

# Seasonal variations of mass absorption efficiency of elemental carbon in PM<sub>2.5</sub> in urban Guangzhou of south China

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## Highlights:

- Vehicle exhaust is the dominant source for carbonaceous aerosols.
- Enhancement of MAE<sub>EC</sub> compared to “pure EC” was least in summer due to a low degree of EC coating.
- High mass fraction of non-carbonaceous and high RH caused high MAE<sub>EC</sub>.

1 **Abstract**

2 This study investigates seasonal variations of mass absorption efficiency of elemental  
3 carbon ( $MAE_{EC}$ ) and possible influencing factors in urban Guangzhou of south China.  
4 Mass concentrations of elemental carbon (EC) and organic carbon (OC) in  $PM_{2.5}$  and  
5 aerosol absorption coefficient ( $b_{ap}$ ) at multi-wavelengths were simultaneously  
6 measured in four seasons of 2018–2019 at hourly resolution. Seasonal average mass  
7 concentrations of EC were in the range of 1.36–1.70  $\mu\text{gC m}^{-3}$  with a lower value in  
8 summer than in the other seasons, while those of OC were in the range of 4.70–6.49  
9  $\mu\text{gC m}^{-3}$  with the lowest value in summer and the highest in autumn. Vehicle exhaust  
10 from local traffic was identified to be the predominant source of carbonaceous aerosols.  
11 The average aerosol absorption Ångström exponents (AAE) were lower than 1.2 in four  
12 seasons, indicating EC and  $b_{ap}$  were closely related with vehicle exhaust. Seasonal  
13  $MAE_{EC}$  at 550 nm was 11.0, 8.5, 10.4 and 11.3  $\text{m}^2 \text{g}^{-1}$ , respectively, in spring, summer,  
14 autumn, and winter. High  $MAE_{EC}$  was related with the high mass ratio of non-  
15 carbonaceous aerosols to EC and high ambient relative humidity (RH).

16 **Keywords:** vehicle exhaust; non-carbonaceous aerosols; absorption enhancement;  
17 relative humidity

## 18 **1. Introduction**

19 Elemental carbon (EC), also termed as black carbon (BC) from an optical  
20 perspective, is the most crucial light absorption matter in atmospheric aerosols  
21 (Andreae and Gelencsér, 2006). EC poses direct warming effect, second only to that of  
22 CO<sub>2</sub> (Bond et al., 2013). EC also affects visibility and atmospheric stability due to its  
23 strong absorption of solar radiation (Ding et al., 2016; Watson, 2002). Thus, knowledge  
24 of the optical properties of EC at high temporal resolution in different environments is  
25 needed to address air quality and climate issues. One of the key optical properties of  
26 EC is its mass absorption efficiency (MAE<sub>EC</sub>), which is an essential parameter for  
27 estimating the contribution of EC to light absorption coefficient ( $b_{ap}$ ) of atmospheric  
28 aerosols. A constant MAE<sub>EC</sub> value of 6.5 m<sup>2</sup> g<sup>-1</sup> at 550nm was recommended by the US  
29 IMPROVE (Interagency Monitoring of Protected Visual Environments) observation  
30 network (Tao et al., 2020). In fact, a wide range of MAE<sub>EC</sub> values has been reported  
31 due to different mixing states of EC with coating aerosols (Cappa et al., 2012; Lack and  
32 Cappa, 2010; Peng et al., 2016; Wu et al., 2016b; Zhang et al., 2018). Theoretically,  
33 MAE<sub>EC</sub> would be enhanced by a factor of 2.0 when an EC particle is fully coated by  
34 non-absorbing materials with a shell to core diameter ratio as large as 2.8 (Zhang et al.,  
35 2017). The dependence of bulk MAE<sub>EC</sub> in fine particle (PM<sub>2.5</sub>) on the mass ratio of non-  
36 absorbing materials to EC is weaker in cleaner than polluted environment where EC  
37 emissions are dominated by vehicle exhaust (Cappa et al., 2012; Cappa et al., 2019;  
38 Lan et al., 2013), mainly because only a small fraction of EC was well coated by non-

39 absorbing materials in real world. Size distribution of EC is another important factor  
40 influencing  $MAE_{EC}$ , e.g.,  $MAE_{EC}$  could decrease by approximately 6% if the mass  
41 median diameter of EC increased from 140 nm to 200 nm (Zhang et al., 2018).

