UNIVERSITYOF BIRMINGHAM University of Birmingham Research at Birmingham

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

Zhang, Guohua; Fu, Yuzhen; Peng, Xiaocong; Sun, Wei; Shi, Zongbo; Song, Wei; Hu, Weiwei; Chen, Duohong; Lian, Xiufeng; Li, Lei; Tang, Mingjin; Wang, Xinming; Bi, Xinhui

DOI: 10.1029/2021JD035226

License: None: All rights reserved

Document Version Peer reviewed version

Citation for published version (Harvard):

Zhang, G, Fu, Y, Peng, X, Sun, W, Shi, Z, Song, W, Hu, W, Chen, D, Lian, X, Li, L, Tang, M, Wang, X & Bi, X 2021, 'Black carbon involved photochemistry enhances the formation of sulfate in the ambient atmosphere: Evidence from in situ individual particle investigation', Journal of Geophysical Research: Atmospheres, vol. 126, no. 19, e2021JD035226. https://doi.org/10.1029/2021JD035226

Link to publication on Research at Birmingham portal

Publisher Rights Statement:

An edited version of this paper was published by AGU. Copyright 2021 American Geophysical Union. Zhang, G., Fu, Y., Peng, X., Sun, W., Shi, Z., Song, W., et al. (2021). Black carbon involved photochemistry enhances the formation of sulfate in the ambient atmosphere: Evidence from in situ individual particle investigation. Journal of Geophysical Research: Atmospheres, 126, e2021JD035226. https://doi.org/10.1029/2021JD035226

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

•Users may freely distribute the URL that is used to identify this publication.

•Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.

•User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?) •Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

1 Black Carbon Involved Photochemistry Enhances the Formation of Sulfate in the

2 Ambient Atmosphere: Evidence from *in-situ* Individual Particle Investigation

- Guohua Zhang^{1,2,3,*}, Yuzhen Fu^{1,2,4}, Xiaocong Peng^{1,2,4}, Wei Sun^{1,2,4}, Zongbo Shi⁵, Wei
 Song^{1,2,3}, Weiwei Hu^{1,2,3}, Duohong Chen⁶, Xiufeng Lian⁷, Lei Li⁷, Mingjin Tang^{1,2,3}, Xinming
 Wang^{1,2,3}, Xinhui Bi^{1,2,3,*}
- 6 ¹ State Key Laboratory of Organic Geochemistry and Guangdong Provincial Key Laboratory of
- 7 Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese
- 8 Academy of Sciences (CAS), Guangzhou 510640, PR China
- 9 ² CAS Center for Excellence in Deep Earth Science, Guangzhou, 510640, China
- 10 ³ Guangdong-Hong Kong-Macao Joint Laboratory for Environmental Pollution and Control,
- 11 Guangzhou Institute of Geochemistry, CAS, Guangzhou 510640, PR China
- ⁴ University of Chinese Academy of Sciences, Beijing 100049, PR China
- ⁵ School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham
- 14 B15 2TT, U.K.
- ⁶ State Environmental Protection Key Laboratory of Regional Air Quality Monitoring, Guangdong
- 16 Environmental Monitoring Center, Guangzhou 510308, PR China
- ⁷ Institute of Mass Spectrometer and Atmospheric Environment, Jinan University, Guangzhou 510632,
- 18 PR China
- 19 *Corresponding to Guohua Zhang (<u>zhanggh@gig.ac.cn</u>) and Xinhui Bi (bixh@gig.ac.cn)
- 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 particles could be well explained ($R^2 = -0.7-0.8$) by the radiation-related parameters (> 30%) 41 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 (NO ₂), sulfur dioxide
74	(SO ₂), ozone (O ₃), and nitric acid (HNO ₃) [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 NO ₂ [Zhang et al.,
78	2020a]. Besides, the photochemical oxidation of some intrinsic organic compositions by O_2
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 $(^{1}O_{2})$ and hydroxyl radical (·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.

B7 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.

In the present study, a Single Particle Aerosol Mass Spectrometer (denoted as Hexin SPAMS to show disparateness with the Aerodyne SP-AMS, which is unique to individual soot particles) was applied to measure the size and chemical compositions of individual particles, in order to accommodate the specific role of BC in the formation of secondary species. The variation of sulfate (with nitrate as a reference) associated with both the BC-containing and 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

- atmosphere and (2) to explore the dependence of sulfate production on atmospheric conditions,
- including their precursors and meteorological parameters.

