2016.

547 Sun, Y., Zhang, Q., Schwab, J. J., Yang, T., Ng, N. L., and Demerjian, K. L.: Factor analysis of combined organic and
548 inorganic aerosol mass spectra from high resolution aerosol mass spectrometer measurements, *Atmos. Chem. Phys.*,

549 12, 8537-8551, 2012.

550 Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components
551 from Positive Matrix Factorization of aerosol mass spectrometric data, *Atmos. Chem. Phys.*, 9, 2891-2918, 2009.

552 Wang, J., Onasch, T. B., Ge, X., Collier, S., Zhang, Q., Sun, Y., Yu, H., Chen, M., Prévôt, A. S. H., and Worsnop, D. R.:
553 Observation of fullerene soot in eastern China, *Environ. Sci. Tech. Lett.*, 3, 121-126, 2016a.

554 Wang, J., Zhang, Q., Chen, M.-D., Collier, S., Zhou, S., Ge, X., Xu, J., Shi, J., Xie, C., Hu, J., Ge, S., Sun, Y., and Coe, H.:
555 First chemical characterization of refractory black carbon aerosols and associated coatings over the Tibetan Plateau
556 (4730 m a.s.l), *Environ. Sci. Tech.*, 51 (24) :14072, 2017a.

557 Wang, J., Wu, Y., Ge, X., Shen, Y., Ge, S., Chen, M.: Characteristics and sources of ambient refractory black carbon aerosols:
558 Insights from soot particle aerosol mass spectrometer. *Atmos. Environ.*, 185, 147-152, 2018.

559 Wang, Q., Huang, R.-J., Cao, J., Tie, X., Shen, Z., Zhao, S., Han, Y., Li, G., Li, Z., Ni, H., Zhou, Y., Wang, M., Chen, Y.,
560 and Su, X.: Contribution of regional transport to the black carbon aerosol during winter haze period in Beijing, *Atmos.*
561 *Environ.*, 132, 11-18, 2016b.

562 Wang, Y., de Foy, B., Schauer, J. J., Olson, M. R., Zhang, Y., Li, Z., and Zhang, Y.: Impacts of regional transport on black
563 carbon in Huairou, Beijing, China, *Environ. Pollut.*, 221, 75-84, 2017b.

564 Wang, Y., Liu, F., He, C., Bi, L., Cheng, T., Wang, Z., Zhang, H., Zhang, X., Shi, Z., and Li, W.: Fractal dimensions and
565 mixing structures of soot particles during atmospheric processing, *Environ. Sci. Technol. Lett.*, 4, 487-493, 2017c.

566 Willis, M. D., Lee, A. K. Y., Onasch, T. B., Fortner, E. C., Williams, L. R., Lambe, A. T., Worsnop, D. R., and Abbatt, J. P.
567 D.: Collection efficiency of the Soot-Particle Aerosol Mass Spectrometer (SP-AMS) for internally mixed particulate
568 black carbon, *Atmos. Meas. Tech.*, 7, 5223-5249, 2014.

569 Willis, M. D., Healy, R. M., Riemer, N., West, M., Wang, J. M., Jeong, C. H., Wenger, J. C., Evans, G. J., Abbatt, J. P. D.,
570 and Lee, A. K. Y.: Quantification of black carbon mixing state from traffic: implications for aerosol optical properties,
571 *Atmos. Chem. Phys.*, 16, 4693-4706, 2016.

572 Wu, Y., Zhang, R., Tian, P., Tao, J., Hsu, S. C., Yan, P., Wang, Q., Cao, J., Zhang, X., and Xia, X.: Effect of ambient
573 humidity on the light absorption amplification of black carbon in Beijing during January 2013, *Atmos Environ.*, 124,
574 217-223, 2016.