42 Benefited from a series of emission control measures across China, annual mass  
43 concentrations of  $PM_{2.5}$  in the Pearl River Delta (PRD) region in south China have  
44 decreased evidently since a decade ago and met the national air quality standard ( $< 35$   
45  $\mu\text{g m}^{-3}$ ) for many years. However, mass concentrations of EC in  $PM_{2.5}$  have not  
46 evidently decreased compared to the case of secondary inorganic aerosols (SIAs, e.g.,  
47 sulfate and nitrate) and organic carbon (OC) due to the large number of vehicle  
48 population in urban areas in this region (Tao et al., 2017a). Recently, continuous  
49 decreases in OC and sulfate concentrations while an elevation of nitrate concentration  
50 and its fraction in  $PM_{2.5}$  were observed in urban Guangzhou, a megacity of the PRD  
51 region (Li et al., 2021). The change of chemical compositions has already affected the  
52 physical and optical properties of  $PM_{2.5}$  in this region, e.g., increased the hygroscopicity  
53 (Xu et al., 2020; Li et al., 2021). Different change patterns of SIA species and OC,  
54 despite the flat EC mass concentration in recent years, certainly would affect  $MAE_{EC}$   
55 in this region. However, previous studies mainly focused on the impact of atmospheric  
56 aging process and deliquescence of aerosol under the high ambient RH on  $MAE_{EC}$  in  
57 this region (Sun et al., 2020; Tao et al., 2021). The impact of changes of non-absorbing  
58 materials (SIAs and OC) relative to EC on  $MAE_{EC}$  has yet to be validated in this region.

59 To shade some light on the causes of seasonal variations in  $MAE_{EC}$ , a measurement

60 campaign was conducted in an urban environment in Guangzhou in April, July and  
61 October of 2018 and January of 2019, which represent four different seasons. During  
62 the campaign, hourly mass concentrations of organic carbon (OC), EC,  $b_{ap}$ , criteria air  
63 pollutants and meteorological parameters were collected. In the following sections,  
64 mass concentrations and potential sources of carbonaceous aerosols were first  
65 characterized (Section 3.1), aerosol absorption coefficient and its wavelength  
66 dependence were then analyzed (Section 3.2), and finally seasonal variations in  $MAE_{EC}$   
67 and associated influencing factors were explored (Section 3.3). Knowledge gained from  
68 this study is useful in evaluating visibility degradation and regional climate change in  
69 South China.

## 70 **2. Methodology**

### 71 **2.1. Sampling site**

72 The measurement campaign was conducted at a national air quality monitoring  
73 site located on the roof of a seven-story building inside the original Guangzhou  
74 Environmental Monitoring Center (GEMC) (23.13°N, 113.26°E) in Guangzhou (Fig.  
75 1). There are no obviously industrial emissions within 10 km surrounding the site, but  
76 the site is affected by local sources such as traffic and residential activities. The site can  
77 be considered to represent typical urban environment in this city. Mass concentrations  
78 of EC ( $C_{EC}$ ) and OC ( $C_{OC}$ ) and  $b_{ap}$  were measured in April, July and October 2018 and  
79 January 2019, representing spring, summer, autumn and winter, respectively.