114 2 Methods

115 2.1 Data collection

On-line measurements were conducted at a representative urban site in Guangzhou (China) [*Zhang et al.*, 2019a], a megacity in the PRD region. The measurements cover four seasons, including spring (21/02 to 11/04, 2014), summer (13/06 to 16/07, 2013), autumn (26/09 to 19/10, 2013), and winter (15/12 to 25/12, 2013). The sampling inlet for fine particle 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_{ya}) based on a calibration

- function created using polystyrene latex spheres (PSL, Duke Scientific Corp., Palo Alto) withpredefined 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
- 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
- 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 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. 148 149 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
- 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 BC-containing particles, as presented in Fig. 2, are carbon ion clusters (e.g., $m/z \pm 12[C]^{+/-}$, 159 $\pm 36[C_3]^{+/-}$, $\pm 48[C_4]^{+/-}$ and $\pm 60[C_5]^{+/-}$), organic carbon (OC) fragments $(m/z \ 27[C_2H_3]^+,$ 160 161 $29[C_2H_5]^+$, $37[C_3H]^+$, $26[CN]^-$, $42[CNO]^-$, and $43[C_2H_3O]^+$), and secondary inorganic species, 162 such as sulfate (-97[HSO₄].), nitrate (-62[NO₃]), and ammonium (18[NH₄])). There are also 163 some metallic species such as $23[Na]^+$ and $39[K]^+$. 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 proportion of variance explained (\mathbb{R}^2). Furthermore, the Relaimpo package is used to assess the 189 190 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 relative importance of the predictor variables can also be obtained, with "Mean DecreaseAccuracy" presenting the capability of each independent variable in explaining the variabilityof SNRs.

198 3 Results and Discussion

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

seasons (Fig. 4b). A sharp increase of the SNRs in the BC-containing particles, rather than the BC-free particles, started at noon hour (~12:00). On the other hand, the SNRs of the BC-containing particles decreased from the highest values during the afternoon hours to the lowest contribution during nighttime or early morning. The diurnal trend of SNRs for the 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 N2O5 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

discussed above, nitrate peaks at our site are most probably attributed to the nighttimechemistry 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 SO₂/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 O_2 , which produces additional ROS, including 1O_2 and $\cdot OH$ [<i>Li et al.</i> ,
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 SO_2
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 O ₃ [Xu et al., 2015; He et al., 2017]. However,
273	the interactions between BC particles and NO ₂ are unlikely to contribute to the formation of
274	nitrate [Han et al., 2013a; Guan et al., 2017].

There are also some possible explanations against the above hypothesis, but are unlikely to be significant. One is that BC and sulfate or their precursors originate from the same primary sources. This seems unlikely given a relatively low correlation ($R^2 = 0.26$, p < 0.01, 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 SO ₂ [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 SO ₂
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 NOx most
285	probably originate from local sources, whereas SO ₂ 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 SO ₂ through the produced in-particle oxidants (OH,
292	NO ₂ , and NO ₂ ⁻ /HNO ₂) [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 H ₂ SO ₄ , 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	μ m, 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 μ m, and thus, particles with sizes smaller than 0.1 μ m are beyond the scope of this

study. More directly, the SNRs show no clear trend with increasing size (Fig. S8), furthersupporting 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 formation of sulfate [Ault et al., 2010; Zhang et al., 2019a] could be negligible due to their 303 304 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 H_2O_2) 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

The main limitation or bias in the present study is the use of RPA in these qualitativeindividual 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

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].

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

18

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].

396	Acknowledgments
397	This work was funded by the National Natural Science Foundation of China (42077322,
398	41775124, and 41877307), Natural Science Foundation of Guangdong Province
399	(2019B151502022), Youth Innovation Promotion Association CAS (2021354), and
400	Guangdong Foundation for Program of Science and Technology Research (2019B121205006
401	and 2020B1212060053).
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

Adachi, K., N. Moteki, Y. Kondo, and Y. Igarashi (2016), Mixing states of light-absorbing
particles measured using a transmission electron microscope and a single-particle soot
photometer in Tokyo, Japan, J. Geophys. Res.-Atmos., 121(15), 2016JD025153,
doi:10.1002/2016JD025153.

Ault, A. P., C. J. Gaston, Y. Wang, G. Dominguez, M. H. Thiemens, and K. A. Prather
(2010), Characterization of the Single Particle Mixing State of Individual Ship Plume Events
Measured at the Port of Los Angeles, *Environ. Sci. Technol.*, 44(6), 1954-1961,
doi:10.1021/es902985h.