575 Wu, Y., Wang, X., Tao, J., Huang, R., Tian, P., Cao, J., Zhang, L., Ho, K. F., Han, Z., and Zhang, R.: Size distribution and
576 source of black carbon aerosol in urban Beijing during winter haze episodes, *Atmos. Chem. Phys.*, 17, 7965-7975,
577 2017.

578 Wu, Z., Wang, Y., Tan, T., Zhu, Y., Li, M., Shang, D., Wang, H., Lu, K., Guo, S., Zeng, L., and Zhang, Y.: Aerosol liquid
579 water driven by anthropogenic inorganic salts: Implying its key role in haze formation over the North China Plain,
580 *Environ. Sci. Technol. Lett.*, 5, 160-166, 2018.

581 Xie, C., Xu, W., Wang, J., Wang, Q., Liu, D., Tang, G., Chen, P., Du, W., Zhao, J., Zhang, Y., Zhou, W., Han, T., Bian, Q.,
582 Li, J., Fu, P., Wang, Z., Ge, X., Allan, J., Coe, H., and Sun, Y.: Vertical characterization of aerosol optical properties
583 and brown carbon in winter in urban Beijing, China, *Atmos. Chem. Phys. Discuss.*, 2018, 1-28, 10.5194/acp-2018-
584 788, 2018.

585 Xu, W., Han, T., Du, W., Wang, Q., Chen, C., Zhao, J., Zhang, Y., Li, J., Fu, P., Wang, Z., Worsnop, D. R., and Sun, Y.:
586 Effects of aqueous-phase and photochemical processing on secondary organic aerosol formation and evolution in
587 Beijing, China, *Environ. Sci. Tech.*, 51, 762-770, 2017.

588 Yan, C., Zheng, M., Sullivan, A. P., Shen, G., Chen, Y., Wang, S., Zhao, B., Cai, S., Desyaterik, Y., Li, X., Zhou, T.,
589 Gustafsson, Ö., and Collett, J. L.: Residential coal combustion as a source of levoglucosan in China, *Environ. Sci.*
590 *Tech.*, 52, 1665-1674, 2018.

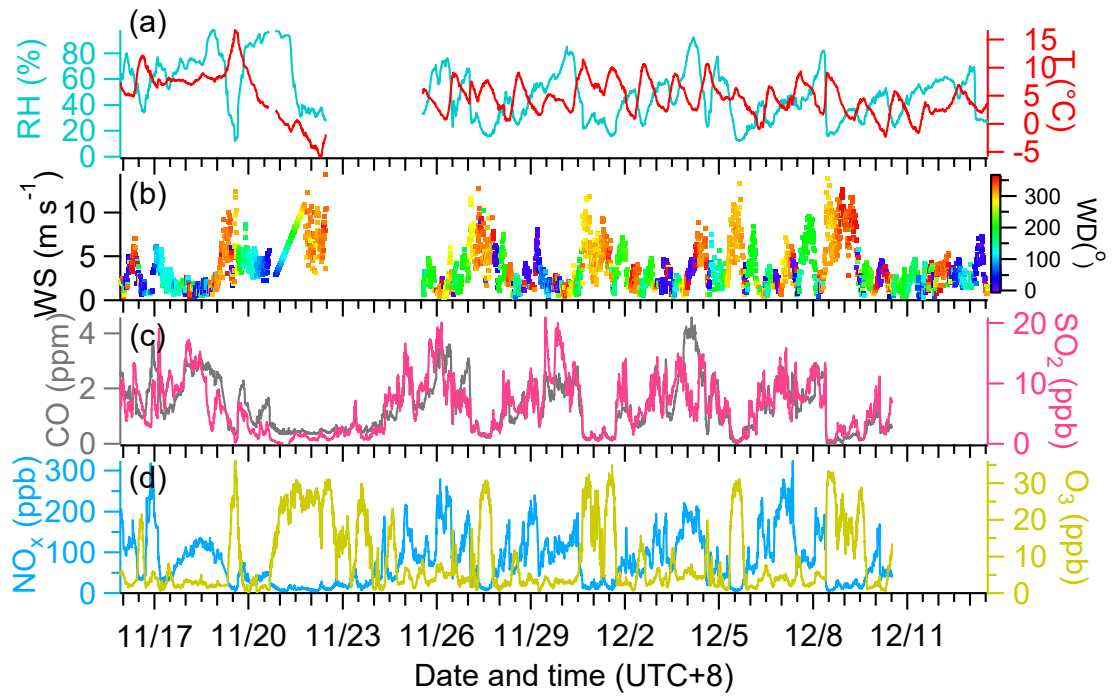
591 Yang, T., Guilin, H., and Zhifang, X.: Atmospheric Black Carbon Deposit in Beijing and Zhangbei, China, *Procedia Earth*
592 *and Planet. Sci.*, 10, 383-387, 2014.