### 80 **2.2. Online measurement of EC and OC mass concentrations**

81 A model RT-4 Sunset semi-continuous carbon analyzer (Sunset Laboratory Inc,  
82 OR, USA) was utilized to measure  $C_{EC}$  and  $C_{OC}$  with a time resolution of 1 hour.  
83 Ambient air, after passing a  $PM_{2.5}$  cutoff inlet, was drawn into the carbon analyzer via  
84 a 2 m stainless steel tube by the internal pump at a flow rate of  $8 \text{ L min}^{-1}$ . A denude was  
85 installed in front of the carbon analyzer to trap volatile OC. Fine particles were retained  
86 on a quartz filter in the first 45 min of each hour, and then delivered into a quartz furnace  
87 for OC and EC analysis in the next 15 min using the thermo-optical approach. OC was  
88 first vaporized by stepwise heating in a pure helium (He) environment. Subsequently,  
89 oxygen was mixed (2 %  $O_2$  in He) to oxidize EC on the filter. The decomposition  
90 products of the above two steps were detected by a flame ionization detector to quantify  
91 the carbon amounts. During the analysis, a laser beam continuously irradiated the quartz  
92 filter. When OC was carbonized with the elevated temperature under the pure He  
93 environment, the intensity of transmitted light of the laser gradually decreased.  
94 Subsequently, the transmitted light progressively increased with the oxidation and  
95 decomposition of carbonized OC and EC under the He/ $O_2$  environment. The moment  
96 when the transmitted light was back to its initial intensity was defined as the split point  
97 to discriminate OC and EC. The carbon amounts detected before this split point was  
98 defined as OC, and that detected afterwards was defined as EC. Operation principle of  
99 the carbon analyzer was described in detail by (Birch and Cary, 1996).

### 100 **2.3. Online measurement of the aerosol absorption coefficient**

101 A model AE-31 aethalometer (Magee Scientific, CA, USA) was used to obtain  $b_{ap}$

102 at seven wavelengths of 370, 470, 520, 590, 660, 880 and 950 nm with a time resolution  
 103 of 5 min. The aethalometer was also equipped with a PM<sub>2.5</sub> cutoff inlet to ensure only  
 104 fine particles were measured. Meanwhile, a heating device was installed in front of the  
 105 aethalometer to dry the sample. The value of  $b_{ap}$  can be obtained from the measured  
 106 attenuation (ATN) together with equations (1), (2) and (3), as described in Weingartner  
 107 et al. (2003):

$$108 \quad b_{ap} = \frac{ATN}{t} \cdot \frac{A}{Q} \cdot \frac{1}{R(ATN) \cdot C} \quad (1)$$

$$109 \quad R = \left( \frac{1}{f} - 1 \right) \cdot \frac{\ln(ATN) - \ln(10)}{\ln(50) - \ln(10)} + 1 \quad (2)$$

$$110 \quad f = \alpha(1 - \omega) + 1 \quad (3)$$

111 where  $t$  is the sampling time for a single measurement,  $A$  is the sampling area on the  
 112 filter membrane, and  $Q$  is the sampling flow rate which was set as 5 L min<sup>-1</sup> in this  
 113 study.  $C$  and  $R$  in Eq. (1) are the two factors introduced to correct the inherent errors in  
 114  $b_{ap}$  determination using the AE-31 aethalometer. Factor  $C$  is used to correct the  
 115 scattering effect of filter membrane and laden particles which was set as a constant of  
 116 3.5 as recommended by WMO (2016). This value is also close to that derived by  
 117 comparing AE-31 measured attenuation coefficient with the reference  $b_{ap}$  obtained by  
 118 a multi-angle absorption photometer (MAAP) (Wu et al., 2021). Factor  $R$  as a function  
 119 of ATN is employed to correct the loading effect (Weingartner et al., 2003). The variable  
 120  $\omega$  in Eq. (3) represents the single scattering albedo which was set as a mean value of  
 121 0.83 in Guangzhou (Andreae et al., 2008), and  $\alpha$  is a constant scale factor which was  
 122 set as 0.86 in this study (Weingartner et al., 2003).

