

Black carbon involved photochemistry enhances the formation of sulfate in the ambient atmosphere

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1 **Black Carbon Involved Photochemistry Enhances the Formation of Sulfate in the**
2 **Ambient Atmosphere: Evidence from *in-situ* Individual Particle Investigation**

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20

21 **Key points:**

- 22 1. Enhanced sulfate to nitrate ratios (SNRs) are observed for the BC-containing particles
23 2. The distinct diurnal variation of the enhanced SNRs is most likely attributed to BC catalytic
24 photochemistry
25 3. SNRs in individual BC-containing particles could be well predicted by the radiation-related
26 parameters and the relative BC content

27 **Abstract**

28 Mixing state of black carbon (BC) with secondary species has been highlighted as a
29 major uncertainty in assessing its radiative forcing. While recent laboratory simulation has
30 demonstrated that BC could serve as a catalyst to enhance the formation of sulfate, its role in
31 the formation and evolution of secondary aerosols in the real atmosphere remains poorly
32 understood. In the present study, the mixing of BC with sulfate/nitrate in the atmosphere of
33 Guangzhou (China) was directly investigated with a single particle aerosol mass spectrometer
34 (SPAMS). The peak area ratios of sulfate to nitrate (SNRs) for the BC-containing particles are
35 constantly higher than those of the BC-free particles (defined as particles with negligible BC
36 signals). Furthermore, the seasonal SNR peak is observed in summer and autumn, and the
37 diurnal peak is found in the afternoon, consistent with the trends of radiation-related
38 parameters (i.e., solar radiation and temperature), pointing to the BC-induced photochemical
39 production of sulfate. Such hypothesis is further supported by the multilinear regression and
40 random forest analysis, showing that the variation of SNRs associated with the BC-containing
41 particles could be well explained ($R^2 = \sim 0.7-0.8$) by the radiation-related parameters ($> 30\%$
42 of the variance) and the relative BC content ($\sim 20\%$) in individual particles, but with limited
43 influence of precursors ($SO_2/NO_x: < 5\%$). Differently, the radiation-related factors only
44 explain $< 10\%$ of the SNR variation for the BC-free particles. These results provide ambient
45 observational evidence pointing to a unique role of BC on the photochemical formation and
46 evolution of sulfate, which merits further quantitative evaluations.

47 **Keywords:** black carbon; sulfate; individual particles; mixing state; SPAMS

48 1 Introduction

49 As a substantial fraction of atmospheric aerosols, black carbon (BC) or soot enhances haze
50 pollution, modifies the regional meteorology, and imposes a tremendous positive forcing on the
51 global climate by absorbing solar radiation [*Bond et al.*, 2013; *Ding et al.*, 2016; *Penner*, 2019].
52 While freshly emitted BC contains limited coating, atmospheric aging such as coagulation with
53 other particles, condensation of vapors, and cloud processing will lead to internally mixed BC
54 particles with complex compositions [*Zhang et al.*, 2018; *Riemer et al.*, 2019]. These aging
55 processes result in considerable variability in morphology, mixing state, and hygroscopic and
56 optical properties of BC particles, subsequently leading to the modification of climatic and
57 health effects [*He et al.*, 2015; *Peng et al.*, 2016; *Hu et al.*, 2020]. Nevertheless, significant
58 discrepancies between standard model predictions and regionally-specific observations are
59 tightly related to distinct compositional heterogeneity (or mixing state) among BC particles
60 [*Liu et al.*, 2017; *Matsui et al.*, 2018; *Fierce et al.*, 2020].

61 As one of the most critical factors determining the absorption of BC, the mixing state of
62 individual BC particles is highly complicated and constantly changing during their transport in
63 the atmosphere. BC particles were observed to be extensively internally mixed worldwide
64 [*Adachi et al.*, 2016; *Liu et al.*, 2017; *Zhang et al.*, 2017; *Motos et al.*, 2019], including various
65 areas around China, such as the Pearl River Delta (PRD) region [*Huang et al.*, 2012; *Zhang et*
66 *al.*, 2014; *Tan et al.*, 2016], Yangtze River Delta region [*Kleffmann and Wiesen*, 2005], and
67 North China Plain [*Zhang et al.*, 2018; *Liu et al.*, 2020a; *Yu et al.*, 2020], leading to
68 significantly enhanced light scattering and absorption capacity of BC. While extensive studies