593 Zhang, Q., Alfarra, M. R., Worsnop, D. R., Allan, J. D., Coe, H., Canagaratna, M. R., and Jimenez, J. L.: Deconvolution
594 and quantification of hydrocarbon-like and oxygenated organic aerosols based on aerosol mass spectrometry, *Environ.*
595 *Sci. Tech.*, 39, 4938-4952, 2005.

596 Zhang, Q., Jimenez, J., Canagaratna, M., Ulbrich, I., Ng, N., Worsnop, D., and Sun, Y.: Understanding atmospheric organic
597 aerosols via factor analysis of aerosol mass spectrometry: a review, *Anal. Bioanal. Chem.*, 401, 3045-3067, 2011.

598 Zhang, S., Wu, Y., Yan, H., Du, X., Max Zhang, K., Zheng, X., Fu, L., and Hao, J.: Black carbon pollution for a major road
599 in Beijing: Implications for policy interventions of the heavy-duty truck fleet, *Transport. Res. D-TR E*, 2017.

600

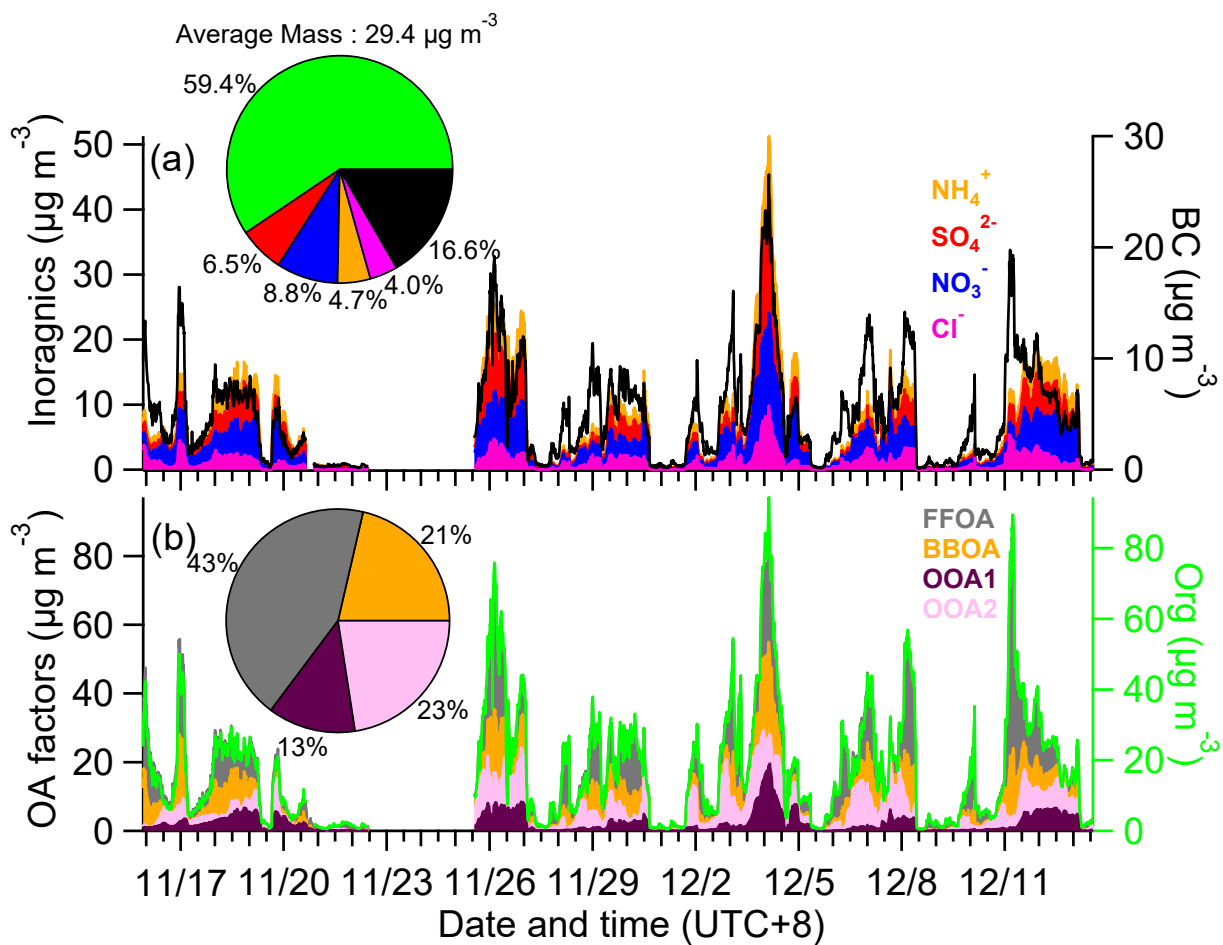


601

602 Figure 1. Temporal variation of (a) relative humidity (RH) and temperature (T, °C), (b) wind speed (WS, m s⁻¹) and wind

603 direction (WD), and (c)(d) mass loadings of CO, SO₂, NO_x and O₃.

