1 **Chemical properties, sources and size-resolved**

2 **hygroscopicity of submicron black carbon-containing**

3 **aerosols in urban Shanghai**

4 Shijie Cui[1], Dan Dan Huang[2], Yangzhou Wu[1,a], Junfeng Wang[1], Fuzhen Shen[1,b], Jiukun

5 Xian[1], Yunjiang Zhang[1], Hongli Wang[2], Cheng Huang[2], Hong Liao[1], Xinlei Ge[1, *]

6

7 [1] Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution

8 Control, Collaborative Innovation Center of Atmospheric Environment and Equipment

9 Technology, School of Environmental Science and Engineering, Nanjing University of

10 Information Science and Technology, Nanjing 210044, China

11 [2] Shanghai Academy of Environmental Sciences, Shanghai 200233, China

12 [a]now at: Department of Atmospheric Sciences, School of Earth Sciences, Zhejiang

13 University, Hangzhou 310027, PR China

14 [b]now at: Department of Meteorology, University of Reading, Reading, RG6 6BX, UK

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16 *Corresponding author: Xinlei Ge (Email: caxinra@163.com)

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Abstract. Refractory black carbon (rBC) aerosols play an important role in air quality and climate change, yet high time-resolved and detailed investigation on the physicochemical properties of rBC and its associated coating is still scarce. In this work, we used a laser-only Aerodyne soot particle aerosol mass spectrometer (SP-AMS) to exclusively measure the rBC-containing (rBCc) particles, and compared their properties with the total non-refractory submicron particles (NR-PM$_1$) measured in parallel by a high-resolution AMS (HR-AMS) in Shanghai. The observation shows that rBC was overall thickly coated with an average mass ratio of coating to rBC core (R_{BC}) of ~5.0. (±1.7). However, mass of rBC coating species only occupied 19.1% (± 4.9)% of those in NR-PM$_1$; sulfate tended to condense preferentially on non-rBC particles therefore its portion on rBC was only 7.4%, (± 2.2)%, while the majority of primary organic aerosols (POA) were associated with rBC (72.7 ± 21.0%). Positive matrix factorization reveals that cooking emitted organics did not coat on rBC, and a portion of organics coated on rBC was from biomass burning which was unidentifiable in NR-PM$_1$ organics. Small rBCc particles were predominantly from traffic, while large-sized ones were often mixed with secondary components and typically had thick coating. During this campaign, sulfateSulfate and secondary organic aerosol (SOA) species were generated mainly through daytime photochemical oxidation (SOA formation likely involved with in-situ chemical conversion of traffic-related POA to SOA), while nocturnal heterogeneous formation was dominant for nitrate; we also estimated the average times of 5~19 hours for those secondary species to coat on rBC. Particles during a short period that was affected by ship emissions, were characterized with a high vanadium concentration (on average 5.86.3 ± 3.1 ng m^{-3}) and a mean vanadium/nickel mass ratio of 2.0. (± 0.6). Furthermore, the size-resolved hygroscopicity parameter (κ_{rBCc}) of rBCc particles was obtained based on its fully chemical characterization, and was parameterized as $\kappa_{rBCc}(x)= 0.29−0.14 \times \exp(-0.006 \times x)$ (x is from 150 to 1000 nm). Under critical supersaturations (SS_C) of 0.1% and 0.2%, the D_{50} values were 166 (± 16) and 110 (± 5) nm, respectively, and with 16 (± 3%)% and 59 (± 4%))% of rBCc in number could be activated into cloud condensation nuclei (CCN). Our findings are valuable to advance the understanding of BC chemistry as well

50   as the effective control of atmospheric BC pollution.

51   **1 Introduction**

52   Refractory black carbon (rBC) aerosols can directly absorb solar radiation,

53   indirectly change the nature of cloud and alter the albedo of snow or glaciers ~~(Jacobi et~~

54   ~~al., 2015)~~(Jacobi et al., 2015), resulting in a positive radiative forcing that is second

55   only to carbon dioxide on both regional and global scales (Ramanathan and Carmichael,

56   2008;Bond et al., 2013). The fresh rBC particles produced by incomplete combustion

57   of biomass and fossil fuel tend to be fractal in morphology and can mix with many other

58   components (Peng et al., 2016;Li et al., 2021). After entering into the atmosphere, fresh

59   rBC can further externally or internally mix with organic/inorganic species which are

60   primarily emitted or secondarily formed, and such aged rBC-containing (rBCc)

61   particles (Chen et al., 2017;Lee et al., 2017) might have contrasting chemical properties

62   and morphologies (or mixing states) (Liu et al., 2017a;Lee et al., 2019;Xie et al., 2019).

63   In addition, when rBC mixes with hydrophilic materials, its hygroscopicity, cloud

64   condensation nuclei (CCN) activity and size distribution, etc., can be significantly

65   changed, which subsquently affect its atmospheric behavior, impact and lifecycle ~~(Liu~~

66   ~~et al., 2013;Lambe et al., 2015)~~(Liu et al., 2013;Lambe et al., 2015). Therefore, it is

67   necessary to elucidate the physicochemical characteristics and sources of rBC cores

68   and associated coating materials, so as to better understand their influences on climate

69   and air quality.

70   Chemical composition of ambient rBCc particles is largely dependent upon

71   atmospheric conditions and emission sources. In general, the thickness of coating, mass

72   contribution of secondary components (such as sulfate, nitrate and secondary organic

73   aerosol (SOA) species) and oxidation degree of the coated organics of rBCc particles,

74   increase with the aging time or oxidation capacity of ambient environment (Cappa et

75   al., 2012;Liu et al., 2015;Wang et al., 2017;Collier et al., 2018;Wang et al., 2019),

76   except in some specific cases that thickly coated rBCc might be dominated by primarily

77   emitted particles (such as from biomass burning (Wang et al., 2017)). Recent field

78   observations report that SOA species coated on rBC cores could account for 35% and

79   41% of the total SOA mass near traffic emission sources and in a polluted offshore

environment, respectively (Massoli et al., 2012;Massoli et al., 2015). A study of rBCc particles in Singapore finds that over 90% of rBC derived from local combustion sources (mainly traffic), while 30% of rBC was associated with fresh SOA generated under the influences of daytime shipping and industrial emissions ~~(Rivellini et al., 2020)~~(Rivellini et al., 2020).The SOA material concentrated on the surface of rBC was found to be chemically different from the SOA that was externally mixed with rBC ~~(Lee et al., 2017)~~(Lee et al., 2017) in Fontana, California, and another study in Shenzhen, China, reveals that more oxidized SOA preferred to mix with rBC due to that abundant transition metals detected on rBC cores might act as catalysts to convert less oxidized SOA to more oxidized SOA in aerosol aqueous phase ~~(Cao et al., 2022)~~(Cao et al., 2022); the rBC could catalyze SO_2 to form sulfate as well, as observed in Beijing ~~(Zhang et al., 2020)~~(Zhang et al., 2020) and Guangzhou ~~(Zhang et al., 2021)~~(Zhang et al., 2021), China. Besides SOA, cooking-related OA is found to be externally mixed with rBC (Lee et al., 2017;Wang et al., 2019), and a unique biomass burning related OA factor was identified and was only present in rBCc rather than non-rBC particles during summertime in Beijing (Wang et al., 2020a).

Size distribution of rBCc particles is also modulated greatly by their original sources and ageing processes. For example, a study in Shanghai shows a bimodal size distribution of rBCc, with a condensation mode dominated by traffic emissions (small core size, thin coating) and a droplet mode including highly aged biomass burning particles (large core size and thick coating) and highly aged traffic particles (small core size and very thick coating) ~~(Gong et al., 2016)~~(Gong et al., 2016). Another study in Beijing ~~(Liu et al., 2019)~~(Liu et al., 2019) further resolves four size modes of rBCc, relevant with traffic (small core, thin coating), coal or biomass burning (moderate coating, both small and large cores), coal combustion (large core, think coating) and secondary process (thick coating, both small and large cores).

Moreover, water uptake and CCN activity of rBCc particles can increase with the encapsulation of water-soluble substances such as sulfate, nitrate, and SOA (Liu et al., 2013;Wu et al., 2019). Based on the measured chemical composition of rBCc, our previous work has established a method for calculating size-resolved hygroscopicity

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110   parameters of rBCc ($\kappa_{r\text{BCc}}$), and determined the CCN activation diameters of rBCc

111   particles for given critical supersaturation (SS_C) values (Wu et al., 2019).

112   Highly time-resolved chemical characterization of rBCc particles were seldom

113   reported in China and is still lacking in Shanghai. In this study, we utilized an Aerodyne

114   soot particle aerosol mass spectrometer (SP-AMS) to determine the concentration,

115   composition and size distribution of rBCc particles exclusively (technical details in

116   Section 2.1) in urban Shanghai for the first time. We also compared the SP-AMS

117   measurement results with those from a co-located Aerodyne high-resolution time-of-

118   flight aerosol mass spectrometer (HR-AMS), to comprehensively investigate the

119   characteristics of rBCc particles. We analyzed $\kappa_{r\text{BCc}}$ and estimated the proportions of

120   activated rBCc numbers at given SS_C as well.

121

122   **2 Experimental methods**

123   **2.1 Sampling site and instrumentation**

124   The field measurement was conducted from October 31 to December 2, 2018,

125   during which the instruments were deployed on 8th floor of the building of Shanghai

126   Academy of Environmental Sciences (SAES) (31°10'33.348" N, 121°26'10.978" E).

127   Shanghai can be a representative of the densely populated megacity across the world;

128   the measurement period also belonged to the cold season when sources of rBCc might

129   be complex, and can offer rich information about the rBCc; of course, future

130   measurements in other seasons are still essential to achieve a complete understanding

131   of rBCc. East of the sampling site is a large commercial shopping center, and the site

132   is surrounded by residential areas with two busy arterial roads directly to the east (~450

133   m) and south (~150 m), respectively (Figure S1 in the supporting information). In

134   addition, the adjacent areas are densely populated with roadside residents, office

135   workers, and market traders, as well as crowds in and out of the Caobao Road Metro

136   station (~100 m). The measurement period was dominated by northeasterly winds,

137   while many international freight companies located on northeastern side of the site, and

138   many freighters were reposing on the Huangpu River. Overall, the sampling site was

139   probably influenced by vehicular emissions, residential activities and the northeast

140 Cargo ship emission plumes, etc.

141   An Aerodyne SP-AMS and an HR-AMS were operated in parallel during the

142 campaign. The two AMSs shared a same sampling line with a $PM_{2.5}$ cyclone (Model

143 URG-2000-30EN) in front to remove coarse particles. Ambient air pulled through the

144 sampling line was dried using a diffusion dryer filled with silicon gel and was

145 subsequently drawn into both instruments. Due to the transmission efficiency of the

146 inlet lens, both AMSs measured mainly particles of 30-1200 nm (denoted as PM_1).

147   The working principle of SP-AMS has been described in detail previously ~~(Onasch~~

148 ~~et al., 2012)~~(Onasch et al., 2012). However, in this work, we used only the intracavity

149 infrared laser vaporizer to selectively measure rBCc particles (rBC cores and associated

150 coating materials), as rBC can absorb 1064 nm laser light. The thermal tungsten

151 vaporizer had to be physically detached otherwise non-rBC particles can still be

152 detected as the filament can heat the vaporizer to ~200 °C even if it was turned off.

153 Before sampling, the SP-AMS was tuned and calibrated following the steps described

154 previously (Lee et al., 2015; Willis et al., 2016; Wang et al., 2017). During sampling, due

155 to relatively low rBCc mass loadings, the SP-AMS was operated with two mass

156 sensitive V modes (2.5 minutes per cycle), one with a particle time-of-flight (PToF)

157 mode (30 s) and another one (120 s) with a mass spectral mode with mass-to-charge

158 (m/z) ratio up to 500. Filtered air was also measured in the middle of campaign (for 60

159 min) to determine the limits of detection (LOD, three times the standard deviation) of

160 various aerosol species and to adjust the air-influenced mass spectral signals ~~(Zhang et~~

161 ~~al., 2005)~~(Zhang et al., 2005).

162   Before removal of the tungsten heater, the calibrations of ionization efficiency (IE)

163 for nitrate and relative ionization efficiency (RIE) of sulfate were performed by using

164 pure ammonium nitrate and ammonium sulfate particles ~~(Jayne et al., 2000)~~(Jayne et

165 al., 2000), and the values were assumed to be unchanged throughout the whole

166 campaign ~~(Willis et al., 2016)~~(Willis et al., 2016). RIE of rBC to nitrate was calibrated

167 by using size-selected (300 nm) BC particles (REGAL 400R pigment black, Cabot

168 Corp.) ~~(Onasch et al., 2012)~~(Onasch et al., 2012), and the average ratio of C_1^+ to C_3^+

169 was calculated to be 0.584 to correct the interference on C_1^+ from other organics. RIEs

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170 of ammonium, nitrate, sulfate and rBC were determined to be 4.53, 1.10, 1.01, and 0.17,

171 respectively, and RIE of organics used the default value of 1.4 (Canagaratna et al., 2007).

172 The size was calibrated by Polystyrene latex (PSL) spheres (100–700 nm) (Duke

173 Scientific Corp., Palo Alto, CA) before the measurement. This study applied a

174 collection efficiency (CE) of 0.5 for SP-AMS.