123  $b_{ap}$  generally exhibits as a power-law function of wavelength ( $\lambda$ ), the exponent of  
124 which is defined as absorption Ångström exponent (AAE):

$$125 \quad b_{ap,\lambda} \propto \lambda^{-AAE} \quad (4)$$

126 In this study, the AAE value is derived from the linear regression of the obtained  
127  $b_{ap}$  against the seven wavelengths in the range of 370–950 nm on a logarithm scale,  
128 thereby denoted as  $AAE_{370-950nm}$ .

#### 129 **2.4. Auxiliary measurements for air pollution and meteorological parameters**

130 Mass concentrations of  $PM_{2.5}$  and mixing ratios of gaseous pollutants including  
131  $SO_2$ ,  $NO_2$ ,  $NO$ ,  $CO$  and  $O_3$  were obtained from a co-located national air quality station.  
132 An automatic weather station (Vaisala Co., Ltd., Finland) was deployed to provide  
133 meteorological data including wind speed, wind direction, temperature, relative  
134 humidity (RH) and air pressure.

### 135 **3. Results and Discussion**

#### 136 **3.1. Mass concentrations and potential sources of carbonaceous aerosols**

137 Seasonal average  $C_{EC}$  was  $1.64 \pm 0.84$ ,  $1.36 \pm 0.57$ ,  $1.68 \pm 0.81$  and  $1.70 \pm 1.20$   
138  $\mu gC m^{-3}$ , and that of  $C_{OC}$  was  $5.17 \pm 2.29$ ,  $4.70 \pm 2.35$ ,  $6.49 \pm 2.43$  and  $6.09 \pm 2.64$   $\mu gC$   
139  $m^{-3}$  in spring, summer, autumn and winter, respectively. Seasonal differences in  $C_{EC}$   
140 were very small among spring, autumn and winter, mainly due to the relatively stable  
141 primary emissions of EC (e.g., vehicle exhaust) in these seasons in urban Guangzhou  
142 (Tao et al., 2017b). The 20% lower  $C_{EC}$  in summer than in the other seasons were mainly  
143 due to the stronger diffusion (e.g., higher mixing height) and more precipitation

144 scavenging in this season (Fig. 2). Due to the same reason, the lowest seasonal value of  
145  $C_{OC}$  also appeared in summer. The highest seasonal average of  $C_{OC}$  in autumn might be  
146 related with, besides primary fossil combustion, the formation of secondary organic  
147 carbon due to the strong photochemical reaction in this season in Guangzhou. Seasonal  
148 variations in  $C_{OC}$  were also slightly larger than those in  $C_{EC}$  due to more factors  
149 affecting  $C_{OC}$ . In contrast, the highest mass concentration of  $PM_{2.5}$  was observed in  
150 winter ( $53.52 \pm 22.89 \mu\text{g m}^{-3}$ ), which was 1.9 times higher than that ( $18.45 \pm 5.48 \mu\text{g}$   
151  $\text{m}^{-3}$ ) in summer. The much larger seasonal variations in  $PM_{2.5}$  than EC and OC  
152 suggested the dominant contributions of secondary inorganic aerosols over  
153 carbonaceous aerosols to  $PM_{2.5}$  in this city.

154 Moderate correlations ( $R^2 \geq 0.58$ ,  $p < 0.01$ ) between hourly  $C_{OC}$  and  $C_{EC}$  were  
155 found in all the seasons (Fig. 3), with the slopes of 2.3, 3.1, 2.7 and 1.9, in spring,  
156 summer, autumn and winter, respectively, implying the homogenic sources of  
157 carbonaceous aerosols in urban Guangzhou (Tao et al., 2017b). The relatively high  
158 slopes (OC/EC ratios) in the present study than reported previously for this city (Tao et  
159 al., 2014; Tao et al., 2017b) were likely due to the different method protocols (e.g.,  
160 NIOSH-TOT protocol and IMPROVE-TOR protocol) (Cheng et al., 2011; Wu et al.,  
161 2016a). On average, the determined  $C_{EC}$  by IMPROVE-TOR protocol (denoted as  $C_{EC-}$   
162  $TOR$ ) was 2.2 times of that by NIOSH-TOT protocol (denoted as  $C_{EC-TOT}$ ) in urban areas  
163 in the PRD region (Wu et al., 2016a). Taking into account this conversion factor, the  
164 seasonal slopes between  $C_{OC}$  and  $C_{EC}$  under the IMPROVE-TOR protocol in this study