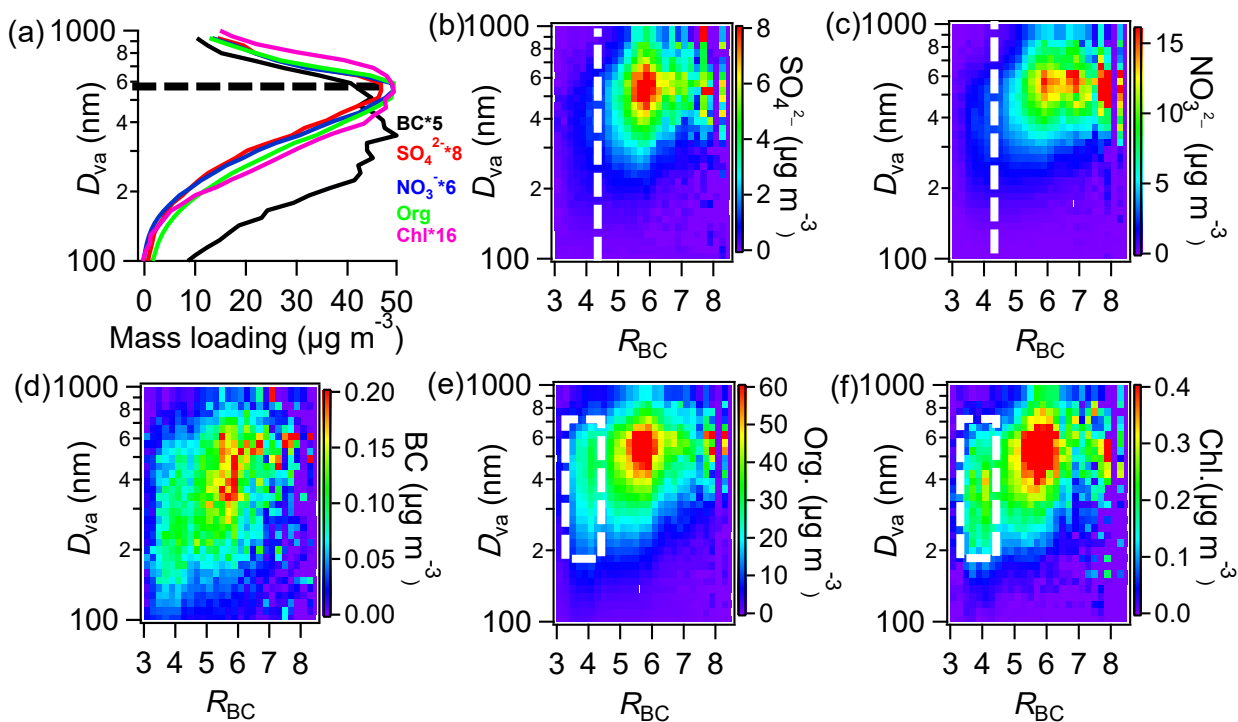
604



606

607 Figure 2. (a) Temporal variations of mass loadings of inorganic coating components (sulfate, nitrate, ammonium and
 608 chloride) and BC cores, and (b) temporal variations of mass loadings of organic coating (Org) and PMF separated OA