175 ~~The co-located HR-AMS (DeCarlo et al., 2006)~~The co-located HR-AMS

176 (DeCarlo et al., 2006) was used to measure all PM$_1$ including both rBCc and non-rBC

177 particles, but it detected only non-refractory species (NR-PM$_1$ species) as its 600 ºC

178 thermal heater is unable to vaporize rBC and other refractory components. In addition,

179 mass concentrations of gaseous pollutants, carbon monoxide (CO), ozone (O$_3$),

180 nitrogen dioxide (NO$_2$), and sulfur dioxide (SO$_2$) were measured by the Thermo

181 Scientific analyzers provided by SAES. Meteorological parameters including air

182 temperature (T), relative humidity (RH), wind speed (WS), wind direction (WD) and

183 precipitation, were obtained from Xujiahui Environmental Monitoring Station of

184 Shanghai (31°11'49.1424"N, 121°26'34.44" E)(~2400 m away from the site). The

185 concentrations of particle-phase vanadium (V) and nickel (Ni) that were used to

186 investigate ship influence were measured independently by an Atmospheric heavy

187 metal analyzer (XHAM-2000A, SAIL HERO., China).

188

189 **2.2 Data analysis**

190 The AMS data (both SP-AMS and HR-AMS) were analyzed using standard ToF-

191 AMS data analysis tool (Squirrel version 1.59D and Pika version 1.19D), based on Igor

192 Pro 6.37 (Wavemetrics, Lake Oswego, OR, USA). The mass concentrations and high

193 resolution mass spectra (HRMS) of rBC and coating species (rBC$_{CT}$) were calculated

194 from high-resolution (HR) fitting of V-mode data. Size distributions of rBCc

195 components were determined by the PToF data with unit mass resolution and were

196 scaled to their mass concentrations obtained above. In particular, size distribution of

197 rBC was scaled to that of m/z 24 (C$_2^+$) (the scaling factor is rBC mass concentration to

198 that of calculated based on its size distribution), because m/z 24 as a rBC fragment, has

199 least interference from other organic or inorganic species; such treatment was adopted

200   in earlier studies too (Collier et al., 2018;Wang et al., 2019;Wang et al., 2016).

201   The HR ion fitting of AMS data is able to distinguish various ions and isotopic

202   ions and calculate elemental ratios of organics such as oxygen-to-carbon (O/C),

203   hydrogen-to-carbon (H/C), nitrogen-to-carbon (N/C), and organic mass to organic

204   carbon (OM/OC) ratios, via the original Aiken-ambient (A-A) method (Aiken et al.,

205   2008) and the improved method (I-A) (Canagaratna et al., 2015b). Outcomes of both

206   methods correlated well. Average O/C, H/C, and OM/OC ratios from the I-A method

207   used in this work were 24.9%, 7.3%, and 5.6%, respectively, higher than those from the

208   A-A method.

209   Furthermore, we performed Positive matrix factorization (PMF) ~~(Paatero and~~

210   ~~Tapper, 1994)~~(Paatero and Tapper, 1994) analysis on the HRMS of organics measured

211   by the SP-AMS via the PMF Evaluation Tool ~~(Ulbrich et al., 2009)~~(Ulbrich et al., 2009).

212   The PMF solutions were thoroughly evaluated following the protocols documented in

213   ~~Zhang et al. (2011)~~Zhang et al. (2011). Finally, a 6-factor solution was chosen as the

214   optimal one. The final result included four primary OA (POA) factors, namely

215   hydrocarbon-like species enriched OA (HOA-rich), rBC-enriched OA (rBC-rich),

216   biomass burning OA (BBOA), water-soluble hydrocarbon-like species enriched OA

217   (WS-HOA), and two secondary OA (SOA) factors including a less oxidized oxygenated

218   OA (LO-OOA$_{rBC}$), and a more oxidized oxygenated OA (MO-OOA$_{rBC}$) (Key diagnostic

219   plots in Fig. S2). As a comparison, the mass spectra of 5-factor and 7-factor solutions

220   are illustrated in Fig. S3 (for the 5-factor solution, factor 3 is a mixed factor of BBOA

221   and WS-HOA, while for the 7-factor solution, MO-OOA clearly splits into factor 5 and

222   factor 2). The HR-AMS data were processed in a similar way, and four factors of NR-

223   PM$_1$ organics were resolved, including hydrocarbon-related OA (HOA$_{NR-PM1}$), cooking

224   OA (COA$_{NR-PM1}$), less oxidized oxygenated OA (LO-OOA$_{NR-PM1}$), and more oxidized

225   oxygenated OA (MO-OOA$_{NR-PM1}$) (Mass spectra and time series shown in Fig. ~~S3~~S4).

226

227   **2.3 Calculation of size-resolved hygroscopicity of rBCc**

228   The hygroscopicity parameter κ is a single parameter representing the

229   hygroscopicity of particles, calculated based on essentially the chemical composition

230 (Petters and Kreidenweis, 2007)(Petters and Kreidenweis, 2007). SP-AMS measured

231 size-resolved chemical compositions of rBCc can thus lead to size-resolved

232 hygroscopicity of rBCc ($\kappa_{r\text{BCc}}$) (Wu et al., 2019;Hu et al., 2021). This study applied a

233 similar method proposed by Wu et al. (2019) and the critical parameters involved in

234 calculation are detailed in Table S1. The procedures are briefly described here: (1)

235 obtain the matrice of size-resolved mass concentrations of each rBCc component from

236 SP-AMS analysis; (2) convert the size-resolved concentration matrice of inorganic ions

237 (SO_4^{2-}, NO_3^- and NH_4^+) to corresponding matrice of inorganic salts (NH_4NO_3, NH_4HSO_4,

238 (NH_4)$_2SO_4$) using a simplified solution of ion pairs (Gysel et al., 2007)(Gysel et al.,

239 2007); (3) convert the size-resolved mass matrice of all components (inorganic salts,

240 OA and rBC) to those of size-resolved volume fractions (Gysel et al., 2007;Chang et

241 al., 2010;Wu et al., 2016); (4) combine with previously reported hygroscopic

242 parameters (Gysel et al., 2007;Chang et al., 2010;Wu et al., 2016) to obtain the

243 volumetric contributions of each component to the hygroscopicity of rBCc; (5) use the

244 Zdanovskii-Stokes-Robinson (ZSR) rule to derive the size-resolved hygroscopicity of

245 rBCc ($\kappa_{r\text{BCc}}$) (Topping et al., 2005a, b2005b, a).

246

247 **3 Results and discussion**

248 **3.1 Overview of chemical characteristics of rBCc and NR-PM$_1$ particles**

249 Figure 1 presents the time series of meteorological parameters, concentrations of

250 gaseous pollutants (CO, NO$_2$, O$_3$, and SO$_2$), ship emission tracers (vanadium and

251 nickel), rBC and rBC$_{CT}$ species and their mass percentages to the total rBCc mass,

252 PMF-resolved OA factors and their corresponding fractional contributions. The

253 sampling period was featured by relatively moderate temperatures and very stagnant

254 conditions with average ($\pm1\sigma$) temperature of 15.3 $\pm$ (($\pm$ 2.9) °C and wind speed (WS)

255 of 0.16 $\pm$ (($\pm$ 0.29) m s^{-1}. CalmThe wind (<with speeds <0.5 m s^{-1}) dominated most of

256 the sampling days and 42% of sampling time was with near-zero wind, therefore overall

257 influence of WS and WD on surface mass loadings of rBCc was insignificant. Yet one

258 should keep in mind that WD can affect rBCc sources, and WS in higher altitude might

259 be stronger therefore long-range transport of air pollutants was still possible. The

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260 average concentrations of CO, NO$_2$, O$_3$, SO$_2$, V, and Ni were determined to be 0.60 (±

261 0.26) ppm, 29.20 (± 17.07) ppt, 27.10 (± 15.97) ppt, 1.27 (± 0.72) ppt, 4.05 (± 3.19)

262 ng m^{-3}, and 3.06 (± 2.45) ng m^{-3}, respectively.

263   The mass loadings of rBC and rBC$_{CT}$ ranged from 0.04 to 11.00 μg m^{-3} and 0.37

264 to 30.47 μg m^{-3} with campaign-mean values (± 1σ) of 0.92 ~~± (~~(± 0.81) μg m^{-3} and 4.55

265 ~~± (~~(± 4.40) μg m^{-3}. The coating materials accounted for ~~83.0%~~81.8 (± 5.3)% of the total

266 rBCc mass, of which organics was the most abundant species (2.54 ± 2.52 μg m^{-3},

267 46.~~0~~6 ± 6.4%), followed by nitrate (1.20 ± 1.30 μg m^{-3}, ~~20~~18.5 ± 8.0%), ammonium

268 (0.44 ± 0.40 μg m^{-3}, ~~9~~8.0 ± 2.0%), sulfate (0.30 ± 0.19 μg m^{-3}, 7.1 ± 3.~~6.0~~%), and

269 chloride (0.07 ± 0.05 μg m^{-3}, 1.7 ± 1.0%). The mass ratio of rBC$_{CT}$ to rBC (R_{BC}) ranged

270 from 2.2 to 9.0, with an average of ~5.0 (±1.7). The average R_{BC} was higher than that

271 in California (R_{BC} = 2.3) ~~(Collier et al., 2018)~~(Collier et al., 2018) and in Shenzhen (R_{BC}

272 = 2.5)~~(Cao et al., 2022)~~(Cao et al., 2022), lower than that in Tibetan Plateau (R_{BC}=7.7)

273 (Wang et al., 2017) and similar to that in Beijing (R_{BC}=5.0) ~~(Wang et al., 2019)~~(Wang

274 et al., 2019), suggesting rBC was relatively thickly coated throughout the campaign.

275 Correlation between rBC and rBC$_{CT}$ was moderate (Pearson's ~~r^2=~~r = 0.~~58~~76).

276 Correlation coefficients (~~r^2~~r) of chloride, nitrate, sulfate and organics with rBC were

277 0.~~52~~72, 0.~~75~~87, 0.~~51~~71 and 0.~~53~~73, respectively, suggesting variability of sources

278 among different coating components.

279   Figure 2 compares the campaign-averaged diurnal patterns of rBC$_C$ and NR-PM$_1$

280 species, chemical compositions of rBCc and NR-PM$_1$, and mass ratios of the species

281 coated on rBC to those of NR-PM$_1$. We found that the diurnal variations of nitrate,

282 sulfate, ammonium, chloride were very similar (~~r^2>~~r > 0.~~86~~92) between the two particle

283 groups, while apparent difference was found for rBCc organics with a much obvious

284 morning rush hour peak~~.~~ (6:00 - 9:00). The results indicate that the formation processes

285 of inorganic salts coated on rBC were similar to those uncoated on rBC, but there were

286 large difference regarding sources/processes existed for organics. For rBC itself, the

287 diurnal cycle presented clearly a morning peak and an evening peak, likely relevant

288 with rush hour traffic emissions (CO showed similar pattern). On the contrary, R_{BC} had

289 a minimum in the morning and dropped to a low level in later afternoon, probably due

290 to influence from traffic-emitted fresh and barely coated rBC particles (details in

291 Section 3.2.1).

292   Distributions of species between rBCc and non-rBC particles were also different,

293 leading to different chemical compositions (Figs. 2g and 2h). Sulfate tended to

294 preferentially condense on non-rBC particles, as its mass contribution to total rBCc

295 mass was only 6.5~~%,~~ (± 4.2)%, while its contribution to total NR-PM$_1$ was 17.6~~%.~~ (±

296 8.3)%. Apportionment of nitrate between rBCc and non-rBC particles was about even

297 as it both occupied ~26% of the total rBCc and NR-PM$_1$ masses. Organics occupied

298 55.9~~%~~ (± 9.2)% of rBCc mass, larger than it in NR-PM$_1$ (43.7 ± 11.7%), due to that

299 primary OA species preferentially associated with rBC. Such result is similar to that

300 observed in winter in Beijing but contrary to the result that SOA was more abundant in

301 rBCc in Shenzhen ~~(Cao et al., 2022)~~(Cao et al., 2022).

302   On average, rBC$_C$ accounted for 19.1% of the total NR-PM$_1$ mass loading (21.61

303 ± 15.80 μg m^{-3})(Fig. 2i), comparable to that in Fontana, California ~~(Lee et al.,~~

304 ~~2017)~~(Lee et al., 2017). The finding reveals that significant fractions of aerosol species

305 were externally mixed with rBC. Individually, sulfate captured by rBC only represented

306 7.4~~%~~ (± 2.2)% of NR-PM$_1$ sulfate, similar to the ~~eariler~~earlier results (Lee et al.,

307 2017;Wang et al., 2020a;Cao et al., 2022;Ma et al., 2020); mass fractions of rBCc

308 nitrate (20.1 ± 5.2%) and chloride (20.4 ± 5.5%) in NR-PM$_1$ were similar to the portion

309 of total rBC$_C$ (19.1 ± 4.9%), while the fraction of organics was higher (26.1~~%).~~ ± 7.3%).

310 The lower fraction of sulfate in rBCc than nitrate was likely due to a few reasons. One

311 probable reason is traffic was a dominant source of rBC (see Section 3.2.1 for details)

312 and NO$_2$ is known to be mainly from traffic as well, therefore secondarily formed nitrate

313 was easy to condense on co-emitted rBC, however SO$_2$ is mainly from other sources

314 rather than traffic. Another possible cause is that rBC concentration was relatively high

315 during nighttime, and nighttime formation of nitrate was significant; Sulfate, on the

316 other hand, was mostly formed in the afternoon due to photochemical oxidation in this

317 study (see Section 3.3.2 for details), whereas afternoon rBC concentration was low.

318 The relatively high ratio of organics was attributed to the fact that majority of POA

319 species were coated on rBC (average ratio of 72.7 ± 21.0%), while rBC-related SOA

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320 was 21.8 ~~%~~(± 7.7)% of the total. Note the rBCc POA here included all four POA factors,

321 and COA_{NR-PM1} did not coat on rBC thus was not included in the calculation.