165 (Fig. S1) are comparable to those (0.77–1.52) directly determined using IMPROVE-  
166 TOR protocol in previous studies (Tao et al., 2017b; Tao et al., 2014). The estimated  
167 OC/EC ratios under IMPROVE-TOR protocol are close to that of vehicle exhaust (1.1)  
168 and generally lower than those of coal combustion (2.7) and biomass burning (9.0)  
169 (Watson et al., 2001). These values implied the predominant contribution of traffic  
170 emissions to carbonaceous aerosols in urban Guangzhou.

171 In addition, moderate correlations ( $R^2 \geq 0.55$ ,  $p < 0.01$ ) between hourly  $C_{EC}$  and  
172  $NO_x$  ( $NO+NO_2$ ) mixing ratio were found in all the seasons except summer (Fig. 4),  
173 further indicating the predominant contribution of traffic emissions to EC (Bos et al.,  
174 2021). The poor correlation in summer was likely due to frequent rainfall, which  
175 removed particles more effectively than did insoluble gases (such as  $NO_x$ ). Similarly,  
176 OC was also very likely mainly from vehicle exhaust emissions followed by secondary  
177 aerosol formation in this city.

### 178 **3.2. Aerosol absorption coefficient and its wavelength dependence**

179  $b_{ap}$  at 950nm ( $b_{ap,950nm}$ ) showed a similar seasonal pattern to that of  $C_{EC}$  due to the  
180 predominant contribution of EC to aerosol light absorption at infrared wavelengths. The  
181 highest seasonal average of  $b_{ap,950nm}$  was found in winter ( $10.43 \pm 7.09 \text{ Mm}^{-1}$ ), which  
182 was 1.6 times of the lowest one in summer ( $6.50 \pm 2.65 \text{ Mm}^{-1}$ ). Note that the average  
183  $C_{EC}$  in winter is only 1.2 times of that in summer. The slightly different scales of  
184 seasonal variations between  $b_{ap,950nm}$  and  $C_{EC}$  suggested other factors besides EC mass  
185 might also affect  $b_{ap,950nm}$ , e.g., coating fraction and coating thickness (Lack and Cappa,

186 2010; Lan et al., 2013; Zhang et al., 2018).

187 Wavelength dependence of  $b_{ap}$  could also be used to investigate the sources of  
188 carbonaceous aerosols. Generally, AAE in urban areas dominated by traffic emissions  
189 has a value of approximately 1.0, and a value larger than 1.6 when dominated by  
190 biomass burning (Blanco-Alegre et al., 2020; Lack and Cappa, 2010). As shown in Fig.  
191 2b, hourly AAE varied in a range of 0.82–1.60 during the whole measurement period,  
192 indicating negligible contributions from biomass burning to  $b_{ap}$ .

193 Seasonal  $AAE_{370-950nm}$  calculated using Eq. 4 was 1.07, 1.09, 1.19 and 1.17 in  
194 spring, summer, autumn and winter, respectively, in urban Guangzhou (Fig. 5).  $AAE_{370-}$   
195  $950nm$  values in all the seasons were evidently lower than those from biomass burning,  
196 suggesting negligible contributions of brown carbon (BrC) from biomass and/or biofuel  
197 burning to  $AAE_{370-950nm}$  in urban Guangzhou. The slightly larger  $AAE_{370-950nm}$  in  
198 autumn and winter than in spring and summer was likely due to the seasonal differences  
199 in EC morphology, size distribution and mixing state (Gyawali et al., 2012; Zhang et  
200 al., 2020). The values of  $AAE_{370-950nm}$  in the present study were consistent with previous  
201 results obtained in urban Guangzhou in 2015–2016 (Tao et al., 2021) and other cities  
202 in the PRD region, e.g., 1.1 in urban Shenzhen (Lan et al., 2013; Li et al., 2018) and  
203 1.0–1.1 in Hong Kong (Lan et al., 2013; Li et al., 2018). These results further supported  
204 that EC was mainly emitted from vehicle emissions in the urban areas of the PRD region.