 609 factors (inset pie charts show the average composition of total BC-containing particles and organics, respectively).

610



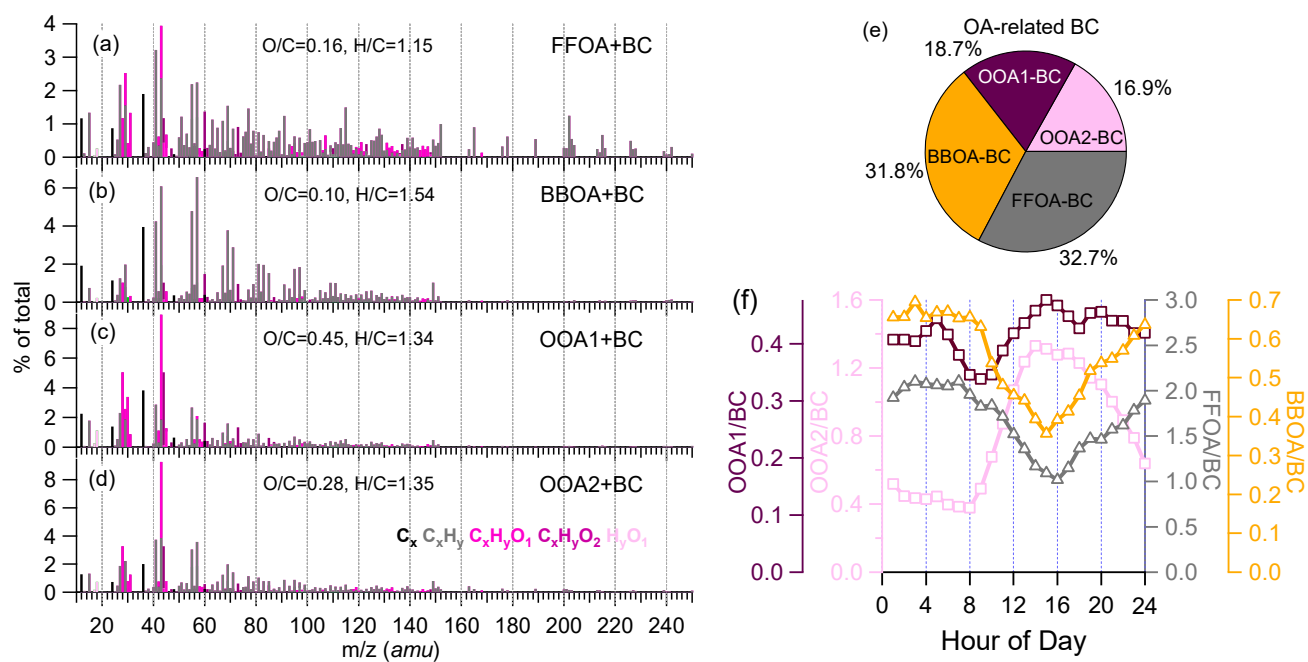
611

612 Figure 3. Mass-based campaign-averaged size distributions: (a) major coating components and BC cores, and (b-f) image