419	Berk, R. A. (2008), Random Forests, in Statistical Learning from a Regression
420	Perspective, edited, pp. 1-63, Springer New York, New York, NY,
421	doi:10.1007/978-0-387-77501-2_5.
422	Bond, T. C., et al. (2013), Bounding the role of black carbon in the climate system: A
423	scientific assessment, J. Geophys. ResAtmos., 118(11), 5380-5552, doi:10.1002/Jgrd.50171.
424	Breiman, L. (2001), Random Forests, Mach. Learn., 45(1), 5-32,
425	doi:10.1023/A:1010933404324.
426	Cahill, J. F., K. Suski, J. H. Seinfeld, R. A. Zaveri, and K. A. Prather (2012), The mixing
427	state of carbonaceous aerosol particles in northern and southern California measured during
428	CARES and CalNex 2010, Atmos. Chem. Phys., 12(22), 10989-11002,
429	doi:10.5194/acp-12-10989-2012.
430	Chen, B., Z. Zhu, X. Wang, A. Andersson, J. Chen, Q. Zhang, and Ö. Gustafsson (2017),
431	Reconciling modeling with observations of radiative absorption of black carbon aerosols, J.
432	Geophys. ResAtmos., 122(11), 5932-5942, doi:10.1002/2017JD026548.
433	Ding, A. J., et al. (2016), Enhanced haze pollution by black carbon in megacities in China,
434	Geophys. Res. Lett., 43(6), 2873-2879, doi:10.1002/2016GL067745.
435	Draxler, R. R., and G. D. Rolph (2012), HYSPLIT (HYbrid Single-Particle Lagrangian
436	Integrated Trajectory) Model access via NOAA ARL READY Website
437	(http://ready.arl.noaa.gov/HYSPLIT.php), MD, Silver Spring.
438	Fierce, L., et al. (2020), Radiative absorption enhancements by black carbon controlled by
439	particle-to-particle heterogeneity in composition, Proc. Natl. Acad. Sci. USA, 117(10),
440	5196-5203, doi:10.1073/pnas.1919723117 %J
441	Fu, H., M. Zhang, W. Li, J. Chen, L. Wang, X. Quan, and W. Wang (2012), Morphology,
442	composition and mixing state of individual carbonaceous aerosol in urban Shanghai, Atmos.

- 443 Chem. Phys., 12(2), 693-707, doi:10.5194/acp-12-693-2012.
- 444 Gaston, C. J., P. K. Quinn, T. S. Bates, J. B. Gilman, D. M. Bon, W. C. Kuster, and K. A.
- 445 Prather (2013), The impact of shipping, agricultural, and urban emissions on single particle

- 446 chemistry observed aboard the R/V Atlantis during CalNex, J. Geophys. Res.-Atmos., 118(10),
- 447 5003-5017, doi:10.1002/Jgrd.50427.
- 448 Gehling, W., and B. Dellinger (2013), Environmentally Persistent Free Radicals and Their
- 449 Lifetimes in PM2.5, *Environ. Sci. Technol.*, 47(15), 8172-8178, doi:10.1021/es401767m.
- 450 Gen, M., R. Zhang, D. D. Huang, Y. Li, and C. K. Chan (2019), Heterogeneous SO2
- 451 Oxidation in Sulfate Formation by Photolysis of Particulate Nitrate, Environ. Sci. Tech. Let.,
- 452 *6*(2), 86-91, doi:10.1021/acs.estlett.8b00681.
- Groemping, U. (2006), Relative Importance for Linear Regression in R: The Package
 relaimpo, J. Stat. Softw., 17(1), 1-27, doi:10.18637/jss.v017.i01.
- 455 Gross, D. S., M. E. Galli, P. J. Silva, and K. A. Prather (2000), Relative sensitivity factors
- 456 for alkali metal and ammonium cations in single particle aerosol time-of-flight mass spectra,
- 457 Anal. Chem., 72(2), 416-422.
- Guan, C., X. Li, W. Zhang, and Z. Huang (2017), Identification of Nitration Products
 during Heterogeneous Reaction of NO2 on Soot in the Dark and under Simulated Sunlight, *J. Phys. Chem. A*, *121*(2), 482-492, doi:10.1021/acs.jpca.6b08982.
- 461 Han, C., Y. Liu, and H. He (2013a), Heterogeneous photochemical aging of soot by NO2
- 462 under simulated sunlight, *Atmos. Environ.*, *64*, 270-276, doi:10.1016/j.atmosenv.2012.10.008.
- 463 Han, C., Y. Liu, and H. He (2013b), Role of Organic Carbon in Heterogeneous Reaction of
- 464 NO2 with Soot, *Environ. Sci. Technol.*, 47(7), 3174-3181, doi:10.1021/es304468n.
- Han, C., Y. C. Liu, J. Z. Ma, and H. He (2012), Key role of organic carbon in the
 sunlight-enhanced atmospheric aging of soot by O-2, *Proc. Natl. Acad. Sci. USA*, 109(52),
- 467 21250-21255, doi:10.1073/pnas.1212690110.
- He, C., K. N. Liou, Y. Takano, R. Zhang, M. L. Zamora, P. Yang, Q. Li, and L. R. Leung
 (2015), Variation of the radiative properties during black carbon aging: theoretical and
 experimental intercomparison, *Atmos. Chem. Phys.*, *15*(20), 11967-11980,
 doi:10.5194/acp-15-11967-2015.
- He, L. Y., X. F. Huang, L. Xue, M. Hu, Y. Lin, J. Zheng, R. Y. Zhang, and Y. H. Zhang
 (2011), Submicron aerosol analysis and organic source apportionment in an urban atmosphere

474 in Pearl River Delta of China using high-resolution aerosol mass spectrometry, J. Geophys.