69 have gained insight into the evolution of mixing state of BC particles, it has been merely
70 linked to the condensation of secondary species, such as sulfate, nitrate, and organics [*Ault et*
71 *al.*, 2010; *Cahill et al.*, 2012; *Gaston et al.*, 2013; *Zhang et al.*, 2013; *Zhang et al.*, 2018; *Yuan et*
72 *al.*, 2019]. Actually, BC can be actively involved in the formation of secondary species, through
73 interacting with atmospheric reactive species, such as nitrogen dioxide (NO₂), sulfur dioxide
74 (SO₂), ozone (O₃), and nitric acid (HNO₃) [*Kleffmann and Wiesen*, 2005; *McCabe and Abbatt*,
75 2009; *Khalizov et al.*, 2010; *Han et al.*, 2013b; *Zhao et al.*, 2017]. A recent laboratory study
76 indicates that the BC catalytic chemistry should play a considerable role in the enhanced sulfate
77 formation during the regional haze in China, in the presence of ammonia and NO₂ [*Zhang et al.*,
78 2020a]. Besides, the photochemical oxidation of some intrinsic organic compositions by O₂
79 might also be an essential aging process for BC [*Han et al.*, 2012]. There is also growing
80 evidence demonstrating that BC is photoactive and could release reactive oxygen species (ROS)
81 including singlet oxygen (¹O₂) and hydroxyl radical (\cdot OH), which may represent a crucial
82 aging pathway of BC [*Gehling and Dellinger*, 2013; *Li et al.*, 2018b; *Li et al.*, 2019]. The
83 results also show that the BC-induced ROS could further initiate the oxidation of OC, through
84 an electron transfer pathway [*Li et al.*, 2018b; *Li et al.*, 2019]. Therefore, the increase oxidation
85 capacity associated with the photochemical aging of BC may potentially contribute to the
86 formation of secondary aerosols, such as sulfate.

87 Despite environmental significance, whether the intrinsic properties of BC particles are
88 significant in the formation and evolution of secondary compositions in the ambient
89 atmosphere remains poorly understood. The main challenge to address such issues in field

90 measurement is to track the heterogeneous reactions unique to the BC-containing particles,
91 which relies on individual particle techniques accompanied with chemical information. For
92 instance, with an Aerodyne soot particle - aerosol mass spectrometer (SP-AMS), various
93 non-refractory species (e.g., sulfate, nitrate, and organics) associated with refractory BC can be
94 quantitatively traced in real-time [Lee *et al.*, 2015; Wang *et al.*, 2016b]. The temporal variation
95 of secondary compositions internally mixed with BC could also be indicated by single-particle
96 mass spectrometry (SPMS), despite only semi-quantitative information obtained [Cahill *et al.*,
97 2012; Healy *et al.*, 2012; Zhang *et al.*, 2014]. Measurements with both techniques have
98 indicated that active photochemical formation of oxidized organics and sulfate could lead to a
99 distinct diurnal cycle of mixing state of BC-containing particles [Moffet and Prather, 2009;
100 Zhang *et al.*, 2014]. However, the role of BC in such chemistry has not been identified yet. In
101 addition, there is still a lack of treatments for heterogeneous reactions on different types of
102 particles in most models [Zheng *et al.*, 2015]. Therefore, it is necessary to comprehensively
103 evaluate the effect of heterogeneous chemistry involving BC particles on the formation of
104 secondary compositions.

105 In the present study, a Single Particle Aerosol Mass Spectrometer (denoted as Hexin
106 SPAMS to show disparateness with the Aerodyne SP-AMS, which is unique to individual soot
107 particles) was applied to measure the size and chemical compositions of individual particles, in
108 order to accommodate the specific role of BC in the formation of secondary species. The
109 variation of sulfate (with nitrate as a reference) associated with both the BC-containing and
110 BC-free particles, and also their diurnal trends, are analyzed and discussed. The main objectives

111 are (1) to verify whether BC regulates the formation and evolution of sulfate in the ambient
112 atmosphere and (2) to explore the dependence of sulfate production on atmospheric conditions,
113 including their precursors and meteorological parameters.

114 **2 Methods**

115 **2.1 Data collection**

116 On-line measurements were conducted at a representative urban site in Guangzhou
117 (China) [Zhang *et al.*, 2019a], a megacity in the PRD region. The measurements cover four
118 seasons, including spring (21/02 to 11/04, 2014), summer (13/06 to 16/07, 2013), autumn
119 (26/09 to 19/10, 2013), and winter (15/12 to 25/12, 2013). The sampling inlet for fine particle
120 characterization was situated ~40 meters above the ground level.