613 plots of size distributions of sulfate, nitrate, BC, organics, and chloride as a function of R_{BC} (mass ratio of coating-to-BC)

614 (Note size distributions of BC and chloride were scaled from those of m/z 24 and m/z 35, respectively)

615



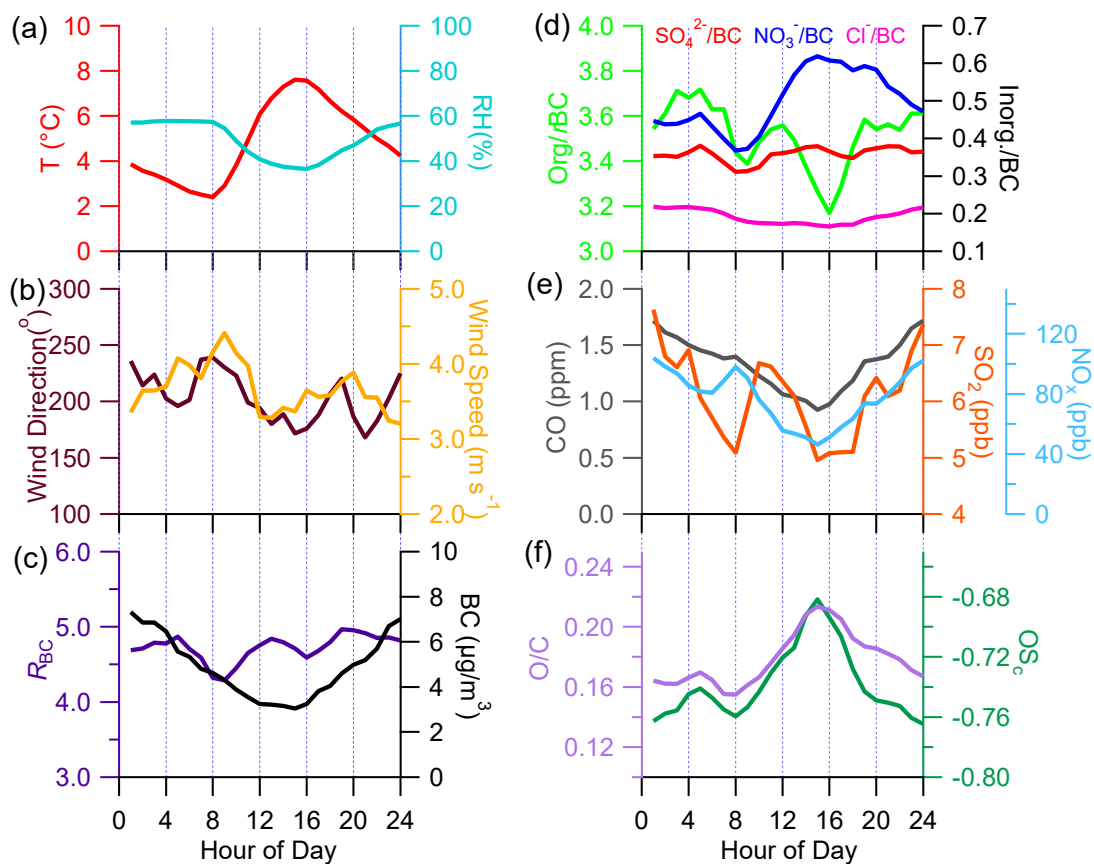
617

618 Figure 4. High-resolution mass spectra of (a) fossil fuel combustion OA (FFOA + BC), (b) biomass burning OA (BBOA +

619 BC), (c) OOA1 + BC, (d) OOA2 + BC, (e) Mass fractions of the BC fragments apportioned in different OA factors, and (f)

620 diurnal cycles of the four OA factors relative to BC.