475 Res.-Atmos., 116(D12304), 1-15, doi:10.1029/2010jd014566.

- He, X., S. Pang, J. Ma, and Y. Zhang (2017), Influence of relative humidity on
 heterogeneous reactions of O₃ and O₃/SO₂ with soot particles: Potential for environmental and
 health effects, *Atmos. Environ.*, *165*, 198-206, doi:10.1016/j.atmosenv.2017.06.049.
- Healy, R. M., et al. (2013), Quantitative determination of carbonaceous particle mixing
 state in Paris using single-particle mass spectrometer and aerosol mass spectrometer
 measurements, *Atmos. Chem. Phys.*, *13*(18), 9479-9496, doi:10.5194/acp-13-9479-2013.
- Healy, R. M., et al. (2012), Sources and mixing state of size-resolved elemental carbon
 particles in a European megacity: Paris, *Atmos. Chem. Phys.*, *12*(4), 1681-1700,
 doi:10.5194/acp-12-1681-2012.
- 485 Hu, K., D. L. Zhao, D. T. Liu, S. Ding, P. Tian, C. J. Yu, W. Zhou, M. Y. Huang, and D. P. 486 Ding (2020), Estimating radiative impacts of black carbon associated with mixing state in the 487 lower atmosphere over the northern North China Plain. Chemosphere, 252. 488 doi:10.1016/j.chemosphere.2020.126455.
- Huang, X. F., T. L. Sun, L. W. Zeng, G. H. Yu, and S. J. Luan (2012), Black carbon
 aerosol characterization in a coastal city in South China using a single particle soot photometer, *Atmos. Environ.*, *51*, 21-28, doi:10.1016/j.atmosenv.2012.01.056.
- Jeong, C. H., M. L. McGuire, K. J. Godri, J. G. Slowik, P. J. G. Rehbein, and G. J. Evans
 (2011), Quantification of aerosol chemical composition using continuous single particle
 measurements, *Atmos. Chem. Phys.*, *11*(14), 7027-7044, doi:10.5194/acp-11-7027-2011.
- Khalizov, A. F., M. Cruz-Quinones, and R. Y. Zhang (2010), Heterogeneous Reaction of
 NO2 on Fresh and Coated Soot Surfaces, *J. Phys. Chem. A*, *114*(28), 7516-7524,
 doi:10.1021/jp1021938.
- Kleffmann, J., and P. Wiesen (2005), Heterogeneous conversion of NO2 and NO on
 HNO3 treated soot surfaces: atmospheric implications, *Atmos. Chem. Phys.*, *5*, 77-83,
 doi:10.5194/acp-5-77-2005.

- Lee, A. K. Y., M. D. Willis, R. M. Healy, T. B. Onasch, and J. P. D. Abbatt (2015), Mixing
- 502 state of carbonaceous aerosol in an urban environment: single particle characterization using
- 503 the soot particle aerosol mass spectrometer (SP-AMS), Atmos. Chem. Phys., 15(4), 1823-1841,
- **504** doi:10.5194/acp-15-1823-2015.
- Lee, S. H., D. M. Murphy, D. S. Thomson, and A. M. Middlebrook (2003), Nitrate and
 oxidized organic ions in single particle mass spectra during the 1999 Atlanta Supersite Project, *J. Geophys. Res.*, *108*(D7), 8417, doi:10.1029/2001jd001455.
- Li, K. N., X. N. Ye, H. W. Pang, X. H. Lu, H. Chen, X. F. Wang, X. Yang, J. M. Chen, and
 Y. J. Chen (2018a), Temporal variations in the hygroscopicity and mixing state of black carbon
 aerosols in a polluted megacity area, *Atmos. Chem. Phys.*, *18*(20), 15201-15218,
 doi:10.5194/acp-18-15201-2018.
- Li, L., et al. (2011), Real time bipolar time-of-flight mass spectrometer for analyzing
 single aerosol particles, *Intl. J. Mass. Spectrom.*, 303(2-3), 118-124,
 doi:10.1016/j.ijms.2011.01.017.
- Li, M., F. Bao, Y. Zhang, H. Sheng, C. Chen, and J. Zhao (2019), Photochemical Aging of
 Soot in the Aqueous Phase: Release of Dissolved Black Carbon and the Formation of 1O2, *Environ. Sci. Technol.*, 53(21), 12311-12319, doi:10.1021/acs.est.9b02773.
- Li, M., F. Bao, Y. Zhang, W. Song, C. Chen, and J. Zhao (2018b), Role of elemental
 carbon in the photochemical aging of soot, *Proc. Natl. Acad. Sci. USA*, *115*(30), 7717-7722,
 doi:10.1073/pnas.1804481115.
- Li, S., et al. (2020), Characterizing the ratio of nitrate to sulfate in ambient fine particles of
 urban Beijing during 2018–2019, *Atmos. Environ.*, 117662,
 doi:10.1016/j.atmosenv.2020.117662.
- Li, W. J., L. Y. Shao, D. Z. Zhang, C. U. Ro, M. Hu, X. H. Bi, H. Geng, A. Matsuki, H. Y.
 Niu, and J. M. Chen (2016), A review of single aerosol particle studies in the atmosphere of
 East Asia: morphology, mixing state, source, and heterogeneous reactions, *J. Clean. Prod.*, *112*,
 1330-1349, doi:10.1016/j.jclepro.2015.04.050.