322

3.2 Distinctive sources of OA in rBCc and in NR-PM$_1$

324 As shown previously, source apportionment results of OA in rBCc and NR-PM$_1$

325 were different. This section discusses in details the characteristics of OA sources in

326 rBCc and in bulk NR-PM$_1$.

3.2.1 Source apportionment of OA in rBCc

328 Figure 3 shows the HRMS and temporal variations of the six OA factors resolved

329 from PMF analysis of rBCc organics. Note the PMF analysis included rBC signals (i.e.,

330 C_x^+ ions) to aid identification of different factors, yet calculations of elemental ratios of

331 these OA factors did not include C_x^+ ions in order to explicitly explore the properties of

332 organic coating. The HRMS of HOA-rich and rBC-rich were similar to the OA

333 previously reported in urban environments near traffic emissions and/or in

334 gasoline/diesel vehicle exhaust (Massoli et al., 2012;Lee et al., 2015;Enroth et al.,

335 2016;Saarikoski et al., 2016;Willis et al., 2016;Lee et al., 2017), therefore both factors

336 were traffic-related. The HOA-rich mass spectrum was featured by intense hydrocarbon

337 ion series (i.e., $C_nH_{2n+1}^+$ and $C_nH_{2n-1}^+$ ions in Fig. 3c), and a lowest O/C ratio of 0.07.

338 Mass fraction of rBC signals (i.e., C_n^+ ions, such as m/z 12, 24, 36, 48, and 60, etc.) in

339 HOA-rich was 8.1%. Mass spectrum of rBC-rich factor had remarkable contribution

340 from rBC (24.2%). Beside C_n^+ ions, the rBC-rich factor contained more oxygenated

341 organic fragments and presented a higher O/C ratio of 0.21 than that of HOA-rich,

342 similar to previous studies (Willis et al., 2016;Lee et al., 2017). This result is reasonable

343 as previous studies (Corbin et al., 2014;Malmborg et al., 2017) found that refractory

344 organics could generate oxygenated ion fragments (such as CO^+ and CO_2^+ derived from

345 oxygenated species on soot surface or inside soot nanostructure). HOA-rich factor

346 correlated very well with the common AMS tracer of vehicular OA, $C_4H_9^+$ (r=0.95, Fig.

347 3i), while rBC-rich factor did match the variation of rBC well (r=0.90, Fig. 3g). Since

348 diesel combustion often releases more rBC than that of gasoline, it is likely that the

349 rBC-rich factor is representative of diesel vehicle exhaust while HOA-rich factor

350 represents gasoline combustion emissions. This result demonstrates that laser-only SP-

351 AMS is capable of distinguishing diesel and gasoline burning particles which typically

352 cannot be separated by other AMS measurements. Further verification should be subject

353 of future work.

354   In this work, a multiple linear regression for the three-dimension size-resolved

355 mass spectra according to the method provided in Ulbrich et al. (2012) was used to

356 resolve the average size distributions of six OA factors. The diagnostic plots are shown

357 in Fig. 4. Overall, the lumped size distribution of six OA factor could reproduce well

358 that of total OA (except for a few size bins, most deviations are within 10%).

359 Correlation between measured and reconstructed OA of all size bins was very tight with

360 r of 0.99 and a slope of 0.97, indicating the robustness of the regressed size distributions

361 of all OA factors. The results together with size distributions of rBCc components, and

362 corresponding mass fractional contributions of different components in all size bins are

363 illustrated in Fig. 5. The average HOA-rich size distribution peaked around 150 nm

364 (D_{va}, vacuum aerodynamic diameter), generally matching with previously reported size

365 distribution of HOA (Sun et al., 2012;Ulbrich et al., 2012;Zhou et al., 2016).

366 Interestingly, size distribution of rBC-rich factor presented two modes, with one

367 peaking ~260 nm, and a more pronounced one peaking ~580 nm (Fig. 5a).

368   The BBOA was identified owing to its obviously higher signals of $C_2H_4O_2^+$ (2.03%)

369 and $C_3H_5O_2^+$ (1.62%) than those in other factors, as these two ions are well-known AMS

370 fragments of the biomass burning tracer, levoglucosan (Mohr et al., 2009;Cubison et

371 al., 2011). In addition, theThe time series of BBOA correlated particularly tightly with

372 both marker ions (r of 0.86 and 0.80, respectively); it in fact also correlated well with

373 K^+ (r=0.79), another tracer of biomass burning emission. The O/C and H/C ratios of

374 BBOA were 0.12 and 1.78, and C_n^+ ions accounted for 9.1% of BBOA, all suggesting

375 that the factor was fresh and might be co-emitted with rBC. A relatively high N/C ratio

376 (0.033) was found for BBOA, which could be attributed to the large amounts of

377 nitrogen-containing organic species enriched in biomass burning OA (Laskin et al.,

378 2009)(Laskin et al., 2009). In addition, the size distribution of BBOA (Fig. 5a) (peak

379 size ~500 nm) was similar to that of biomass burning BC-containing particles obtained

380 using single particle mass spectrometry in Shanghai (Gong et al., 2016)(Gong et al.,

381 2016).

382   The PMF analysis deconvoluted a unique OA factor coated on rBC, namely WS-

383 HOA. Firstly, the WS-HOA mass spectrum had a series of hydrocarbon ion fragments

384 and its time series correlated well with them (e.g., r of 0.90 and 0.92 for WS-HOA vs.

385 $C_4H_7^+$ and $C_4H_9^+$, respectively). Secondly, this factor correlated the best (r=0.57) with

386 aerosol liquid water content (ALWC) (Fig. 3j) compared with the other five OA factors

387 (all r<0.2). Thirdly, a previous study (Ye et al., 2017)Thirdly, a previous study (Ye et

388 al., 2017) that investigated specially the water-soluble fraction of OA via PMF analysis,

389 separated also a HOA factor that contained significant nitrogen-containing organic

390 fragments, with a highest N/C ratio among all other factors, and correlated well those

391 nitrogenated fragments. The WS-HOA defined here showed similar characteristics with

392 the highest N/C (0.037) among all factors and tight correlations with nitrogen-

393 containing fragments (r>0.80). At last, although WS-HOA had a relatively high O/C

394 (0.31) with remarkable contributions from $C_2H_3O^+$ and CO_2^+, yet its correlations with

395 these two ions were in fact not strong (r of 0.46 and 0.44, respectively); and WS-HOA

396 had the least fraction of rBC fragments (0.9%) (note rBC is hydrophobic), even less

397 than the two SOAs (Fig. 3d). Both results suggest that this factor is a collection of

398 water-soluble primary OA species. The peak of WS-HOA size distribution was ~150

399 nm, close to that of HOA-rich (Figs. 5a). Aqueous-phase processed SOA (aqSOA) were

400 typically with very high O/C ratio (Xu et al., 2019)Aqueous-phase processed SOA

401 (aqSOA) were typically with very high O/C ratio (Xu et al., 2019), and size distribution

402 of aqSOA often presented a droplet mode, peaking in relatively large sizes (such as

403 500~600 nm)(Gilardoni et al., 2016;Wang et al., 2021;Ge et al., 2012). Therefore, the

404 moderate O/C (0.31) and small mode size of WS-HOA again manifest it was not from

405 aqueous-phase reactions but more likely the water-soluble fraction of POA.

406   The PMF analyses separated two SOA factors, LO-OOA$_{rBC}$ and MO-OOA$_{rBC}$.

407 Mass spectral features of the two SOAs were consistent with previous studies: The LO-

408 OOA$_{rBC}$ was rich in $C_xH_yO_1^+$ ions (38.7%) (such as $C_2H_3O^+$ at m/z 43) but with less

409 contribution from $C_xH_yO_2^+$ ions (7.6%) and an overall moderate O/C (0.25), while MO-

410 OOA$_{rBC}$ had much more contribution from C$_x$H$_y$O$_2^+$ ion family (22.7%) (such as CO$_2^+$

411 at m/z 44) and C$_x$H$_y$O$_1^+$ ions (44.7%), with a high O/C ratio (0.56). In addition, LO-

412 OOA$_{rBC}$ correlated better with nitrate (r=0.83) than it with sulfate (r=0.69), while the

413 correlation between MO-OOA$_{rBC}$ and sulfate (r=0.84) is better than it with nitrate

414 (r=0.76). Size distributions of the two SOAs were also in accord with their secondary

415 behaviors, both accumulating at larger sizes (~450 nm for LO-OOA$_{rBC}$, and a bit larger

416 mode size of ~500 nm for MO-OOA$_{rBC}$), in agreement with previous observations (Sun

417 et al., 2012;Ulbrich et al., 2012;Zhou et al., 2016).

418   In total, traffic-related POA (sum of HOA-rich, rBC-rich and WS-HOA) was the

419 most abundant source of rBCc organics (39.1%); BBOA occupied ~18.4%; the

420 contributions of two SOAs were on par with each other (20.2% for LO-OOA$_{rBC}$, and

421 22.3% for MO-OOA$_{rBC}$) (Fig. 2g). Among traffic POA, gasoline derived HOA-rich

422 factor outweighed the diesel derived rBC-rich factor (11.4% $vs.$ 6.3% of the total rBCc).

423 Contributions of different factors varied greatly for different sizes of rBCc particles

424 (Fig. 5b). Small-sized particles were overwhelmingly dominated by traffic POA; SOA

425 contributions increased with increase of size, and dominated over POA for 300-800 nm

426 ones; contribution of BBOA was also relative larger for 300-800 nm than for other-

427 sized ones; the very large particles (800-1000 nm) were found to be affected mainly by

428 traffic POA in this work. Correspondingly, for the total rBCc particles, rBC cores

429 peaked at ~170 nm, while other secondary inorganic components, behaving like SOA

430 factors, all peaked at a big size (~550 nm) (Fig. 5c) and their mass percentages were

431 also large for large-sized particles (Fig. 5d).

432   Figure 6a further demonstrates the changes of mass fractions of each rBCc

433 component as a function of R_{BC}. R_{BC} is a proxy of coating thickness. It was found that

434 the thinly coated rBCc (R_{BC}<3) were dominated (up to ~80%) by traffic-related POA.

435 With the increase of R_{BC}, contribution of secondary components increased gradually,

436 especially the two SOAs and nitrate (sulfate showed little changes across the whole R_{BC}

437 range); SOA and nitrate contributions reached 40.2% and 31.3% at R_{BC} = 8, respectively.

438 Accordingly, the oxidation degree (OSc = 2*O/C-H/C) (Kroll et al., 2011)(Kroll et al.,

439 2011) of coated organics increased with R_{BC}. In Fig. 6b, we presented the mass

15

contributions of OA factors to the rBC mass at different R_{BC} values. The rBC was as expected, predominantly associated with POA (from 94% at $R_{BC}<2$ to 66% at $R_{BC} >8$), similar to those from Fontana (Lee et al., 2017). Contribution of rBC-rich factor decreased obviously, and those of SOA factors increased with R_{BC}. The contributions of HOA-rich, WS-HOA and BBOA factors changed little.

3.2.2 Comparisons with NR-PM₁ organics

As shown in Fig. ~~S3~~S4, PMF analysis separated four OA factor for NR-PM₁ organics. Two SOA factors (LO-OOA and MO-OOA) were resolved for both rBCc and NR-PM₁, and their contributions to them were also close (Figs. 2g and 2h). Correlations of time series between the two LO-OOA factors and between the two MO-OOA factors were also tight (r of 0.94 and 0.90, respectively), indicating similar formation processes for each SOA. But, of course, the SOAs from rBCc and from NR-PM₁ were not entirely the same, as later ones had higher O/C ratios (0.52 of LO-OOA$_{NR-PM1}$ and 0.62 of MO-OOA$_{NR-PM1}$). On average, the portion of LO-OOA coated on rBC took up 21.6% mass of LO-OOA in total NR-PM₁, and the portion was 26.0% for MO-OOA. This result suggests that there were some ~~but not big~~ differences regarding the partitioning of LO-OOA and MO-OOA onto rBCc and non-rBC particles.

Compared with SOAs, source apportionment results of POA were quite distinct. Firstly, there was only one HOA factor resolved for NR-PM₁, while three HOA factors were separated for rBCc. Note the rBC-rich and WS-HOA factors occupied merely 3.1% and 2.1% of NR-PM₁ OA mass, respectively, probably the cause that they were not identified in NR-PM₁ OA. Nevertheless, mass loadings of the sum of HOA-rich, rBC-rich and WS-HOA factors (termed as HOA$_{rBC}$) agreed quite well with that of HOA$_{NR-PM1}$ (r=0.95) (Fig. 7a), verifying both source apportionment results. And, HOA$_{rBC}$ took up 63.7% of HOA$_{NR-PM1}$, while previous studies reported that 81% ~~(Massoli et al., 2012) and 87 % (Massoli et al., 2015) of HOA were associated with~~ ~~rBC. These results imply that HOA species in NR-PM₁ were largely internally mixed~~ ~~with rBC affected by vehicular emissions. Secondly, COA$_{NR-PM1}$ was only identified in~~ ~~NR-PM₁ OA. AMS-resolved COA$_{NR-PM1}$ is mainly from cooking oil and food itself,~~

470 ~~therefore it negligibly internally mixes with rBC. This result is consistent with previous~~

471 ~~observations~~ (Massoli et al., 2012) and 87 % (Massoli et al., 2015) of HOA were

472 associated with rBC. These results imply that HOA species in NR-PM$_1$ were largely

473 internally mixed with rBC affected by vehicular emissions. Secondly, COA$_{NR-PM1}$ was

474 only identified in NR-PM$_1$ OA. AMS-resolved COA$_{NR-PM1}$ is mainly from cooking oil

475 and food ingredients, therefore it negligibly internally mixes with rBC. This result is

476 consistent with previous observations (Lee et al., 2015;Willis et al., 2016;Lee et al.,

477 2017;Collier et al., 2018)~~. At last, BBOA was identified in rBCc OA but not in NR-PM$_1$~~

478 ~~OA. One plausible reason was that the BBOA mass contribution was minor (equivalent~~

479 ~~to <5% of NR-PM$_1$ OA mass); another speculation is that laser only SP-AMS can detect~~

480 ~~refractory species that HR-AMS cannot, some of them might be originated from~~

481 ~~biomass burning (Wang et al., 2020a).~~. At last, BBOA was identified in rBCc OA but

482 not in NR-PM$_1$ OA. One plausible reason was that the BBOA mass contribution was

483 minor (equivalent to <5% of NR-PM$_1$ OA mass) therefore was not able to be separated

484 from other OA factors; another speculation is that laser only SP-AMS can detect

485 refractory species that HR-AMS cannot, and a portion of these refractory species are

486 likely rich in biomass burning OA. Identification of BBOA in rBCc rather than in

487 simultaneously measured total NR-PM$_1$ was also found in Tibet (Wang et al., 2017) and

488 Beijing (Wang et al., 2020a), role of such BBOA and its interplay with rBC core remain

489 a subject of future work.