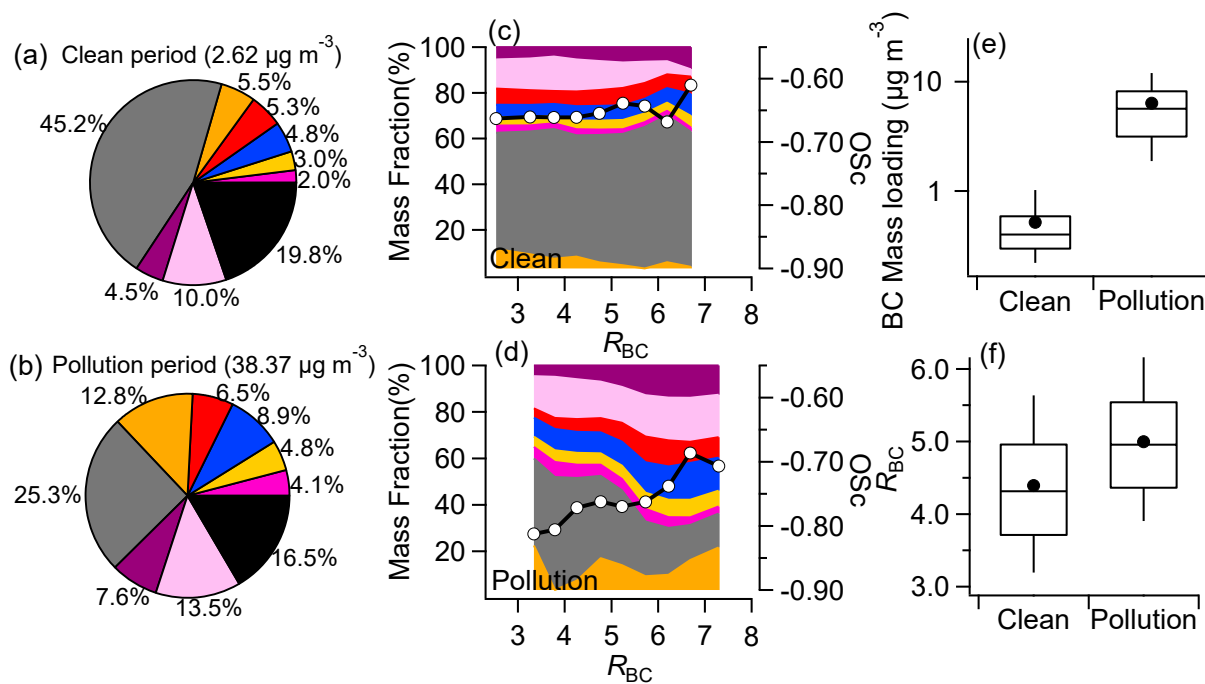
621



623

624 Figure 5. Diurnal cycles of (a) T and RH, (b) wind direction and wind speed, (c) mass ratio of coatings to BC (R_{BC}) and
 625 BC, (d) Org/BC, SO_4^{2-}/BC , NO_3^-/BC and Cl/BC, (e) mass loadings of gaseous species (CO, SO_2 , NO_x), and (f) O/C and
 626 oxidation state ($OS_c=2*O/C-H/C$).