- Liu, D., et al. (2020a), Black Carbon Emission and Wet Scavenging From Surface to the
 Top of Boundary Layer Over Beijing Region, J. Geophys. Res.-Atmos., 125(17),
 doi:10.1029/2020jd033096.
- Liu, D. T., et al. (2017), Black-carbon absorption enhancement in the atmosphere determined by particle mixing state, *Nature Geosci.*, *10*(3), 184-U132, doi:10.1038/Ngeo2901.

533 Liu, H., X. L. Pan, D. T. Liu, X. Y. Liu, X. S. Chen, Y. Tian, Y. L. Sun, P. Q. Fu, and Z. F.

534 Wang (2020b), Mixing characteristics of refractory black carbon aerosols at an urban site in

535 Beijing, Atmos. Chem. Phys., 20(9), 5771-5785, doi:10.5194/acp-20-5771-2020.

Liu, Q., J. Quan, X. Jia, Z. Sun, X. Li, Y. Gao, and Y. Liu (2019a), Vertical Profiles of

537 Aerosol Composition over Beijing, China: Analysis of In Situ Aircraft Measurements, J. Atmos.

538 *Sci.*, *76*(1), 231-245, doi:10.1175/JAS-D-18-0157.1 %J Journal of the Atmospheric Sciences.

Liu, Y., Z. Wu, X. Huang, H. Shen, Y. Bai, K. Qiao, X. Meng, W. Hu, M. Tang, and L. He

540 (2019b), Aerosol Phase State and Its Link to Chemical Composition and Liquid Water Content

541 in a Subtropical Coastal Megacity, *Environ. Sci. Technol.*, 53(9), 5027-5033,
542 doi:10.1021/acs.est.9b01196.

Matsui, H. (2016), Black carbon simulations using a size- and mixing-state-resolved
three-dimensional model: 1. Radiative effects and their uncertainties, *J. Geophys. Res.-Atmos.*, *121*(4), 1793-1807, doi:10.1002/2015jd023998.

Matsui, H., D. S. Hamilton, and N. M. Mahowald (2018), Black carbon radiative effects
highly sensitive to emitted particle size when resolving mixing-state diversity, *Nat. Commun.*, 9,
doi:10.1038/s41467-018-05635-1.

- McCabe, J., and J. P. D. Abbatt (2009), Heterogeneous Loss of Gas-Phase Ozone on
 n-Hexane Soot Surfaces: Similar Kinetics to Loss on Other Chemically Unsaturated Solid
 Surfaces, J. Phys. Chem. C, 113(6), 2120-2127, doi:10.1021/jp806771q.
- Moffet, R. C., and K. A. Prather (2009), In-situ measurements of the mixing state and
 optical properties of soot with implications for radiative forcing estimates, *Proc. Natl. Acad. Sci. USA*, *106*(29), 11872-11877, doi:10.1073/pnas.0900040106.