490   Diurnal cycles of the POA and SOA factors from both PMF analyses are compared

491 in Figs. 7b and 7c. The diurnal pattern of stacked HOA$_{rBC}$ indeed agreed with that of

492 HOA$_{NR-PM1}$, both with two peaks in the morning and evening rush hours, and, the

493 patterns of rBC-rich, HOA-rich, and WS-HOA factors showed similar behaviors

494 individually (Fig. 7b). The diurnal variation of COA$_{NR-PM1}$ had pronounced peaks

495 during lunch and dinner times, and its percentage in NR-PM$_1$ OA reached 54% at night.

496 Diurnal patterns of two LO-OOA factors were somewhat different (r=0.35). LO-

497 OOA$_{rBC}$ has a major peak in the afternoon, while though LO-OOA$_{NR-PM1}$ concentration

498 rose in the afternoon too but peaked in early evening (~~~8 pm~~20:00). The daily variations

499 of two MO-OOA factors were similar (r=0.83), both peaking at 16:00. The afternoon

500   increases of both SOAs indicate an important role of photochemical reactions, yet

501   differences in formation mechanisms, volatilities and partitioning behaviors of SOA

502   products could lead to diversities of their diurnal patterns and HRMS.

503

504   **3.3 Evolution and formation rBCc components**

505   **3.3.1 Behaviors of rBC cores**

506   Size distribution of rBC cores shown in Fig. 5c was relatively wide. Beside the

507   main peak at ~170 nm, it extended significantly into large sizes and had a small peak at

508   ~550 nm, which was close to the peak of secondary components. With results shown in

509   Fig. 5a, we found that small rBC cores were often thinly coated, while thickly coated

510   rBCc particle were often highly aged and a portion of them also had large-sized rBC

511   cores. This result is likely owing to that oxidation of rBC-bounded organics and/or

512   condensation of secondary species onto rBC surface can induce restructuring of soot

513   aggregates to form compact and large cores (Chen et al., 2018;Chen et al., 2016). Such

514   phenomenon is in line with earlier studies (Liu et al., 2019;Gong et al., 2016). We

515   further show the image plot of size distributions of rBC at different R_{BC} in Fig. ~~S5a~~S6a.

516   It can be found that the rBC mass in a large part concentrated in particles with R_{BC} of

517   5-8, and there was indeed a significant portion of rBC appearing in large size range

518   (400-800 nm) with very thick coating (R_{BC} of 8-9).

519

520   **3.3.2 Formation of inorganic salts**

521   Sulfate and nitrate both peaked at a big size ~550 nm (Fig. 5c) and were mainly

522   associated with thickly coated rBCc (R_{BC}>6, Figs. ~~S5d~~S6d and ~~S5e~~S6e). To investigate

523   the impacts of photochemistry and aqueous/heterogeneous chemistry on the formation

524   of rBC$_{CT}$ species, we plotted the image plots of size distributions of nitrate, sulfate and

525   organics versus O_X ($O_3 + NO_2$) and relative humidity (RH) in Fig. 8. Here O_X is used

526   as a proxy of photochemical activity (Xu et al., 2017), and RH is an indicator of aqueous

527   reactions ~~(Wu et al., 2018)~~(Wu et al., 2018). Nitrate significantly concentrated in 65-

528   100 ppb O_X range but there was a weak accumulation in low O_X as well (Fig. 8a), while

529   in Fig. 8d, nitrate had a prominent hotspot in RH>85%. Generally, both strong

photochemical activity and high RH could promote nitrate formation. For sulfate, although the distribution was scattered due to low level of mass loadings, high Ox level seemed to favor sulfate formation (Fig. 8b); sulfate was scattered in the whole RH range and there were some enhancements at high RH (>80%) but was much less clear-cut (Fig. 8e). Therefore aqueous-phase production of sulfate was not important in this campaign.

We further calculated the sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) ~~(Xu et al., 2014)~~(Xu et al., 2014), and plotted their variations against O_X and RH in Figs. 9a and 9e, respectively. The NOR rose substantially at O_X >60 ppb but showed no increase at O_X < 60 ppb, while it increased continuously with RH. Mass ratio of nitrate to rBC stayed at a high level during nighttime when RH was high as well (overall diurnal trend of NO_3^-/rBC was similar to that of RH, see Figs. ~~S6a~~S7a and ~~S6d~~S7d). This result indicates a likely more important role of nocturnal nitrate formation (N_2O_5 hydrolysis) ~~(Pathak et al., 2011)~~(Pathak et al., 2011) ~~(Sun et al., 2011)~~(Sun et al., 2011) than photochemical production of nitrate during this campaign; moreover, low temperature and high RH favor nitrate partitioning into the particle phase during nighttime too ~~(Gao et al., 2011)~~(Gao et al., 2011). For sulfate, The SOR increased with O_X while it increased with RH under relatively dry conditions (<60%) but decreased with RH when RH>60%. This result, on the other hand, highlights that photochemical production is more important than aqueous/heterogenous formation for sulfate. In addition, mass ratios of sulfate to rBC were enhanced remarkably during daytime and peaked in the afternoon (Fig. ~~S6e~~S7e), supporting the key role of photochemical formation of sulfate. Sulfate precursor SO_2 was at a high level during daytime too. The main formation pathway of sulfate is strikingly different from that observed in winter Nanjing ~~(Wu et al., 2018)~~(Wu et al., 2018), suggesting significant seasonal variability of sulfate formation even in the same region.

3.3.3 Evolution of organics

Organics had a broad average size distribution (Fig. 5c), but unlike rBC, its main peak appeared at 500~600 nm. Figure ~~S5b~~S6b shows that the majority of organics

560   partitioned in rBCc with R_{BC} of 5.0-9.0 and wide size coverage (300-800 nm).

561   Regarding its dependences on O_X and RH, it mainly accumulated at O_X>70 ppb (Fig.

562   8c) and very high RH (~90%) (Fig. 8f). Consistently, O/C ratio and OSc both peaked

563   in the afternoon (Fig. ~~S6b~~S7b), all suggesting a critical role of photochemistry in

564   affecting the behavior of organics.

565   Figure 9 illustrates the mass ratios of each OA factor to rBC varying with O_X and

566   RH. Mass ratios of all four POA factors generally presented decreasing trends (despite

567   some fluctuations) against O_X (Fig. 9b), and the total POA$_{rBC}$ showed evident decrease

568   with increase of O_X (Fig. 9d). Instead, both LO-OOA$_{rBC}$ and MO-OOA$_{rBC}$, as well as

569   their sum (SOA$_{rBC}$) increased continuously with O_X (Figs. 9c and 9d). This result proves

570   that photochemical oxidation contributed significantly to both LO-OOA$_{rBC}$ and MO-

571   OOA$_{rBC}$ formations. Comparatively, decreases of POA$_{rBC}$ perhaps point to its reaction

572   loss upon photochemical oxidation. With regard to RH, besides WS-HOA, the other

573   three POA$_{rBC}$ factors showed almost no dependences on RH (Fig. 9f); note the increase

574   of WS-HOA with RH did not indicate the aqueous production of WS-HOA (see

575   discussion in Section 3.2.1), but a result of enhanced dissolution with increase of

576   moisture. Overall small increase of POA$_{rBC}$ (Fig. 9h) with RH then mainly attributed to

577   WS-HOA. Contrary to the trends with O_X, mass ratios of two SOA factors as well as

578   the total SOA to rBC went down with increase of RH (Figs. 9g and 9h), indicating a

579   trivial role of aqueous/heterogenous oxidation for the SOA coated on rBC observed

580   during this campaign.

581   The aging of OA is generally characterized by the increase of O/C and decrease of

582   H/C (Ng et al., 2011;Zhao et al., 2019).The different aging pathways of OA follow

583   different slopes in the Van Krevelen (VK) diagram ~~(Heald et al., 2010)~~(Heald et al.,

584   2010). For example, addition of only one oxygen atom to the carbon skeleton results in

585   a slope equal to 0, while replacement of the hydrogen atom with a carboxylic acid group

586   (−COOH) results in a slope of −1 without fragmentation (C-C bond breaking), and −0.5

587   with fragmentation (Heald et al., 2010;Ng et al., 2011;Zhao et al., 2019). As presented

588   in Fig. 10a, fitting of all OA data yielded a slope of −0.96, very close to −1, suggesting

589   that OA ageing process resembled the hydrogen substitution with a –COOH group

590 (carboxylation). Interestingly, the four OA factors (HOA-rich, WS-HOA, LO-OOA$_{rBC}$

591 and MO-OOA$_{rBC}$) aligned almost in a straight line with a slope of -0.77 (Fig. 10a), also

592 close to -1. Figure S7S8 further reveals that there was a strong anti-correlation between

593 mass fractions of sum of HOA-rich and WS-HOA and sum of LO-OOA$_{rBC}$ and MO-

594 OOA$_{rBC}$ ($r=-0.97$); the slope of fitted line was -0.86. All these results suggest that OA

595 evolution may contain a channel of photochemical transformations from HOA-rich and

596 WS-HOA to LO-OOA$_{rBC}$ and then to MO-OOA$_{rBC}$. This result is also in line with the

597 observed decrease of POA$_{rBC}$ and increase of SOA$_{rBC}$ against O$_X$.

598 　　　　CHO$^+$, CHO$_2^+$ and C$_2$H$_2$O$_2^+$ are the AMS tracer ions for carbonyl, carboxylic acid

599 and glyoxal, respectively (Wang et al., 2020b;Canagaratna et al., 2015a;Yu et al., 2014).

600 Mass fractions of these three fragment ions presented decreasing trends (or no clear

601 trends) against RH (Fig. S8S9), suggesting again that aqueous processing is not an

602 important pathway in OA evolution during this campaign. Conversely, fractional

603 contributions of these three ions presented increasing trends versus O$_X$, supporting the

604 dominance of photochemical oxidation pathway (Figs. 10b-d). Figures 10e-g show the

605 scatter plots of H/C versus O/C at different O$_X$ concentrations. The regressed slope was

606 -1.03 for low O$_X$ (<60 ppb) conditions (Fig. 10e), indicating that the OA aging at low

607 O$_X$ level is mainly analogue to the carboxylation process. This result corresponds

608 precisely to the fact that mass fractions of CHO$_2^+$ and C$_2$H$_2$O$_2^+$ increased gradually with

609 O$_X$ at low O$_X$, whereas that of CHO$^+$ remained essentially unchanged (Figs. 10e-g). The

610 fitted slope was -1.14 for moderate O$_X$ conditions (60-80 ppb), and it changed to -0.43

611 for high O$_X$ level (>80 ppb) but correlation became weaker ($r=-0.57$). This result

612 implies that the OA evolution under high O$_X$ conditions might include oxidations by

613 the additions of alcohols, peroxides and carboxylation. In all, the evolution of rBCc OA

614 in Shanghai during this campaign is governed by photochemistry rather than aqueous

615 chemistry, but with different oxidation pathways at different O$_X$ levels.

616

3.3.4 Coating time of secondary species onto rBC

618 　　　　Although the rBCc organics was dominated by primary sources (Fig. 2g), the

619 diurnal variations of OSc, O/C and H/C of the total organics, were controlled

21

predominantly by the two SOA factors. Correlations between the diurnal cycles of MO-OOA$_{rBC}$/rBC and OSc were extremely well (r=0.97 with OS$_C$ and r=0.98 with O/C), and those of LO-OOA/rBC were also tight (r=0.91 with OS$_C$ and r=0.92 with O/C). The correlations with LO-OOA$_{rBC}$ were a bit weaker than those of MO-OOA$_{rBC}$, indicating that MO-OOA$_{rBC}$ was probably the final products and was more important in governing the overall oxidation level of organic coating. Figure 11a depicts the diurnal variations of SOA$_{rBC}$/rBC and POA$_{rBC}$/rBC. Diurnal variations of POA$_{rBC}$/rBC and rBC were overall similar, while the daily pattern of SOA$_{rBC}$/rBC was almost opposite to that of rBC. This result likely indicates that most POA$_{rBC}$ species were co-emitted and coated on rBC cores originally, therefore the coating process during rBCc lifecycle was mainly relevant with SOA species rather than POA species. This process is mainly through photochemical reactions, including in-situ oxidation of originally coated POA species (for example, oxidation of HOA-rich plus WS-HOA to LO-OOA$_{rBC}$, then to MO-OOA$_{rBC}$), and partitioning of secondary species formed in gas-phase reactions onto rBC surface. In addition, sulfate and nitrate were both secondarily formed, but sulfate was dominated by photochemical production while nitrate was governed by nocturnal heterogenous formation (as discussed in Section 3.3.2); different diurnal patterns of them (Fig. ~~S6~~S7) point to different coating processes too.