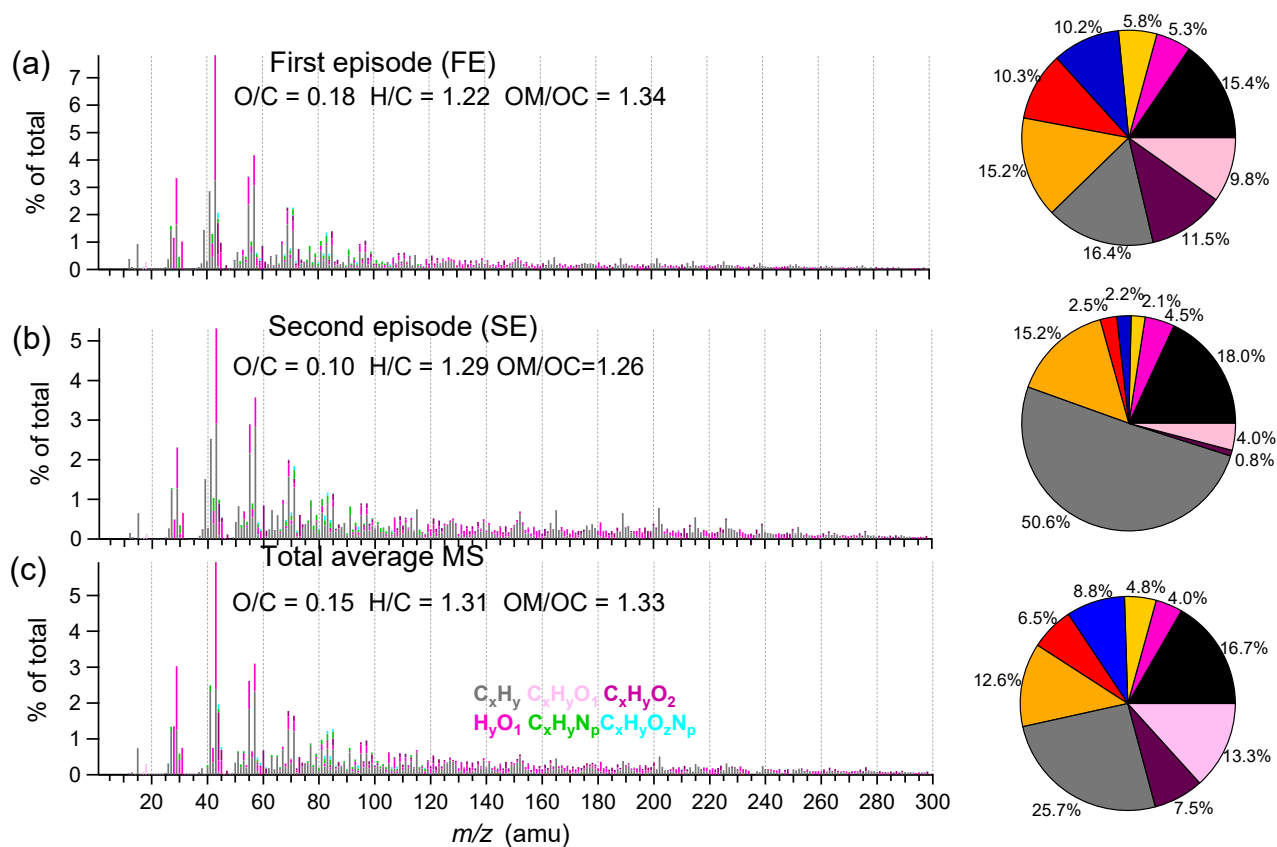
627



629

630 Figure 6. (a)(b) Average compositions of BC-containing particles during clean and pollution periods, (c)(d) mass fractions
 631 of the non-BC coating components (left y-axis) and OS_c (right y-axis) during clean and pollution periods as a function of
 632 R_{BC} , box plots of BC mass loadings (e) and R_{BC} during clean and pollution periods (colors of the components are consistent
 633 with those in Fig. 2).

634



636

637 Figure 7. High-resolution mass spectra of the average OA at different episodes: (a) first episode (FE), (b) second episode
 638 (SE) and (c) whole campaign (inset pies show the average compositions during corresponding episodes; colors of
 639 different components are consistent with those in Fig. 2).

640

641

642

643

644