- 555 Motos, G., J. Schmale, J. C. Corbin, M. Zanatta, U. Baltensperger, and M. Gysel-Beer
- 556 (2019), Droplet activation behaviour of atmospheric black carbon particles in fog as a function
- 557 of their size and mixing state, *Atmos. Chem. Phys.*, 19(4), 2183-2207,
 558 doi:10.5194/acp-19-2183-2019.
- Novakov, T., S. G. Chang, and A. B. Harker (1974), Sulfates as Pollution Particulates:
 Catalytic Formation on Carbon (Soot) Particles, *Science*, *186*(4160), 259,
 doi:10.1126/science.186.4160.259.
- Peng, J. F., et al. (2016), Markedly enhanced absorption and direct radiative forcing of
 black carbon under polluted urban environments, *Proc. Natl. Acad. Sci. USA*, *113*(16),
 4266-4271, doi:10.1073/pnas.1602310113.
- 565 Penner, J. E. (2019), Soot, sulfate, dust and the climate three ways through the fog,
 566 *Nature*, 570(7760), 158-159, doi:10.1038/d41586-019-01791-6.
- Ramana, M. V., V. Ramanathan, Y. Feng, S. C. Yoon, S. W. Kim, G. R. Carmichael, and J.
 J. Schauer (2010), Warming influenced by the ratio of black carbon to sulphate and the
 black-carbon source, *Nature Geosci.*, *3*(8), 542-545, doi:10.1038/Ngeo918.
- 570 Riemer, N., A. P. Ault, M. West, R. L. Craig, and J. H. Curtis (2019), Aerosol Mixing
 571 State: Measurements, Modeling, and Impacts, *Rev. Geophys.*, 57(2), 187-249,
 572 doi:10.1029/2018rg000615.
- Song, X. H., P. K. Hopke, D. P. Fergenson, and K. A. Prather (1999), Classification of
 single particles analyzed by ATOFMS using an artificial neural network, ART-2A, *Anal. Chem.*, 71(4), 860-865.
- Sultana, C. M., G. C. Cornwell, P. Rodriguez, and K. A. Prather (2017), FATES: a flexible
 analysis toolkit for the exploration of single-particle mass spectrometer data, *Atmos. Meas. Tech.*, *10*(4), 1323-1334, doi:10.5194/amt-10-1323-2017.
- Sun, J. X., et al. (2018), Key Role of Nitrate in Phase Transitions of Urban Particles:
 Implications of Important Reactive Surfaces for Secondary Aerosol Formation, *J. Geophys. Res.-Atmos.*, *123*(2), 1234-1243, doi:10.1002/2017JD027264.

582 Tan, H. B., L. Liu, S. J. Fan, F. Li, Y. Yin, M. F. Cai, and P. W. Chan (2016), Aerosol

- 583 optical properties and mixing state of black carbon in the Pearl River Delta, China, *Atmos.*
- 584 *Environ.*, *131*, 196-208, doi:10.1016/j.atmosenv.2016.02.003.
- Wang, G., et al. (2016a), Persistent sulfate formation from London Fog to Chinese haze, *Proc. Natl. Acad. Sci. USA*, *113*(48), 13630, doi:10.1073/pnas.1616540113.
- 587 Wang, H., et al. (2019a), Aerosols in an arid environment: The role of aerosol water
- 588 content, particulate acidity, precursors, and relative humidity on secondary inorganic aerosols,
- 589 Sci. Total. Environ., 646, 564-572, doi:<u>https://doi.org/10.1016/j.scitotenv.2018.07.321</u>.
- Wang, J., et al. (2020a), Fast sulfate formation from oxidation of SO2 by NO2 and HONO
 observed in Beijing haze, *Nat. Commun.*, *11*(1), 2844, doi:10.1038/s41467-020-16683-x.
- 592 Wang, J., et al. (2017), First Chemical Characterization of Refractory Black Carbon

593 Aerosols and Associated Coatings over the Tibetan Plateau (4730 m a.s.l), Environ. Sci.

594 *Technol.*, *51*(24), 14072-14082, doi:10.1021/acs.est.7b03973.

595 Wang, J. F., X. L. Ge, Y. F. Chen, Y. F. Shen, Q. Zhang, Y. L. Sun, J. Z. Xu, S. Ge, H. Yu,

and M. D. Chen (2016b), Highly time-resolved urban aerosol characteristics during springtime

597 in Yangtze River Delta, China: insights from soot particle aerosol mass spectrometry, *Atmos*.

598 *Chem. Phys.*, *16*(14), 9109-9127, doi:10.5194/acp-16-9109-2016.