In this regard, we hereby propose a concept of average coating time (ACT), which is used to roughly estimate the timescales required for secondary components coated onto rBC. The specific method is listed as follows:

1. Move forward the diurnal variation of SA$_{rBC}$/rBC (SA represents a secondary aerosol species) for n hours to get a new SA$_{rBC}$/rBC diurnal pattern, labelled as "SA$_{rBC}$/rBC(r-nh-ahead)". Here, the r value is the linear correlation coefficient between the new SA$_{rBC}$/rBC diurnal pattern with that of rBC.

2. Choose the best correlation coefficient (r-nh-ahead), and nh corresponds to the ACT for this secondary component.

Diurnal patterns of LO-OOA$_{rBC}$/rBC and MO-OOA$_{rBC}$/rBC are depicted in Fig. 11b. They were both opposite to the trend of rBC, and they were similar to each other, except that MO-OOA$_{rBC}$/rBC peaked hours later in the afternoon, signifying that the

22

MO-OOA$_{r\text{BC}}$ needs longer time to coated on rBC than LO-OOA$_{r\text{BC}}$ does, consistent with the fact that MO-OOA$_{r\text{BC}}$ was "more aged". Correspondingly, we obtained an ACT of 7 hours for MO-OOA$_{r\text{BC}}$ (*0.35-7*h-ahead) and 5 hours for LO-OOA $_{r\text{BC}}$ (*0.57-5*h-ahead) (Fig. 11c) using the method described above. The ACT of sulfate (*0.65-7*h-ahead) and nitrate (*0.30-19*h-ahead) were 7 and 19 hours, respectively (Fig. 11d). The results suggest that the rBC emitted mainly in the morning rush hours requires a few hours to be adequately coated by LO-OOA$_{r\text{BC}}$, MO-OOA$_{r\text{BC}}$ and sulfate, as these three species are mainly produced in the afternoon by photochemical reactions; while photochemical production of nitrate is insignificant, thus rBC was coated by nitrate until later night when nitrate was formed efficiently by heterogenous N_2O_5 hydrolysis. Note the best r values were not high (for example, 0.35 for MO-OOA$_{r\text{BC}}$ and 0.30 for nitrate), yet the adjusted trends of all secondary components (Figs. 11c and 11d) matched that of rBC quite well during 3:00~12:00 (r of 0.90, 0.91, 0.84 and 0.84 for MO-OOA$_{r\text{BC}}$, LO-OOA$_{r\text{BC}}$, sulfate and nitrate, respectively), likely meaning that daytime variations of two SOAs and sulfate were indeed controlled by the coating process while governing factors of their nighttime variations might be complex, and *vice versa* for nitrate.

3.4 Size-resolved hygroscopicity of rBCc

By using the method in Section 2.3, we calculated the size-resolved hygroscopicity parameters for the total rBCc ($\kappa_{r\text{BCc}}$) and the coatings materials (κ_{CT}) across the whole campaign. The image plots are illustrated in Figs. 12a and b. Generally, large $\kappa_{r\text{BCc}}$ and κ_{CT} values occurred at big particle sizes, and this result was overall similar to that in Nanjing during winter (Wu et al., 2019). We further illustrate the size-resolved $\kappa_{r\text{BCc}}$ as a function of R_{BC} in Fig. 12c. The figure shows that $\kappa_{r\text{BCc}}$ overall became larger with increasing particle size regardless of the coating thickness. However, there were some (though not significant) relatively high $\kappa_{r\text{BCc}}$ values in the range of 80-150 nm (bottom left and bottom right in Fig. 12c).

In Figs. 13a and b, we further determined the average size-resolved $\kappa_{r\text{BCc}}$ and κ_{CT} as a function of coated diameter ($D_{r\text{BCc}}$). Both $\kappa_{r\text{BCc}}$ and κ_{CT} values were relatively high at $D_{r\text{BCc}}<100$ nm and presented slight decreases from 100 to 150 nm. This is distinctive

680   from those observed in Nanjing, where κ_{CT} increased with D_{rBCc} from 50 nm (Wu et al.,

681   2019). From Figs. 5b and 5d, it can be seen the rBCc with D_{rBCc}<150 nm was dominated

682   by a portion of ammonium and sulfate (8-10%) and organics (~60%), of which organics

683   was dominated by WS-HOA. Such composition explains the relatively high

684   hygroscopicity at D_{rBCc}<150 nm as both ammonium sulfate and WS-HOA are

685   hydrophilic; a slight decrease of the hygroscopicity from 100 to 150 nm D_{rBCc} was also

686   a response of decreased mass contributions of ammonium sulfate and WS-HOA (and

687   increase of hydrophobic HOA-rich contribution).

688   Figures 13a and b provide the fitted exponential functions for the mean κ_{rBCc} and

689   κ_{CT} with D_{rBCc}. The equations are: $\kappa_{rBCc}(x)$= 0.29−0.14 × exp(-0.006 × x) and $\kappa_{CT}(x)$ =

690   0.35 − 0.09 × exp (−0.003 × x) (x is D_{rBCc}, 150<x<1000 nm). Here, 0.29 and 0.35 are

691   the upper limits of κ_{rBCc} and κ_{CT}, higher than those reported in Nanjing (0.28 and 0.30

692   for κ_{rBCc} and κ_{CT}); yet the increasing rates of κ_{rBCc} and κ_{CT} with D_{rBCc} are 0.14 and 0.09,

693   respectively, which are much lower than those from Nanjing (0.35 and 0.27 for κ_{rBCc}

694   and κ_{CT})(Wu et al., 2019). Smaller increased contributions of hydrophilic secondary

695   species from 150 to 1000 nm in Shanghai than those from 100 to 1000 nm in Nanjing

696   are likely the cause of smaller increasing rates of hygroscopicity parameters. In addition,

697   it should be noted that the hygroscopicity is not only determined by the bulk

698   composition, but also affected by the phase state of particles. For instance, a recent

699   study reveals that the hygroscopic growth of phase-separated particles (with ammonium

700   sulfate as cores) can be reduced by the secondary organic shells and is dependent on

701   the thickness of organic coating ~~(Li et al., 2021).~~(Li et al., 2021).

702   The critical supersaturation (SS_C) for a selected dry diameter (D_{rBCc} measured by

703   SP-AMS) of a rBCc particle with a hygroscopicity parameter κ_{rBCc}, can be calculated

704   by the "κ-Kohler theory" equation ~~(Petters and Kreidenweis, 2007)~~(Petters and

705   Kreidenweis, 2007). Based on the size-resolved κ_{rBCc}, the CCN activation diameter (D_{50})

706   of particles at a given critical SS_C can be calculated (Wu et al., 2019). Then, by

707   combining the measured rBCc number size distribution and the D_{50} value, activation

708   fraction (f_{AC}) of rBCc number population (i.e., the fraction greater than the D_{50}) can be

709   obtained. Figure 13c shows the SS_C as a function of D_{rBCc} for the entire sampling period

710   to obtain the D_{50} at a specific SS_C. The D_{50} values of the rBCc particles were determined

711   to be 166 (± 16) nm and 110 (± 5) nm for SS_C of 0.1% and 0.2%, respectively. The two

712   D_{50} values are both smaller than those determined for rBCc particle in Nanjing (Wu et

713   al., 2019), likely owing to the presence of WS-HOA in Shanghai. Figure 13d shows the

714   f_{AC} at SS_C of 0.1% (D_{50} of 166 nm) was 16 (± 3%,)%, and the f_{AC} at SS_C of 0.2% (D_{50}

715   of 110 nm) was 59 (± 4%.)%.

716

717   **3.5 A case study influenced by ship emissions**

718   **3.5.1 Potential source areas of rBCc**

719   To explore the potential geographic origins of rBCc at the receptor site, the hybrid

720   single-particle Lagrangian integrated trajectory (HYSPLIT) model (version 4.9) was

721   applied here. Figure 14a shows that the backward trajectories were classified into four

722   air mass clusters, including one long-range transport from northern sea (Cluster1), one

723   long-range transport from northeastern sea (Cluster2), a local one from eastern ports

724   (Cluster3), and one from northwestern inland region (Cluster4). The four clusters

725   occupied 23.8%, 33.8%, 37.3%, and 5.0% of the total trajectories, respectively. It is

726   clear that the sampling period was influenced by offshore air masses in most of the time

727   (95%). Cluster3 had the highest mean rBCc concentrations (13.2 ± 10.9 μg m^{-3}) while

728   the mean concentrations of the other three clusters were apparently lower (4.3~5.2 μg

729   m^{-3}). This result is plausible as Cluster3 was the shortest in length therefore was least

730   diluted compared with other three clusters. Average chemical compositions of the rBCc

731   from four clusters (Fig. 14b) showed some differences as well: Cluster1 and Cluster2

732   had higher MO-OOA$_{rBC}$ contributions, possibly owing to the interceptions of more

733   aged SOA species during the long-range transports; While Cluster4 had less MO-

734   OOA$_{rBC}$ but a bit more POA$_{rBC}$ contributions, likely attributing to more primary species

735   emitted in inland regions (similarly, a higher fraction of nitrate was likely because of

736   enhanced NO$_2$ emissions).

737

738   **3.5.2 A typical case of rBCc affected by ship emissions**

739   Ship emissions are found to have an important impact on the air quality of

740　Shanghai and the Yangtze River Delta (Zhao et al., 2013;Fan et al., 2016;Liu et al.,

741　2017b;Chen et al., 2019). The ship engines usually burn heavy fuel oil (HFO), and

742　vanadium (V) and nickel (Ni) can be adopted as reliable tracers for the ship-emitted

743　particles (Ault et al., 2009;Moldanová et al., 2009;Ault et al., 2010). The long-term

744　variation of Ni/V ratio in ship-emitted particles in Shanghai has been recently reported

745　(Yu et al., 2021). The main conclusion is that Ni/V ratio was close to 0.4 in 2018, while

746　it became to be greater than 2.0 in 2020. Our measurement was carried out in 2018, and

747　we therefore chose a period from November ~~3~~3rd to ~~5~~5th as a typical case affected by

748　ship emissions (SEP period), since the average Ni/V ratio was ~0.50 and high

749　concentrations of both Ni and V were found. Figure ~~S9~~S10 shows the concentration-

750　weighted trajectories (CWT) of ship emission tracers (V, Ni), rBC and rBC-rich factor

751　during SEP, displaying that these components were mainly from sea. During SEP, the

752　correlation coefficient (r) between V(Ni) and rBC was 0.69 (0.74), indicating the SEP

753　was indeed impacted by ship emissions.

754　　　Figure 15 displays the chemical characteristics of rBCc and NR-PM$_1$ components

755　(especially the OA factors), V and Ni, gaseous pollutants and the meteorological

756　parameters during SEP. As a comparison, we also selected a period with no ship

757　emissions with the same time span as SEP (from 0:00 on November 10 to 0:00 on

758　November 12, termed as non-SEP), and a similar plot during non-SEP is presented in

759　Fig. ~~S10~~S11. During SEP, the wind was mainly from east, and the average wind speed

760　was ~0.5 (± 0.3) m s^{-1} (Fig. 15a); Wusong, Luojing and Waigaoqiao ports located

761　northeast of the sampling site (Fig. S1). Instead, the wind was mainly from north during

762　non-SEP (Fig. ~~S10a~~S11a). During SEP, the average mass concentrations of V and Ni

763　were ~~5.8 ng m^{-}~~6.3 (± 3.1) ng m^{-3} and ~~3.2.~~9 (± 1.4) ng m^{-3}, respectively, while those

764　during non-SEP were only 2.9 (± 1.4) ng m^{-3} and 2.6 (± 1.6) ng m^{-3}. The average mass

765　ratio of V/Ni during SEP was 2.0 in agreement with those reported in ship-influenced

766　PM$_1$ (Mazzei et al., 2008;Mar et al., 2009), and within the range of 1.9 to 3.5 for

767　domestic HFO ~~(Zhao et al., 2013)~~(Zhao et al., 2013), while the average ratio of V/Ni

768　(1.1± 0.8) during non-SEP was outside the range. Moreover, the major air pollutants

769　emitted from ships include nitrogen oxides (NO$_x$), sulfur oxides (SO$_2$), carbon

monoxide (CO), hydrocarbons and primary/secondary particles (Becagli et al., 2017;Wu et al., 2021). As demonstrated in Fig. 15d and Fig. ~~S10d~~S11d, SO_2 concentration was overall higher during SEP (10:00-16:00 on November 11 not included); mass loading of NO_2 was higher during the rush hours of non-SEP, but was higher at night (no traffic) during SEP. Mass proportion of sulfate in NR-PM$_1$ during SEP was also higher than that during non-SEP (~~21.0~~22.7 ± 8.1 % *vs.* ~~18.7~~19.1± 5.3 %), but *vice versa* for nitrate (~~18~~17.8~~%~~ (± 9.9)% during SEP *vs.* ~~25.4%~~26.2 (± 9.1)% during non-SEP).

We further investigated the dependences of rBCc and NR-PM$_1$ species on V during SEP and non-SEP, as shown in Fig. ~~S11~~S12. Here we only used V since Ni level might be influenced by other emission sources, such as refining industry (Jang et al., 2007;Kim et al., 2014) in urban Shanghai, and during non-SEP, Ni still presented a good correlation with rBC (r=0.80). During SEP, V concentrations (most of them >4 ng m^{-3}) overall positively correlated with both sulfate and nitrate (except for rBCc sulfate) (Fig. ~~S11a~~S12a). Considering that V concentration was independently measured for all fine particles, a better correlation with total NR-PM$_1$ sulfate than it with rBCc sulfate is reasonable. Similarly, V-rich particles had positive correlations with traffic-related OA and LO-OOA no matter in rBCc or in total NR-PM$_1$ (Fig. ~~S11b~~S12b). Conversely, during non-SEP, particles with low-V content (most of them <4 ng m^{-3}) had no clear links with sulfate, nitrate, POA and SOA species (even anti-correlations for V>2.5 ng m^{-3}) (Figs. ~~S11c~~S12c and ~~S11d~~S12d; a detailed comparison of the correlation coefficients of V with OA factors of rBCc and NR-PM$_1$ organics are provided in Table S2). The results above ~~do demonstrate~~demonstrate that during SEP, chemical properties of the particles (both fresh and aged ones) were clearly linked with ship influences.