121 The size and chemical composition of dried individual particles were obtained by the
122 Hexin SPAMS (Hexin Analytical Instrument Co., Ltd., China) in real-time [Li *et al.*, 2011].
123 Briefly, particles are introduced into the SPAMS through a critical orifice. They are focused
124 and accelerated to specific velocities determined by two diode Nd:YAG laser beams (532 nm)
125 located 6 cm apart. Based on the measured velocities, a pulsed laser (266 nm) downstream
126 can be triggered to desorb/ionize these individual particles, and ion fragments were produced
127 and measured by a dual polarity time-of-flight mass spectrometer. We set up the instrument at
128 given peak thresholds that can record only those peaks with areas greater than 5 units to
129 distinguish peaks from the background noise (< 1 unit) in the mass spectra. As a result,
130 velocity, detection moment, and mass spectrum for each ionized particle are recorded. The
131 velocity could be converted to vacuum aerodynamic diameter (d_{va}) based on a calibration

132 function created using polystyrene latex spheres (PSL, Duke Scientific Corp., Palo Alto) with
133 predefined sizes.

134 The back trajectories arriving the sampling site (100 m above the sea level) at daytime
135 (12:00 local time, left panel) and nighttime (0:00 local time, right panel) for each season, as
136 shown in Fig. S1 (Supporting Information), were simulated based on the back-trajectory
137 analysis (HYSPLIT 4.9, available at <http://ready.arl.noaa.gov/HYSPLIT.php>) by Air
138 Resources Lab [Draxler and Rolph, 2012]. The auxiliary meteorological data, including
139 ambient temperature (T), relative humidity (RH), wind direction, and wind speed (WS), and
140 concentration of gaseous pollutants (SO₂, NO_x, and O₃), BC, and PM_{2.5}, provided by
141 Guangdong Environmental Monitoring Center, are shown as seasonal (Fig. 1) and diurnal
142 trends (Fig. S2).

143 **2.2 Data analysis**

144 **2.2.1 SPAMS Data**

145 The SPAMS data analysis was performed by importing size and mass spectra of individual
146 particles into Matlab (The MathWorks, Inc.) using the FATEs toolkit [Sultana *et al.*, 2017].
147 BC-containing particles were classified according to the relative peak area (RPA) of carbon ion
148 cluster (i.e., $m/z \pm 12[C]^{+/-}$, $\pm 36[C_3]^{+/-}$, $\pm 48[C_4]^{+/-}$ or $\pm 60[C_5]^{+/-}$), which is set as larger than 0.05.
149 And thus, particles with $RPA < 0.05$ are regarded as BC-free particles. The potential influence
150 of the arbitrarily defined RPA for BC screening on the conclusions is also evaluated in section
151 3.4. Defined as the peak area of each m/z divided by the total ion mass spectral peak areas, RPA
152 is generally applied to indicate the relative fraction of a single species in individual particles

153 [Gross *et al.*, 2000]. The BC-containing particles ruled out with such criteria account for ~60-
154 -80% of all the measured particles (Table S1), which are in the range of those reported in the
155 urban atmosphere [Healy *et al.*, 2013].

156 The majority of the BC-containing particles distribute in a size range of 0.2–1.0 μm (Fig.
157 S3a), which is similar for the BC-free particles. The size range is consistent with dominant
158 mass fraction of BC in the PRD region [Huang *et al.*, 2012]. Representative ion peaks for the
159 BC-containing particles, as presented in Fig. 2, are carbon ion clusters (e.g., $m/z \pm 12[\text{C}]^{+/-}$,
160 $\pm 36[\text{C}_3]^{+/-}$, $\pm 48[\text{C}_4]^{+/-}$ and $\pm 60[\text{C}_5]^{+/-}$), organic carbon (OC) fragments (m/z 27 $[\text{C}_2\text{H}_3]^+$,
161 29 $[\text{C}_2\text{H}_5]^+$, 37 $[\text{C}_3\text{H}]^+$, 26 $[\text{CN}]^-$, 42 $[\text{CNO}]^-$, and 43 $[\text{C}_2\text{H}_3\text{O}]^+$), and secondary inorganic species,
162 such as sulfate ($-97[\text{HSO}_4]^-$), nitrate ($-62[\text{NO}_3]^-$), and ammonium ($18[\text{NH}_4]^+$). There are also
163 some metallic species such as 23 $[\text{Na}]^+$ and 39 $[\text{K}]^+$. Compared with the BC-free particles, the
164 major enhanced ion peaks are the carbon ion clusters for the BC-containing particles.