- Wang, Q., et al. (2020b), Measurement report: Source and mixing state of black carbon
 aerosol in the North China Plain: implications for radiative effect, *Atmos. Chem. Phys.*, 20(23),
 15427-15442, doi:10.5194/acp-20-15427-2020.
- Wang, Q. Y., et al. (2016c), Physicochemical characteristics of black carbon aerosol and
 its radiative impact in a polluted urban area of China, *J. Geophys. Res.-Atmos.*, *121*(20),
 12505-12519, doi:10.1002/2016jd024748.
- Wang, S., S. Zhou, Y. Tao, W. G. Tsui, J. Ye, J. Z. Yu, J. G. Murphy, V. F. McNeill, J. P.
- 606 D. Abbatt, and A. W. H. Chan (2019b), Organic Peroxides and Sulfur Dioxide in Aerosol:
- 607 Source of Particulate Sulfate, *Environ. Sci. Technol.*, doi:10.1021/acs.est.9b02591.
- Wang, X., et al. (2020c), Atmospheric Photosensitization: A New Pathway for Sulfate
 Formation, *Environ. Sci. Technol.*, doi:10.1021/acs.est.9b06347.

610 Wang, X. F., S. Gao, X. Yang, H. Chen, J. M. Chen, G. S. Zhuang, J. D. Surratt, M. N.

611 Chan, and J. H. Seinfeld (2010), Evidence for High Molecular Weight Nitrogen-Containing

612 Organic Salts in Urban Aerosols, *Environ. Sci. Technol.*, 44(12), 4441-4446.

Wang, X. F., Y. P. Zhang, H. Chen, X. Yang, J. M. Chen, and F. H. Geng (2009),
Particulate Nitrate Formation in a Highly Polluted Urban Area: A Case Study by
Single-Particle Mass Spectrometry in Shanghai, *Environ. Sci. Technol.*, 43(9), 3061-3066,
doi:10.1021/es8020155.

Kiao, R., et al. (2009), Formation of submicron sulfate and organic aerosols in the outflow
from the urban region of the Pearl River Delta in China, *Atmos. Environ.*, *43*(24), 3754-3763.

Ku, W., et al. (2017), Effects of Aqueous-Phase and Photochemical Processing on
Secondary Organic Aerosol Formation and Evolution in Beijing, China, *Environ. Sci. Technol.*, *51*(2), 762-770, doi:10.1021/acs.est.6b04498.

Xu, W., Q. Li, J. Shang, J. Liu, X. Feng, and T. Zhu (2015), Heterogeneous oxidation of
SO2 by O3-aged black carbon and its dithiothreitol oxidative potential, *J. Environ. Sci.*, *36*,
56-62, doi:https://doi.org/10.1016/j.jes.2015.02.014.

Xu, X. Z., et al. (2018), The influence of photochemical aging on light absorption of
atmospheric black carbon and aerosol single-scattering albedo, *Atmos. Chem. Phys.*, *18*(23),
16829-16844, doi:10.5194/acp-18-16829-2018.

628 Xue, J., X. Yu, Z. Yuan, S. M. Griffith, A. K. H. Lau, J. H. Seinfeld, and J. Z. Yu (2019),

Efficient control of atmospheric sulfate production based on three formation regimes, *Nature Geosci.*, *12*(12), 977-982, doi:10.1038/s41561-019-0485-5.

Xue, J., Z. Yuan, S. M. Griffith, X. Yu, A. K. H. Lau, and J. Z. Yu (2016), Sulfate
Formation Enhanced by a Cocktail of High NOx, SO2, Particulate Matter, and Droplet pH
during Haze-Fog Events in Megacities in China: An Observation-Based Modeling
Investigation, *Environ. Sci. Technol.*, *50*(14), 7325-7334, doi:10.1021/acs.est.6b00768.

Yu, C. J., D. T. Liu, K. Broda, R. Joshi, J. Olfert, Y. L. Sun, P. Q. Fu, H. Coe, and J. D.
Allan (2020), Characterising mass-resolved mixing state of black carbon in Beijing using a

637 morphology-independent measurement method, *Atmos. Chem. Phys.*, 20(6), 3645-3661,
638 doi:10.5194/acp-20-3645-2020.

639 Yuan, Q., J. Xu, Y. Wang, X. Zhang, Y. Pang, L. Liu, L. Bi, S. Kang, and W. Li (2019),

640 Mixing State and Fractal Dimension of Soot Particles at a Remote Site in the Southeastern

641 Tibetan Plateau, *Environ. Sci. Technol.*, *53*(14), 8227-8234, doi:10.1021/acs.est.9b01917.

542 Zauscher, M. D., Y. Wang, M. J. K. Moore, C. J. Gaston, and K. A. Prather (2013), Air

643 Quality Impact and Physicochemical Aging of Biomass Burning Aerosols during the 2007 San

644 Diego Wildfires, *Environ. Sci. Technol.*, 47(14), 7633-7643, doi:10.1021/es4004137.

Zhang, F., et al. (2020a), An unexpected catalyst dominates formation and radiative
forcing of regional haze, *Proc. Natl. Acad. Sci. USA*, *117*(8), 3960-3966,
doi:10.1073/pnas.1919343117.