### 205 **3.3. Seasonal variations in $MAE_{EC}$ and influencing factors**

206 Good correlations ( $R^2 \geq 0.85$ ,  $p < 0.01$ ) between  $b_{ap}$  and  $C_{EC}$  were found in four

207 seasons (Fig. 6), indicating the dominant impact of EC mass on  $b_{ap}$  at infrared  
208 wavelengths. Considering the negligible contribution of BrC to  $b_{ap}$  at infrared  
209 wavelengths, the slope of zero-intercept linear regression of  $b_{ap}$  against  $C_{EC}$  can be  
210 considered as the bulk  $MAE_{EC}$  at 950 nm ( $MAE_{EC,950nm}$ ). The derived bulk  $MAE_{EC,950nm}$   
211 showed pronounced seasonal variations, with values of 6.13, 4.69, 5.44 and 5.97  $m^2 g^{-1}$   
212 in spring, summer, autumn and winter, respectively, indicating seasonal variations in  
213 microphysical properties (e.g., mixing state, size distribution) of EC.

214 Bulk  $MAE_{EC}$  at 550 nm ( $MAE_{EC,550nm}$ ), an intermediate wavelength in solar  
215 spectrum commonly concerned by previous studies (Bond and Bergstrom, 2006), can  
216 be estimated from  $MAE_{EC,950nm}$  and seasonal AAE using Eq. (4). The derived  
217  $MAE_{EC,550nm}$  are 11.00, 8.51, 10.42 and 11.32  $m^2 g^{-1}$  in spring, summer, autumn and  
218 winter, respectively. Compared to “pure EC” with a mean  $MAE_{EC,550nm}$  of 7.5  $m^2 g^{-1}$ ,  
219 seasonal  $MAE_{EC,550nm}$  were enhanced by 47%, 13%, 39% and 51% in spring, summer  
220 autumn and winter, respectively (Bond and Bergstrom, 2006). The lowest enhancement  
221 in summer was likely due to a low degree of coating of EC in this season. Low  
222 amplifications of MAE in summer (or wet season) were also found in previous studies  
223 in urban areas of the PRD region (Lan et al., 2013; Sun et al., 2020).

224 The amplifications of  $MAE_{EC}$  observed in the present study were comparable to  
225 those previously obtained in other urban regions worldwide (Andreae et al., 2008;  
226 Favez et al., 2009; Kondo et al., 2009; Lan et al., 2013; Liu et al., 2019; Ma et al., 2020;  
227 Sun et al., 2020; Wang et al., 2014; Wu et al., 2016b). Ma et al. (2020) observed a

228 slightly wavelength-dependent absorption enhancement of 1.35–1.42 in Nanjing of the  
229 Yangtze River Delta region, which was attributed to the coating of particulate nitrate  
230 on BC particles from traffic emissions. Liu et al. (2019) found 1.4- and 1.6-times  
231 enhancements of BC absorption (870 nm) for summer and winter respectively in urban  
232 Beijing of the North China Plain region when  $PM_{10} > 50 \mu\text{g m}^{-3}$ . Wang et al. (2014)  
233 obtained an average enhancement of 1.8 for BC absorption at 870 nm in a severely  
234 polluted urban region (Xi'an) of Northwest China. Generally, polluted environments  
235 combined with humid conditions are conducive to EC absorption enhancement by  
236 providing abundant secondary components for coating aged EC particles (Ma et al.,  
237 2020; Wu et al., 2016b). The amplifications of  $MAE_{EC}$  in this study were also  
238 comparable to those obtained in urban Guangzhou in previous years of 2017–2018  
239 presented by Sun et al. (2020), although a different approach named minimum R  
240 squared method was used to determine absorption enhancement in their study. However,  
241 increases in the  $MAE_{EC}$  enhancements were observed when compared to those obtained  
242 in all the seasons of 2015–2016 except summer, likely related to the increasing nitrate  
243 fraction in  $PM_{2.5}$  (Li et al., 2021). Increasing nitrate not only provided abundant  
244 materials for EC coatings but also increased aerosol hygroscopicity (Xu et al., 2020),  
245 which is further conducive to the internal mixing of EC with water-soluble matters  
246 (Tao et al., 2021).