Previous studies (Ault et al., 2009;Ault et al., 2010;Liu et al., 2017b) have shown that the fresh ship-emitted V-rich particles are typically accompanied by high sulfate contribution, while those aged V-containing ship particles are on the other hand with relatively high nitrate contribution. In order to further probe chemical characteristics and evolution processes of particles influenced by ship emissions, we divided SEP into three episodes (i.e., EP1-EP3) (marked in Fig. 15). During EP1, rBC content was

800 highest (Fig. 15k) and coating was thinnest (Fig. ~~S12i~~S13i) indicating the particles were

801 relatively fresh, nevertheless the SOA contents were not low (Figs.15j and 15l), OS_C

802 was moderate (Fig. ~~S12j~~S13j), sulfate portions in NR-PM$_1$ and rBCc were both the

803 highest (26.5%), and nitrate portion was the lowest (9.8%) among three episodes

804 (Figs.15i and 15k). Such composition is not common in other cases, demonstrating it

805 was a specific period impacted by fresh ship emissions. EP2 had the highest mass

806 loadings of V, gas pollutants as well as the lowest planetary boundary layer (PBL)

807 height (~200 meters) (Fig. ~~S12~~S13). Mass contributions of nitrate increased and sulfate

808 decreased, and rBC content decreased from those during EP1, signifying that the

809 particle population likely contained some aged ship-emitted particles. ~~Of course~~Surely,

810 particle composition during EP2 was also influenced by the formation mechanisms of

811 secondary species: EP2 was mostly during nighttime, therefore photochemical

812 formation of sulfate and SOA were weak (~~contributions were low~~ as shown in Figs. 15i-

813 ~~l),~~ and 15l, sulfate contribution was only 15.1%, and SOA contribution was only 33.7%),

814 while nitrate formation was enhanced due to the nocturnal process. During EP3, rBC

815 was the lowest, sulfate and V were moderate, nitrate and SOA were highest in both

816 rBCc and NR-PM$_1$, OS_C and R_{BC} were highest in rBCc among the three episodes (Figs.

817 15i-l and Figs. ~~S12i~~S13i-k), therefore it was also a period with influence from aged

818 ship-emitted particles; the difference from EP2 is that photochemically formed sulfate

819 and SOA were still significant as EP3 was in the later afternoon and early evening,

820 though heterogeneously formed nitrate played a non-negligible role too (see the

821 increase of RH, increase of nitrate and decrease of O_3 concentrations from the

822 beginning of EP3 in Fig. 15).

4. Conclusions and implications

825 We conducted a field measurement during November of 2018 in urban Shanghai,

826 China, focusing on the elucidation of physical and chemical properties of the ambient

827 particles containing rBC cores (rBCc) by using a laser-only SP-AMS together with a

828 HR-AMS. The campaign-average rBCc was 4.6 (± 4.4) μg m^{-3}, occupying ~19.1 (±

829 4.9) % mass of the total NR-PM$_1$. The average mass ratio of coating to rBC cores (R_{BC})

830   was ~5.0, (± 1.7), indicating an overall thick coating, compared with the rBCc near

831   combustion source. Sulfate was found to preferentially condense on non-rBC particles

832   thus led to a low fraction of rBCc sulfate to that in NR-PM$_1$ (7.4% ± 2.2 %), while

833   distribution of nitrate between rBCc and non-rBC particles showed no obvious

834   difference. PMF analysis on rBCc and NR-PM$_1$ OA reveals that cooking-related

835   organics were externally mixed with rBC, and a small portion of organics from biomass

836   burning was only present in rBCc; the traffic-related OA species, however, was in a

837   large part internally mixed with rBC.

838   A regression algorithm was applied to deconvolute the size distributions of

839   individual rBCc OA factors, and results show that small rBCc particles were

840   predominantly generated from traffic, and such particles could grow bigger because of

841   condensation of secondary inorganic and organic components, resulting in thick coating.

842   Investigation on diurnal patterns of the rBCc species reveals that sulfate and two SOA

843   factors (LO-OOA$_{r\mathrm{BC}}$ and MO-OOA$_{r\mathrm{BC}}$) were generated mainly through daytime

844   photochemical oxidation; nitrate, on the other hand, was governed mainly by the

845   nocturnal N_2O_5 hydrolysis. Partial SOA was found to be produced from in-situ

846   photochemical conversion from traffic-related POA. An average coating time (ACT)

847   was proposed to roughly estimate the timescales for the secondary species to coat on

848   rBC, and the ACT of sulfate, LO-OOA$_{r\mathrm{BC}}$, MO-OOA$_{r\mathrm{BC}}$ and nitrate were approximately

849   57, 5, 7 and 19 hours, respectively.

850   Moreover, the size-resolved hygroscopicity parameters of rBCc particles ($\kappa_{r\mathrm{BCc}}$)

851   and the coating material (κ_{CT}) were obtained based on the elucidated composition of

852   rBCc particles. The fitted equations are: $\kappa_{r\mathrm{BCc}}(x)= 0.29-0.14 \times \exp(-0.006 \times x)$ and

853     $\kappa_{\mathrm{CT}}(x) = 0.35 - 0.09 \times \exp(-0.003 \times x)$ (x is $D_{r\mathrm{BCc}}$, $150<x<1000$ nm). The minimums

854   of both $\kappa_{r\mathrm{BCc}}$ and κ_{CT} were at ~150 nm due to the abundances of hydrophobic rBC cores

855   and traffic-related HOA at this size. Under critical supersaturations (SS_C) of 0.1% and

856   0.2%, the D_{50} values were estimated to be 166 (± 16) and 110 (± 5) nm, and the

857   activated number fractions of rBCc particles were 16 (± 3%)% and 59 (± 4%,)%,

858   respectively. Finally, a typical case with influence from ship emissions was investigated.

859   During this period, the rBCc particles were enriched in V (on average 5.86.3 ± 3.1 ng

860   m^{-3}), with a V/Ni ratio of 2.0, (± 0.6), and various secondary formation processes affect

861   the ship-emitted particles at different times of the day.

862   In summary, the findings from this comprehensive study on *r*BCc provide rich

863   information regarding the various primary sources and secondary formation pathways

864   of species coated on *r*BC, as well as the features of distributions of those species

865   between *r*BC and non-rBC particles. In particular, different types of *r*BCc particles

866   from diesel and gasoline vehicle emissions were resolved and elucidation of their

867   properties are useful to their future effective control. Understanding of the formation

868   processes and coating timescales of secondary components is helpful to understand the

869   impact of ambient BC particles too. At last, the parameterized relationship of

870   hygroscopicity with size distribution is useful for modelling the climate effect of *r*BC

871   (alternation of cloud properties).

872

873   *Data availability.* The data in this study are available from the authors upon request

874   (caxinra@163.com).

875

876   *Supplement.* The supplement related to this article is available online at: XXX

877

878   *Author contributions.* SJC, DDH, YZW, JFW, FZS, and XLG conducted the field

879   measurement. SJC, DDH, YZW, JFW, and JKX analyzed the data. YJZ, HLW, CH and

880   HL reviewed the paper and provide useful suggestions. SJC and XLG wrote the paper.

881

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895

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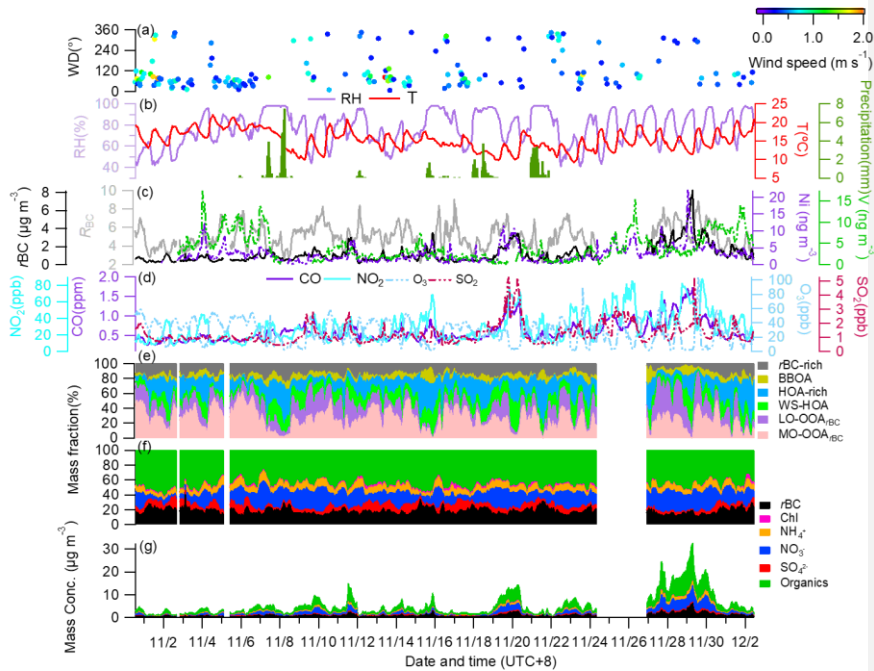
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Figure 1. Time series of (a) wind direction (WD) colored by wind speed (WS), (b) air

temperature (T), relative humidity (RH) and precipitation, (c) mass concentrations of

rBC, Ni, V, and R_{BC} (mass ratio of all coating species to rBC), (d) mass concentrations

of gas pollutants of CO, NO$_2$, O$_3$ and SO$_2$, (e) mass fractions (%) of different OA factors

to the total rBCc OA, (f) mass fractions (%) of different components to the total rBCc

mass, and (g) mass concentrations of stacked rBCc components.
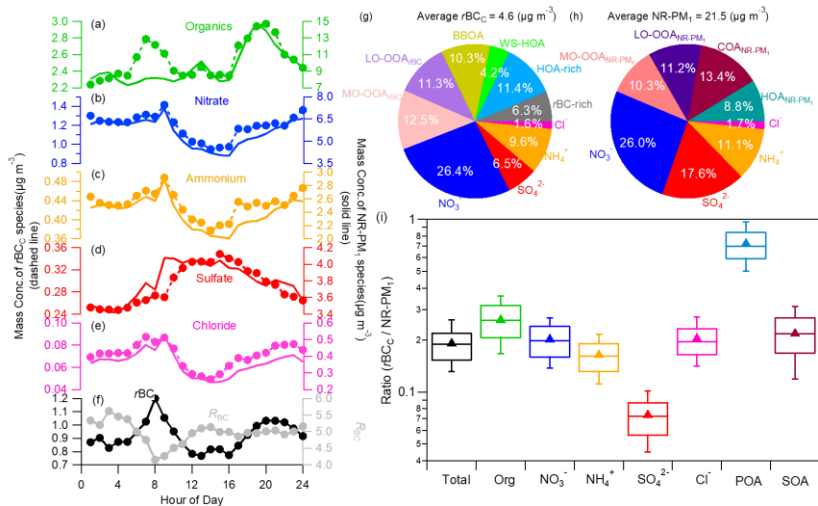
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Figure 2. Diurnal cycles of mass concentrations of (a–e) rBCc and NR-PM$_1$ species (organics, nitrate, ammonium, sulfate, and chloride), and (f) rBC and R_{BC}. Campaign-average chemical composition of rBCc (g) and NR-PM$_1$ (h). (i) Mass ratios of species in rBCc to those in NR-PM$_1$ (the whiskers above and below the boxes mark the 90% and 10% percentiles, respectively; the upper and lower edge of the boxes represent the 75% and 25% percentiles, respectively; and the lines and triangles inside the boxes denote the median and mean values, respectively; SOA represents ([LO-OOA$_{rBC}$] + [MO-OOA$_{rBC}$])/([LO-OOA$_{NR-PM1}$] + [LV-OOA$_{NR-PM1}$]), and POA represents ([rBC-rich + HOA-rich + BBOA + WS-HOA])/HOA$_{NR-PM1}$).
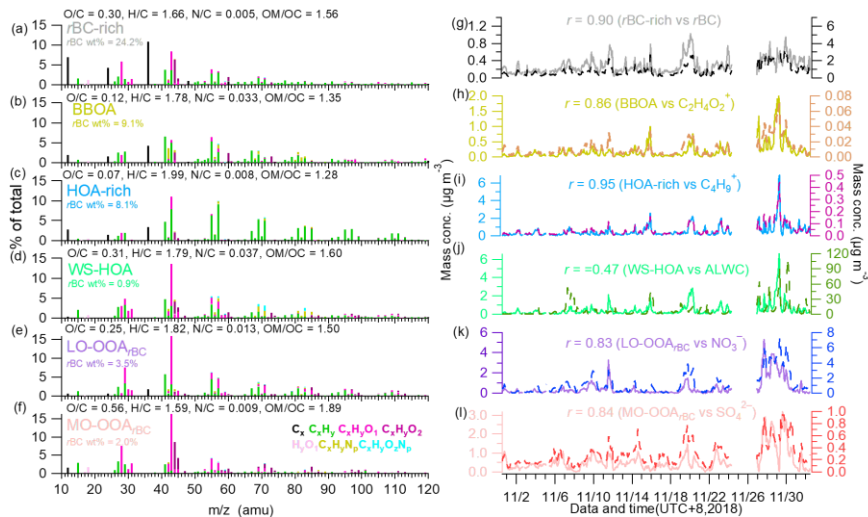
Figure 3. High resolution mass spectra of (a) *r*BC-rich, (b) BBOA, (c) HOA-rich, (d) WS-HOA, (e) LO-OOA*rBC*, and (f) MO-OOA*rBC*. (g-l) Time series of corresponding factors, their tracers (*r*BC, $C_2H_4O_2^+$, $C_4H_9^+$, ALWC, nitrate and sulfate) as well as the correlation coefficients (ALWC refers to aerosol liquid water content, which was estimated by using 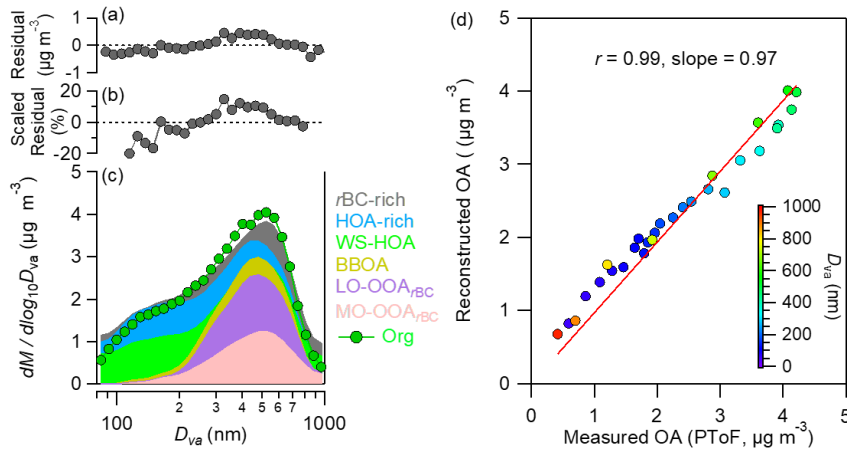the ~~extended aerosol inorganic model (Clegg et al., 1998). Calculated ALWC at different RH values is shown in Fig. S4~~model II of extended aerosol inorganic model (E-AIM II)(Clegg et al., 1998); calculation details and results at different RH values are described in the caption and shown in Fig. S5)