165 An adaptive resonance theory-based neural network algorithm (ART-2a) was further
166 applied to classify the measured individual particles based on the presence and intensity of ion
167 peaks, with a vigilance factor of 0.7, a learning rate of 0.05, and 20 iterations [Song *et al.*, 1999].
168 Through additional manually merging of similar clusters, seven major particle types (i.e.,
169 BC-rich, organic carbon rich (OC-rich), internally mixed OC and BC (OC-BC), potassium rich
170 (K-rich), Seasalt, Dust, Metal-rich) with distinct chemical patterns were obtained (Fig. S4),
171 representing > 98% of the population of all the measured particles. The majority of particle
172 types are similar for the BC-containing and BC-free particles, except for BC-rich particles that
173 only found in the BC-containing particles (Fig. S3b).

174 In the present study, we mainly focus on the difference of sulfate to nitrate ratio (SNR)
175 between the BC-containing and BC-free particles. The respective RPA ratios of sulfate and
176 nitrate between the BC-containing and BC-free particles are compared over the seasons, as
177 shown in Fig. 3. These ratios show significant variations, with higher values for sulfate RPA
178 ratios and lower values for nitrate RPA ratios in the BC-containing particles, indicating a
179 relatively higher fraction of sulfate rather than nitrate in these particles. It is also noted that the
180 sulfate RPAs are lower for the BC-containing particles than the BC-free particles, which is
181 likely attributable to the matrix effect during the ionization. And thus, only the SNR is applied
182 to make it comparable between the BC-containing and BC-free particles.

183 **2.2.2 Multiple linear and random forest regression**

184 Multiple linear and random forest analysis, explicitly describing a relationship between
185 predictor and response variables (i.e., regressors) [Berk, 2008], are applied to estimate the
186 relative contribution of several factors to the variations of SNRs for the BC-containing and
187 BC-free particles, respectively. In the multiple linear models, the least-squares fit is used, and
188 two of the most common measures of model fit are the residual standard error and the
189 proportion of variance explained (R^2). Furthermore, the Relaimpo package is used to assess the
190 relative importance of regressors in the linear model and offers the possibility of bootstrapping
191 them [Groemping, 2006]. Differently, random forest is for nonlinear multiple regression and
192 has been widely applied for prediction and classification, using trees as building blocks to
193 construct powerful prediction models [Breiman, 2001]. The algorithm first creates multiple
194 decision trees, where each tree is grown by using the bootstrap re-sampling method. The

195 relative importance of the predictor variables can also be obtained, with “Mean Decrease
196 Accuracy” presenting the capability of each independent variable in explaining the variability
197 of SNRs.

198 **3 Results and Discussion**

199 **3.1 Distinct variations of SNR associated with the BC-containing particles**

200 It can be seen from Fig. 4 that the seasonal and diurnal variations of SNR are distinguished
201 between the BC-containing and BC-free particles. The SNR shows an apparent seasonal
202 variation, with higher values in summer and autumn but lower in spring and winter. Despite
203 the similar SNR variations for both particle types over the seasons, the SNRs in the
204 BC-containing particles are obviously higher than those in the BC-free particles. In particular,
205 the average SNR for the BC-containing particles is ~2 times those for the BC-free particles in
206 summer and autumn. Such a seasonal variation of SNR is similar to the concentration ratio
207 observed for fine particles in Beijing, with the mean SNR in warmer seasons more than two
208 times that in cold seasons [Li *et al.*, 2020]. However, the difference of SNRs between the
209 BC-containing and BC-free particles cannot be ruled out based on previous bulk analysis.