Chang, G., et al. (2020b), High secondary formation of nitrogen-containing organics
(NOCs) and its possible link to oxidized organics and ammonium, *Atmos. Chem. Phys.*, 20(3),
1469-1481, doi:10.5194/acp-20-1469-2020.

Zhang, G., et al. (2017), The single-particle mixing state and cloud scavenging of black
carbon: a case study at a high-altitude mountain site in southern China, *Atmos. Chem. Phys.*, *17*(24), 14975-14985, doi:10.5194/acp-17-14975-2017.

Zhang, G., et al. (2019a), Oxalate Formation Enhanced by Fe-Containing Particles and
Environmental Implications, *Environ. Sci. Technol.*, 53(3), 1269-1277,
doi:10.1021/acs.est.8b05280.

657 Zhang, G. H., X. H. Bi, J. J. He, D. H. Chen, L. Y. Chan, G. W. Xie, X. M. Wang, G. Y. 658 Sheng, J. M. Fu, and Z. Zhou (2014), Variation of secondary coatings associated with elemental 659 carbon single analysis, 92. 162-170, by particle Atmos. Environ., 660 doi:10.1016/j.atmosenv.2014.04.018.

Zhang, G. H., X. H. Bi, L. Li, L. Y. Chan, M. Li, X. M. Wang, G. Y. Sheng, J. M. Fu, and
Z. Zhou (2013), Mixing state of individual submicron carbon-containing particles during spring
and fall seasons in urban Guangzhou, China: a case study, *Atmos. Chem. Phys.*, *13*(9),
4723-4735, doi:10.5194/acp-13-4723-2013.

29

- 565 Zhang, Y., F. Bao, M. Li, C. Chen, and J. Zhao (2019b), Nitrate-Enhanced Oxidation of
- 666 SO2 on Mineral Dust: A Vital Role of a Proton, *Environ. Sci. Technol.*, 53(17), 10139-10145,

667 doi:10.1021/acs.est.9b01921.

- Zhang, Y., et al. (2018), Sizing of Ambient Particles From a Single-Particle Soot
 Photometer Measurement to Retrieve Mixing State of Black Carbon at a Regional Site of the
 North China Plain, J. Geophys. Res.-Atmos., 123(22), 12778-12795,
 doi:10.1029/2018jd028810.
- 672 Zhao, Y., Y. Liu, J. Ma, Q. Ma, and H. He (2017), Heterogeneous reaction of SO2 with673 soot: The roles of relative humidity and surface composition of soot in surface sulfate formation,

674 *Atmos. Environ.*, 152, 465-476, doi:http://dx.doi.org/10.1016/j.atmosenv.2017.01.005.

675 Zheng, B., Q. Zhang, Y. Zhang, K. B. He, K. Wang, G. J. Zheng, F. K. Duan, Y. L. Ma,676 and T. Kimoto (2015), Heterogeneous chemistry: a mechanism missing in current models to

explain secondary inorganic aerosol formation during the January 2013 haze episode in North
China, *Atmos. Chem. Phys.*, *15*(4), 2031-2049, doi:10.5194/acp-15-2031-2015.

Zhou, Y., et al. (2016), A field measurement based scaling approach for quantification of
major ions, organic carbon, and elemental carbon using a single particle aerosol mass
spectrometer, *Atmos. Environ.*, *143*, 300-312, doi:10.1016/j.atmosenv.2016.08.054.

Zhu, J., J. Shang, Y. Chen, Y. Kuang, and T. Zhu (2020), Reactive Oxygen
Species-Related Inside-to-Outside Oxidation of Soot Particles Triggered by Visible-Light
Irradiation: Physicochemical Property Changes and Oxidative Potential Enhancement, *Environ. Sci. Technol.*, doi:10.1021/acs.est.0c01150.

686

687 Figure Captions

- **688** Figure 1. The auxiliary meteorological data, including solar radiation (SR), oxidants ($O_x =$
- $NO_x + O_3$, 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].
- **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.
- **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).
- **Figure 4.** (a) Seasonal variation of SNRs for the BC-containing and BC-free particles,
- respectively. Box and whisker plot shows lower, median, and upper lines, denoting the 25th,
- 50th, and 75th percentiles, respectively; the lower and upper edges denote the 10th and 90th
- percentiles, respectively. (b) Diurnal variation of SNRs for the BC-containing and BC-free
- particles, respectively. The shadings indicate the 95% confidence intervals of the hourly meanvalues.
- **Figure 5.** The diurnal trends of sulfate and nitrate RPA in the (a) BC-containing and (b)
- 705 BC-free particles, respectively.
- **Figure 6.** Comparison between the measured and regressed SNRs, and the relative
- 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
- 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.