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1344 Figure 4. Summary of key diagnostic plots of derivation of size distributions of

1345 individual *r*BCc OA factors. (a) Absolute and (b) relative residuals between the

1346 reconstructed and measured OA mass concentrations in different size bins. (c) Stacked

1347 size distributions of the six OA factors compared to the size distributions of total OA.

1348 (d) Reconstructed OA mass concentrations compared to the measured values for
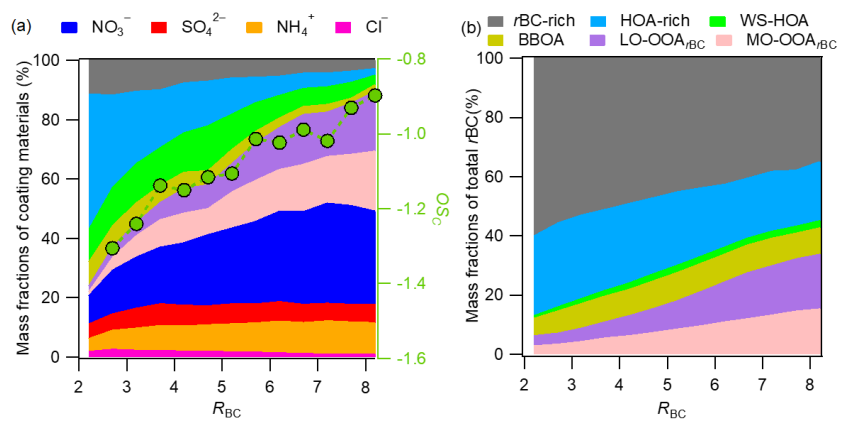
1349 different size bins (80-1000 nm).

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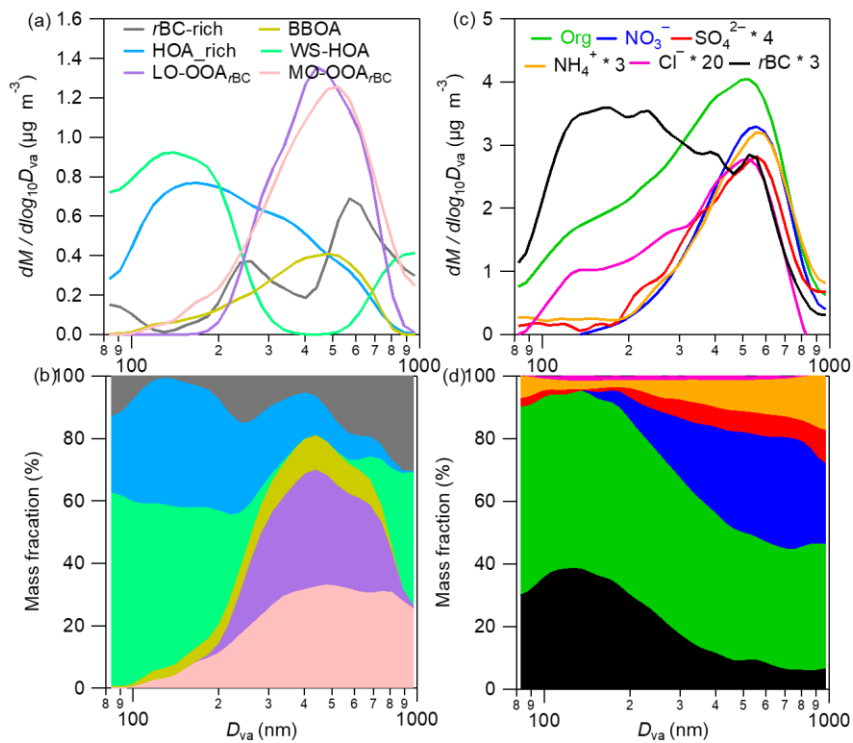
Figure 5. Campaign-average size distributions of six rBCc OA factors (a) and individual rBCc components (b), and corresponding mass contributions of the six factors to the total rBCc OA (c), and the major components to the total rBCc (d) at different sizes (80-1000 nm).
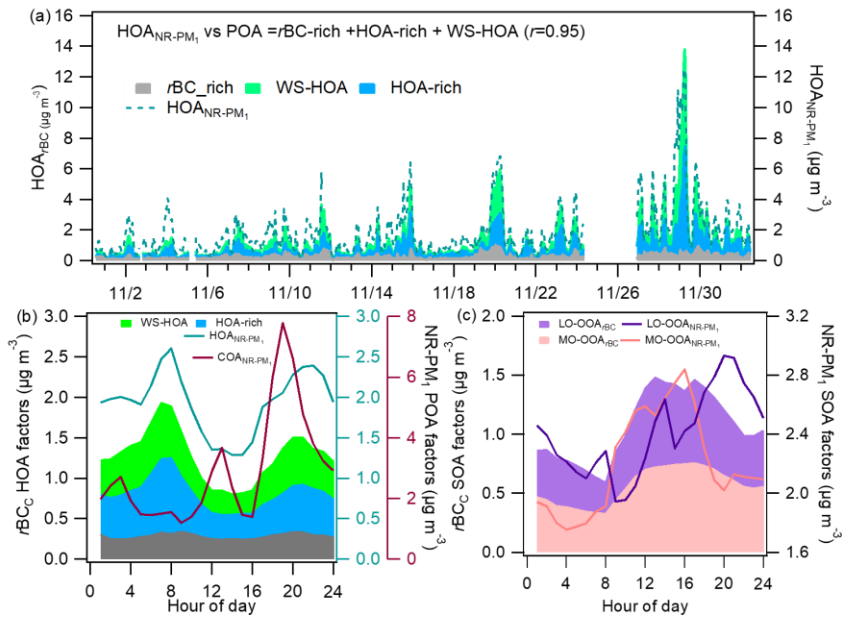
1359 Figure 6. (a) Variations of mass fractions of the major rBCc components against R_{BC}.

1360 (b) Variations of mass contributions of individual rBCc OA factors to rBC against R_{BC}.
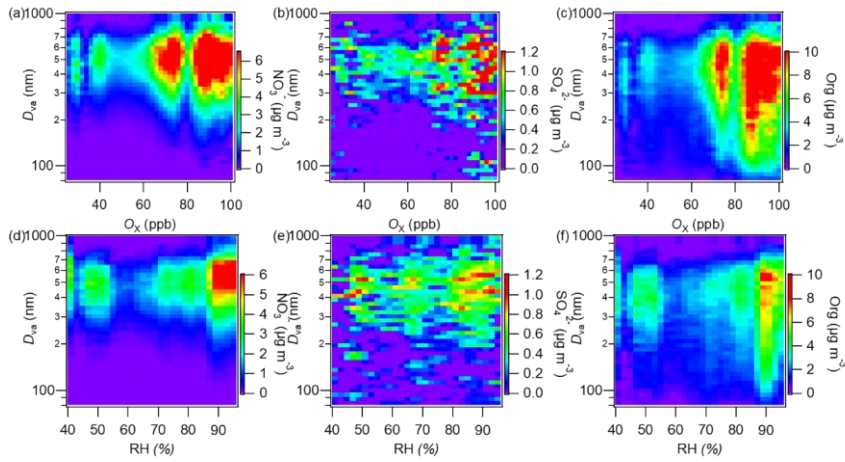
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Figure 7. (a) Time series of stacked three rBCc POA factors (i.e., rBC-rich, HOA-rich, and WS-HOA) and HOA$_{NR-PM1}$. Comparisons of the diurnal patterns of different POA factors (b) and SOA factors (c) of rBCc and NR-PM$_1$.
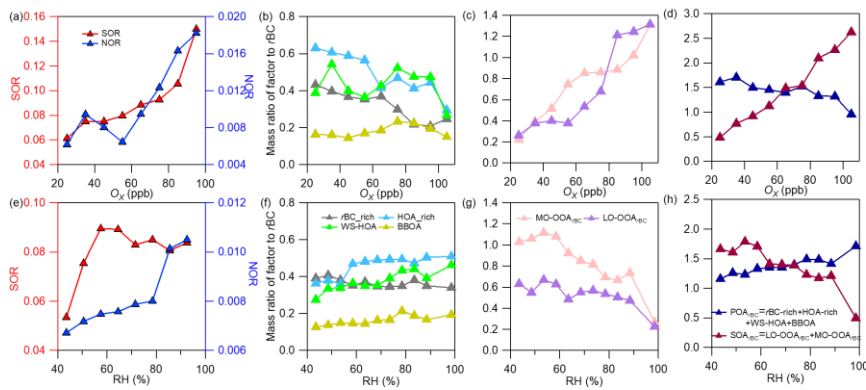
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1369   Figure 8. Image plots of size distributions of *r*BCc nitrate, sulfate, organics as a function

1370   of (a-c) O_X and (d-f) RH, respectively (color represents its concentration).