210 There is a pronounced diurnal variation of SNRs for the BC-containing particles over the
211 seasons (Fig. 4b). A sharp increase of the SNRs in the BC-containing particles, rather than the
212 BC-free particles, started at noon hour (~12:00). On the other hand, the SNRs of the
213 BC-containing particles decreased from the highest values during the afternoon hours to the
214 lowest contribution during nighttime or early morning. The diurnal trend of SNRs for the
215 BC-containing particles is generally similar to that of temperature (Fig. S2). In both the

216 BC-containing and BC-free particles, nitrate varies in a similar trend, decreasing during the
217 afternoon but increasing during nighttime (Fig. 5), most probably attributed to the
218 heterogeneous uptake of N_2O_5 onto the wet aerosols during the high RH period [Lee *et al.*,
219 2003; Wang *et al.*, 2009]. The different SNR trends between the BC-containing and BC-free
220 particles could be mainly attributed to the increase of sulfate RPA during the afternoon,
221 specific for the BC-containing particles. Sulfate associated with the BC-free particles does not
222 show a clear trend, but with a distinct afternoon peak in the BC-containing particles (Fig. 5).
223 And thus, the diurnal variation of SNR is most probably driven by the variation of nitrate in
224 the BC-free particles.

225 Distinct diurnal cycles of secondary compositions associated with BC-containing
226 particles in Yangtze River Delta, China were similar observed [Wang *et al.*, 2016b; Li *et al.*,
227 2018a], with the increase of sulfate and low volatile oxidized organics in the afternoon due to
228 photochemical oxidation; however, with nitrate peaking during nighttime, driven by
229 thermodynamic equilibria and gas-to-particle partitioning [Wang *et al.*, 2016b]. Fast coating
230 of BC was typically found during noontime corresponding to high photochemistry intense and
231 oxidants levels [Moffet and Prather, 2009; Zhang *et al.*, 2018; Liu *et al.*, 2020b]. There are
232 also several studies reporting a correlation between the fraction of internally mixed BC and
233 photochemical activities [Wang *et al.*, 2017; Xu *et al.*, 2018], mainly attributed to the
234 condensation of secondarily formed compositions, including sulfate and oxidized organics.
235 Differently, Moffet and Prather [2009] also observed an increase of nitrate in the
236 BC-containing particles, due to the photochemical formation of nitric acid. However, as

237 discussed above, nitrate peaks at our site are most probably attributed to the nighttime
238 chemistry during the high RH period [Lee *et al.*, 2003; Wang *et al.*, 2009].

239 **3.2 Most possible mechanism for the BC-enhanced SNRs**

240 Overall, the SNR for the BC-containing particles is significantly higher than that for the
241 BC-free particles, reflecting a distinct behavior of the BC-containing particles towards the
242 formation and evolution of sulfate. Consistently, the presence of BC ion peaks represent the
243 major mass spectral difference between the BC-containing and BC-free particles (Fig. 2). The
244 diurnal trend of nitrate and sulfate associated with both the BC-containing and BC-free
245 particles, as discussed above, further indicates that it is the enhanced photochemical formation
246 of sulfate on the BC-containing particles that leads to the higher SNRs. Therefore, it is the
247 heterogeneous processes involving BC that are important since the condensation of gaseous
248 sulfuric and nitric acid gases is expected to be similar for different kinds of particles. The first
249 evidence is the consistent trends between the seasonal and diurnal trends of the SNRs (Fig. 4)
250 and temperature (Figs. 1 and S2), which implies a substantial role of photochemistry in the
251 evolution of the BC-containing particles. Compared with the BC-free particles, the role of
252 such chemistry involving BC is evident with a distinctly higher SNR peak in the afternoon
253 hours. In contrast, it seems that the variations of SNRs cannot be simply explained by
254 atmospheric oxidants ($O_x = O_3 + NO_x$) and the trend of their precursors SO_2/NO_x ($R^2 = 0.05$, p
255 < 0.01) (Figs. 1 and 3). The second evidence comes from that the increase of SNRs towards
256 higher relative BC content (Fig. S5), indicating that the BC fraction increase might contribute
257 to additional oxidants. The relative importance of these factors, including radiation-related

258 parameters (i.e., solar radiation and temperature) and the relative BC content in individual
259 particles, in the variation of SNRs for the BC-containing particles, as discussed in section 3.3,
260 further supports the significance of BC-induced photochemistry. In order to eliminate the
261 interference of different particle types, the K-rich particles were used as the surrogate to make
262 a comparison of SNRs, because it is the major particle type for both the BC-containing and
263 BC-free particles (Fig. S3b). This analysis further confirms the unique role of BC in this
264 heterogeneous process, as SNRs in the K-rich particles with BC signals are obviously higher
265 than those without BC signals (Fig. S5a).

266 As demonstrated by laboratory results, elemental carbon in BC-containing particles can
267 act as a photoactive substrate and has notable catalytic effects on reactions through electronic
268 transfer in the presence of O₂, which produces additional ROS, including ¹O₂ and ·OH [Li *et al.*,
269 2018b; Li *et al.*, 2019; Zhu *et al.*, 2020]. Furthermore, there are also studies reporting the
270 direct contribution of the additional ROS to the formation of sulfate from the oxidation of SO₂
271 on the surface of BC particles [Novakov *et al.*, 1974; Zhao *et al.*, 2017], which could be
272 significantly enhanced with the coexistence of O₃ [Xu *et al.*, 2015; He *et al.*, 2017]. However,
273 the interactions between BC particles and NO₂ are unlikely to contribute to the formation of
274 nitrate [Han *et al.*, 2013a; Guan *et al.*, 2017].

275 There are also some possible explanations against the above hypothesis, but are unlikely
276 to be significant. One is that BC and sulfate or their precursors originate from the same
277 primary sources. This seems unlikely given a relatively low correlation ($R^2 = 0.26$, $p < 0.01$,
278 Fig. S6) between the temporal profiles of the concentration of BC and SO₂. BC is generally

279 produced by incomplete combustion, whereas sulfate is most probably from the secondary
280 process involving the oxidation of its precursor SO₂ [Xiao *et al.*, 2009; Xue *et al.*, 2019],
281 which could be co-emitted with BC. BC is most attributable to the traffic emission in the
282 studied region, with a higher correlation with NO_x ($R^2 = 0.63$, $p < 0.01$, Fig. S6), whereas SO₂
283 or sulfate is mainly produced by coal combustion or biomass burning [Wang *et al.*, 2016c]. It
284 is further revealed from the polar plot with wind direction in Fig. S7 that BC and NO_x most
285 probably originate from local sources, whereas SO₂ is most likely contributed by regional
286 sources. Secondly, one may expect that BC facilitates the depletion of nitrate, including
287 evaporation and photochemical degradation. While the additional heat due to the
288 light-absorbing nature of BC may enhance the evaporation of nitrate, our data show that such an
289 effect is limited, as indicated by the similar variation of nitrate in the BC-containing and
290 BC-free particles (Figs. 5 and S2). Although photochemical degradation of nitrate may
291 improve the heterogeneous oxidation of SO₂ through the produced in-particle oxidants (OH,
292 NO₂, and NO₂⁻/HNO₂) [Gen *et al.*, 2019; Zhang *et al.*, 2019b], there is still no evidence showing
293 the influence of BC in the photochemistry of nitrate. Thirdly, higher SNRs associated with BC
294 may also be explained by the fact the freshly emitted smaller BC particles facilitate the
295 condensation of H₂SO₄, due to their larger surface area concentration. However, as shown in
296 Fig. S3a, the majority of the BC-containing particles were located in the size range of 0.2-1.0
297 μm, and extensively mixed with secondary components, which could be regarded as aged
298 particles. It is also noted that the SPAMS data is restricted to particles in the size range of
299 0.1-1.6 μm, and thus, particles with sizes smaller than 0.1 μm are beyond the scope of this

300 study. More directly, the SNRs show no clear trend with increasing size (Fig. S8), further
301 supporting the limited influence of particle size on the variation of SNRs.

302 In addition, the role of the transition metals, such as Fe and V, that catalyzed the
303 formation of sulfate [Ault *et al.*, 2010; Zhang *et al.*, 2019a] could be negligible due to their
304 limited number fraction (< 3% on average) and no preferential association with the
305 BC-containing particles (Fig. S3b). The influence of air masses and wind on the diurnal
306 variations of SNRs could also be limited, as no obvious difference is observed for daytime
307 and nighttime (Figs. S1 and S2). It is also possible that other oxidants (e.g., organic radicals,
308 H₂O₂) play an indispensable role in the evolution of sulfate, yet it is beyond the scope of the
309 present study.

310 **3.3 Factors determining the variations of SNRs**

311 To elucidate the relative importance of various meteorological and chemical factors on
312 the variation of SNRs, multilinear regression is applied to include the most possible
313 influencing factors, i.e., T, RH, O_x, solar radiation (SR), and SO₂/NO_x [Xu *et al.*, 2015; He *et*
314 *al.*, 2017; Wang *et al.*, 2019a], on the variations of SNRs during the daytime, when the SR
315 data are available. An additional factor, i.e., the relative BC fraction, is added to the
316 regression for the BC-containing particles. It is also noted that the influence of air masses on
317 the seasonal variations of SNRs could be limited, as SNRs share similar values in summer and
318 autumn associated with obviously different air masses (Fig. S1). Furthermore, contrasting
319 SNRs in autumn and winter were observed under the influence of similar air masses.