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Figure 9. Variations of nitrogen oxidation ratio (NOR) and sulfur oxidation ratio, mass
ratios of different POA factors, SOA factors and total POA and SOA to rBC against O_X
(a-d) and RH (e-h) (NOR= $n\mathrm{NO_3^-}/(n\mathrm{NO_3^-}+n\mathrm{NO_2}+n\mathrm{NO})$ and SOR= $n\mathrm{SO_4^{2-}}/(n\mathrm{SO_4^{2-}}+n\mathrm{SO_2})$,
where $n\mathrm{NO_3^-}$, $n\mathrm{SO_4^{2-}}$, $n\mathrm{NO_2}$, $n\mathrm{NO}$ and $n\mathrm{SO_2}$ are the molar concentrations of particle-
phase sulfate, nitrate, gaseous $\mathrm{NO_2}$, NO and $\mathrm{SO_2}$, respectively).
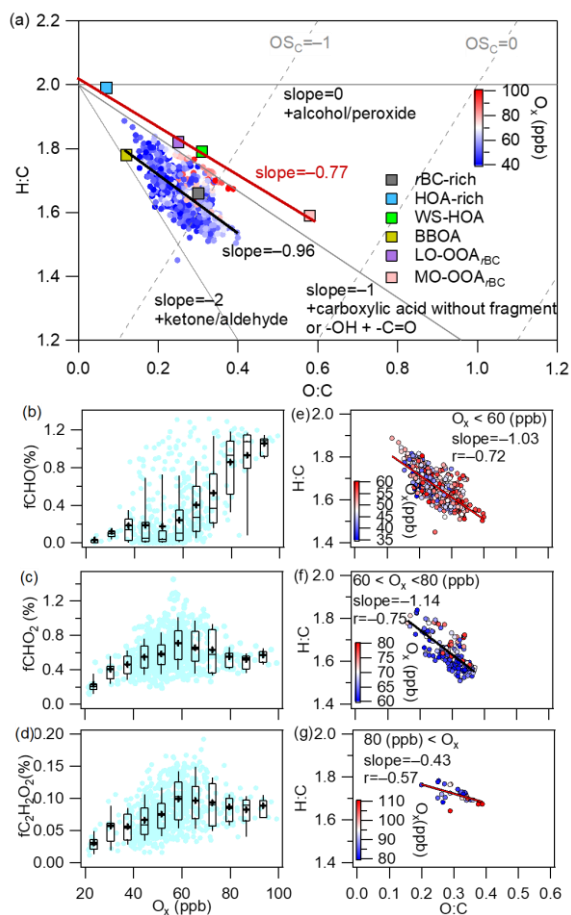
Figure 10. (a) Van Krevelen diagram of H/C versus O/C ratios for all rBCc OA and the six factors colored by O_X concentrations (the black line represents the linearly fitted line of all OA data, and the red line is the fitted line of the four OA factors). (b-d) Mass fractions of selected oxygenated ion fragments as a function of O_X (meanings of the boxes are the same as those described in Fig. 2). (e-g) Scatter plots of H/C versus O/C ratios under different O_X levels (data are colored by O_X concentrations).
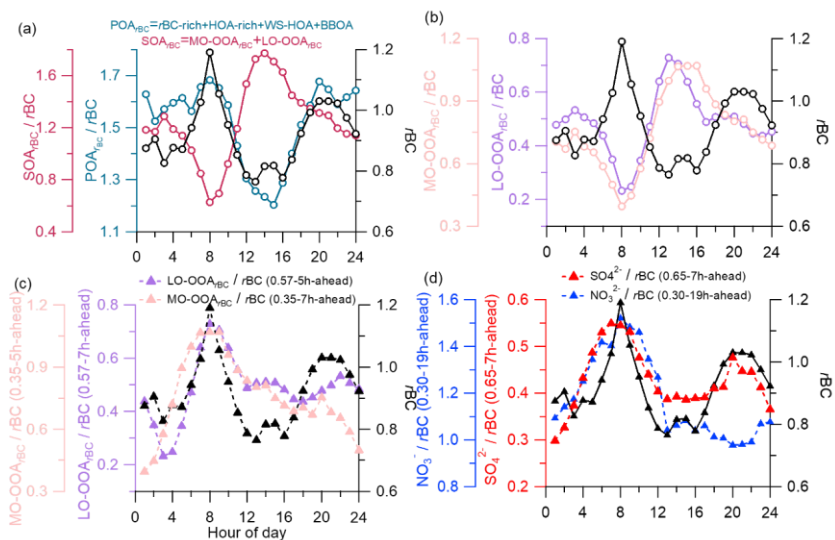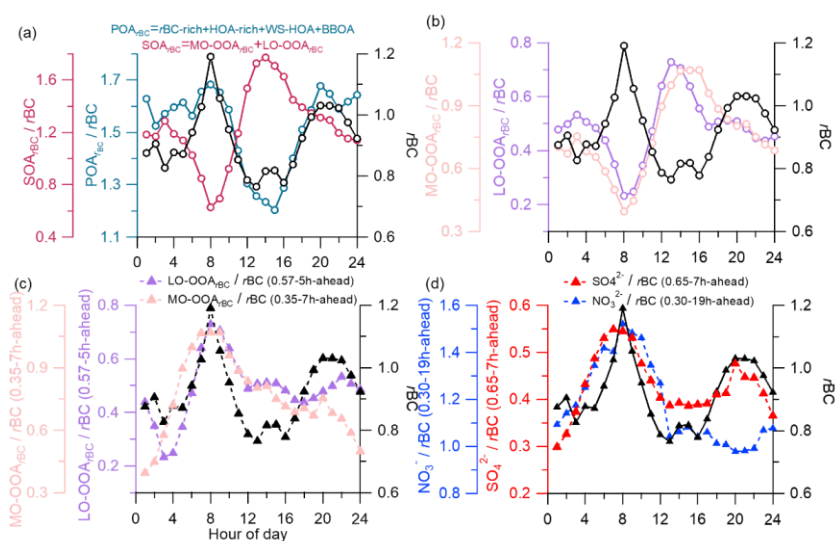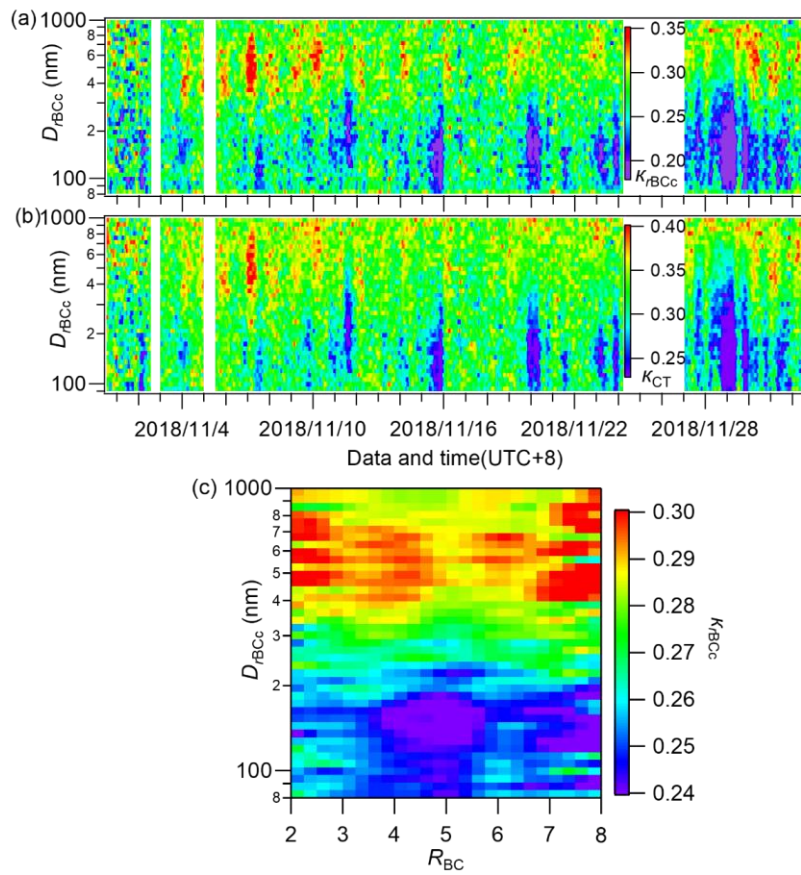
Figure 11. Campaign-average diurnal patterns of (a) rBC, POA$_{r\text{BC}}$/rBC and SOA$_{r\text{BC}}$/rBC, and (b) rBC, MO-OOA$_{r\text{BC}}$/rBC and LO-OOA$_{r\text{BC}}$/rBC. Adjusted diurnal patterns by the average coating time (ACT) for (c) LO-OOA$_{r\text{BC}}$/rBC, MO-OOA$_{r\text{BC}}$/rBC, and (d) SO$_4^{2-}$/rBC, NO$_3^-$/rBC.

Figure 12. Image plots of size-resolved hygroscopicity parameters of (a) rBCc ($\kappa_{r\text{BCc}}$), (b) its coating materials (κ_{CT}) during the whole campaign, and (c) the campaign-average size-resolved $\kappa_{r\text{BCc}}$ at different R_{BC}.

(a) $K_{rBCc}(x) = 0.29 - 0.14 * \exp(-0.006 * x)$

$x = D_{rBCc}$

$150 < x < 1000$ nm

K_{rBCc}

(b) $K_{CT}(x) = 0.35 - 0.09 * \exp(-0.003 * x)$

$x = D_{rBCc}$

$150 < x < 1000$ nm

K_{CT}

(c) $SS_c(\%)$

$SS_C = 0.20\%$

$SS_C = 0.10\%$

D_{rBCc} (nm)

(d) $dN/dlog_{10}D_{rBCc}$ (cm^{-3})

$SS_C = 0.2\%$
$D_{50} = 110$ nm

activated fraction

$SS_C = 0.1\%$
$D_{50} = 166$ nm

D_{rBCc} (nm)

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(a) $\kappa_{rBCc}(x) = 0.29 - 0.14 * \exp(-0.006 * x)$

$x = D_{rBCc}$

$150 < x < 1000$ nm

Coefficient ± SD
Coef1 = 0.29 ± 0.00
Coef2 = 0.14 ± 0.02
Coef3 = 0.006 ± 0.00

κ_{rBCc}

(b) $\kappa_{CT}(x) = 0.35 - 0.09 * \exp(-0.003 * x)$

$x = D_{rBCc}$

$150 < x < 1000$ nm

Coefficient ± SD
Coef1 = 0.29 ± 0.00
Coef2 = −0.09 ± 0.01
Coef3 = 0.003 ± 0.00

κ_{CT}

(c) $SS_C = 0.20\%$

$SS_C = 0.10\%$

$SS_c(\%)$

D_{rBCc} (nm)

(d) $dN/dlog_{10}D_{rBCc}$ (cm^{-3})

$SS_C = 0.2\%$
$D_{50} = 110$ nm

activated fraction

$SS_C = 0.1\%$
$D_{50} = 166$ nm

D_{rBCc} (nm)

Figure 13. Campaign-average size-resolved hygroscopic parameters for rBCc (κ_{rBCc}) and (a) for its coatings (κ_{CT}) (b) (the red lines are exponential fits of the data of 150-1000 nm). (c) Campaign-average size-resolved critical supersaturation (SS_C), and (d) the predicted activated fraction of rBCc number concentration based on D_{50} at SS_C of 0.1% (166 nm) and 0.2% (110 nm) (the solid circles are mean values, the upper and lower lines are the 75th and 25th percentiles, respectively).
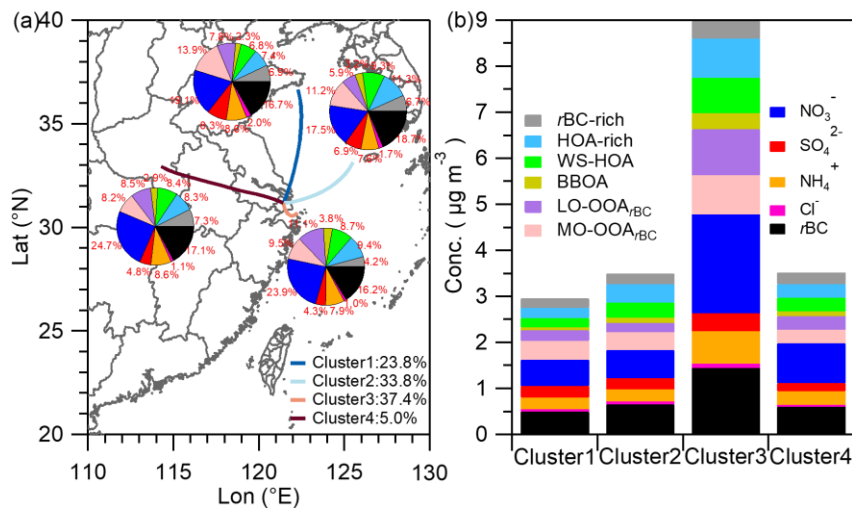
Figure 14. (a) Four clusters of 24-h backward trajectories (at altitude of 500 m) analyzed by NOAA HYSPLIT model (http://www.arl.noaa.gov/ready/hysplit4.html) embedded in Zefir(Petit et al., 2017)(Petit et al., 2017), with the pie chart showing the average *r*BCc chemical compositions in each cluster. (b) Stacked mass concentrations of the *r*BCc components of the four clusters.
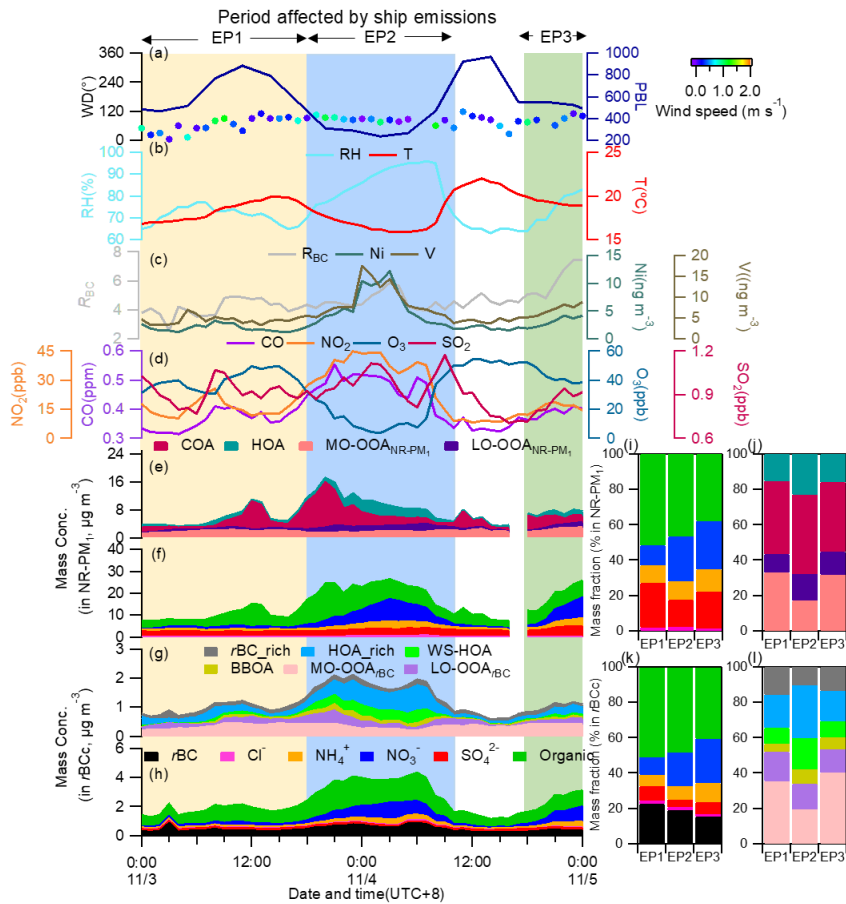
Figure 15. Time series of (a) wind direction (WD) colored by wind speed (WS), planetary boundary layer (PBL) height, (b) relative humidity (RH) and temperature (T), (c) mass concentrations of particle-phase Ni and V, and R_{BC}, (d) mass concentrations of CO, NO_2, O_3, SO_2, stacked concentrations of (e) NR-PM$_1$ OA factors, (f) NR-PM$_1$ species, (g) rBCc OA factors, and (h) rBCc components during the ship emission period (SEP). Mass contributions of different components to NR-PM$_1$ (i), different OA factors to total NR-PM$_1$ OA (j), different components to rBCc (k), and different OA factors to total rBCc OA (l) for the three episodes (EP1, EP2 and EP3).