320 SNRs in both the BC-containing and BC-free particles could be well explained by these
321 factors (Fig. 6), with the evaluation of the model performance provided in Fig. S9. Notably,
322 the variation of the SNRs for the BC-containing particles can be better predicted ($R^2 = 0.68$, p
323 < 0.01) by these variables than that for the BC-free particles ($R^2 = 0.40$, $p < 0.01$). The
324 addition of the relative BC fraction in the regression improves the correlation coefficient R^2
325 from 0.54 to 0.68 for the BC-containing particles. An estimation of the relative importance of
326 the predictors shows that the SNRs for the BC-containing particles are mainly dependent on
327 the T (27%), RH (17%), and relative BC content (13%), but with limit dependence on the
328 SO_2/NO_x (2%). Differently, the SNRs for the BC-free particles are dominantly determined by
329 RH (19%), with modest contribution from SO_2/NO_x (7%), O_x (7%), and T (5%).

330 Consistently, random forest analysis could predict ~80% of the SNR variation for the
331 BC-containing particles, and the most important three predictors are T (26%), relative BC
332 content (25%), and RH (17%), as shown in Fig. S10. Since the diurnal variation of T typically
333 tracks the strength of photochemistry [He *et al.*, 2011; Xu *et al.*, 2017], such results further
334 support the importance of photochemistry and the relative BC content in the evolution of
335 sulfate associated with BC. While the analysis may not reliably inform the complex chemical
336 mechanisms of BC involved production of sulfate, the well-fitted results could still indicate
337 the significance of these factors in the variation of SNRs.

338 **3.4 Limitations**

339 The main limitation or bias in the present study is the use of RPA in these qualitative
340 individual mass spectral data rather than the absolute mass concentrations for individual species.

341 It should be noted that it is still quite challenging for the SPAMS based on laser-ablation to
342 provide quantitative information for individual species, due to various uncertainties induced by
343 the laser ionization, such as matrix effects and incomplete ionization [Jeong *et al.*, 2011; Healy
344 *et al.*, 2013; Zhou *et al.*, 2016]. Despite this, the variation of RPA is still a good indicator for the
345 investigation of atmospheric processing and mixing state of various particle types, including
346 BC-containing particles, at an individual particle level [Wang *et al.*, 2010; Zauscher *et al.*, 2013;
347 Zhang *et al.*, 2014]. In the present study, even though it is insufficient to provide a quantitative
348 assessment of SNRs on the BC-containing particles, our results do successfully identify a
349 distinct behavior of BC-containing particles in the ambient atmosphere and thus have an
350 advantage of providing a qualitative or semi-quantitative understanding of the evolution of
351 SNRs associated with BC. Future work should target a quantitative understanding of the
352 laboratory kinetics of the photochemical reactions of BC-containing particles, e.g., with
353 Aerodyne SP-AMS.

354 Another limitation is related to identifying the individual BC-containing particles based
355 on the arbitrary defined RPA of carbon ion clusters (i.e., > 0.05). However, as can be seen in
356 Fig. S5b, the average SNRs generally increase towards higher relative BC content, regardless of
357 the deviation. It indicates that the methodology for the identification of the BC-containing
358 particles would not lead to an ambiguous conclusion on the distinct behavior of the
359 BC-containing and BC-free particles. While some particle types, including pure ammonium
360 sulfate, and certain organic, cannot simply be ionized by SPAMS, the measured BC-free
361 particles should be still representative of the majority of particle types observed in the urban

362 atmosphere. As shown by microscopic analysis, such pure compounds limitedly contribute to
363 the particle population in a typical urban atmosphere [Fu *et al.*, 2012; Li *et al.*, 2016].

364 **4 Conclusions and Implications**

365 Our results provide observational evidence, extending the laboratory results to the
366 ambient atmosphere that BC could act as a photoactive and absorbing substrate [Li *et al.*,
367 2018b; Li *et al.*, 2019], leading to an enrichment of sulfate. Since there is considerable debate
368 regarding the mechanism for SO₂ oxidation [Wang *et al.*, 2016a; Xue *et al.*, 2016; Gen *et al.*,
369 2019; Wang *et al.*, 2019b; Wang *et al.*, 2020a; Wang *et al.*, 2020c], our finding further
370 underscores the importance of the intrinsic property of BC on the photochemical evolution of
371 sulfate, in particular, during summer and autumn. Given that BC accounts for an essential part
372 of particles in the urban atmosphere [Ding *et al.*, 2016; Tan *et al.*, 2016; Wang *et al.*, 2020b],
373 such a role might be critical for the formation and evolution of sulfate. Liu *et al.* [2019a]
374 observed increasing SNR with altitude over Beijing and attributed the vertical profile to
375 various factors, including plenary boundary layer structure, regional transportation, emission
376 variation, and the aging process of aerosols and gaseous precursors during vertical diffusion.
377 Our analysis may provide an additional explanation associated with photochemistry on the
378 BC-containing particles. The mechanism might also be particularly important during haze
379 episodes when heterogeneous chemistry is thought to play a considerable role in sulfate
380 production [Zheng *et al.*, 2015; Li *et al.*, 2020].

381 A most recent chamber simulation reveals that efficient sulfate formation from BC
382 catalyzed SO₂ oxidation in the presence of NO₂ and NH₃ under dark conditions [Zhang *et al.*,

383 2020a]. Our evidence further suggests that the photochemical activities during the daytime
384 might also be significant for the production of sulfate and influencing the evolution of BC in
385 the atmosphere. Regarding that sulfate is one of the primary drivers of the BC absorption
386 enhancement in the severely polluted areas in China [*Chen et al.*, 2017], the relative enrichment
387 of sulfate on BC may also partly explain the substantial diurnal variability of light absorption
388 enhancement and single-scattering albedo for BC in eastern China [*Xu et al.*, 2018]. However,
389 the influence of BC on the formation of secondary compositions is rarely considered in models
390 [*Matsui*, 2016], although it is well-known that accounting for variability in per-particle
391 composition and properties would help improve absorption enhancement predictions [*Fierce et*
392 *al.*, 2020]. Therefore, to account for the evolution and climate impact of BC accurately, it is
393 essential to include BC involved photochemistry in the regional aerosol-climate modeling,
394 since the associated sulfate are critical to evaluate the hygroscopic, phase, and optical
395 properties of BC-containing particles [*Ramana et al.*, 2010; *Sun et al.*, 2018; *Liu et al.*, 2019b].

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402

403 **Conflict of Interest**

404 There are no conflicts of interest in the article.

405

406 **Data Availability Statement**

407 The processed data supporting this paper are available on Zenodo
408 (10.5281/zenodo.5162927).

409

410 **References**

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686

687 **Figure Captions**

688 **Figure 1.** The auxiliary meteorological data, including solar radiation (SR), oxidants ($O_x =$
689 $NO_x + O_3$), T, RH, and concentration of BC and $PM_{2.5}$. SR and the concentration of BC are
690 not available in winter. The mean values for meteorological data and O_x , are also outlined for
691 each season in our previous publication [Zhang *et al.*, 2020b].

692 **Figure 2.** The representative mass spectra for (a) the BC-containing particles and (b) BC-free
693 particles. Red bars mark the enhanced ion peaks in the BC-containing particles, compared
694 with the BC-free particles.

695 **Figure 3.** (a) The respective RPA ratio of sulfate and nitrate between the BC-containing and
696 BC-negligible particles over the seasons, and (b) the seasonal variation of concentration ratio
697 between SO_2 and NO_x (SO_2/NO_x).

698 **Figure 4.** (a) Seasonal variation of SNRs for the BC-containing and BC-free particles,
699 respectively. Box and whisker plot shows lower, median, and upper lines, denoting the 25th,
700 50th, and 75th percentiles, respectively; the lower and upper edges denote the 10th and 90th
701 percentiles, respectively. (b) Diurnal variation of SNRs for the BC-containing and BC-free
702 particles, respectively. The shadings indicate the 95% confidence intervals of the hourly mean
703 values.

704 **Figure 5.** The diurnal trends of sulfate and nitrate RPA in the (a) BC-containing and (b)
705 BC-free particles, respectively.

706 **Figure 6.** Comparison between the measured and regressed SNRs, and the relative
707 importance of various factors on the variations of SNRs for the (a and c) BC-containing and

708 (b and d) BC-free particles, respectively. The shadings for the regressed line (a and b) indicate
709 the 95% confidence intervals. The error bars (in c and d) provide confidence intervals for the
710 relative importance with 100 bootstrap replicates to evaluate the results.