247       Regarding diurnal pattern of  $MAE_{EC}$  in urban areas of the PRD region, a clear  
248 afternoon peak was previously observed, corresponding well to the peak of number

249 fraction of core-shell mixed rBC particles out of total rBC-containing particles (an  
250 indicator of rBC coating degree) and the peak of O<sub>3</sub> mixing ratio (Lan et al., 2013).  
251 Thus, MAE<sub>EC</sub> was considered to be largely affected by photochemical processes.  
252 However, in the present study, no evident diurnal variations of MAE<sub>EC</sub> were found in  
253 any of the four seasons in urban Guangzhou, despite apparent afternoon peaks of  
254 OC/EC ratio and O<sub>3</sub> concentration (Fig. 7). Note that hourly MAE<sub>EC</sub> investigated in the  
255 diurnal variations was calculated by hourly  $b_{ap,950nm}$  divided by hourly  $C_{EC}$ . In addition,  
256 no significant correlation ( $R^2=0.02$ ) was found between daily MAE<sub>EC,950nm</sub> and OC/EC  
257 ratio, implying limited influence of OC on the mixing state of EC in this city. A large  
258 fraction of OC was attributed to secondary OC (SOC) mostly generated from gas-phase  
259 reactions rather than heterogeneous reactions in urban Guangzhou (Chen et al., 2021),  
260 implying SOC is likely externally mixed with EC, thereby has limited contribution to  
261 the absorption enhancement of EC.

262 By contrast, daily MAE<sub>EC,950nm</sub> positively correlated with mass fraction of non-  
263 carbonaceous aerosol components in PM<sub>2.5</sub> ( $R^2=0.50$ ,  $p<0.01$ ) (Fig. 8a). Note that the  
264 mass concentration of non-carbonaceous aerosol components is calculated as the  
265 difference between PM<sub>2.5</sub> and the total of EC and organic matter ( $1.6\times OC$ ) (Zhang et  
266 al., 2013). Because the relatively low contributions of mineral aerosols and trace metals  
267 to PM<sub>2.5</sub> in urban Guangzhou (Tao et al., 2014), the non-carbonaceous aerosol  
268 components are mostly attributed to secondary inorganic aerosols (SIAs), such as  
269 sulfate, nitrate and ammonium. The lowest MAE<sub>EC,950nm</sub> in summer was likely due to

270 the lowest mass fraction of non-carbonaceous aerosols in  $PM_{2.5}$  (triangles in Fig. 8a).  
271 In addition, higher  $MAE_{EC,950nm}$  was also closely related with higher RH under the same  
272 mass fraction of non-carbonaceous aerosols in  $PM_{2.5}$  (Fig. 8a). High RH leads to high  
273 water content in aerosols, which is conducive to EC core embedding into water-soluble  
274 SIA components. Furthermore, high RH also favors the heterogeneous formation of  
275 SIAs on the surface of EC particles, thereby increasing the probability of core-shell  
276 mixing (Wu et al., 2016b). Thus, ambient RH also plays a role on the variation of  
277  $MAE_{EC,950nm}$ , which partly interpreted the relatively lower  $MAE_{EC,950nm}$  in autumn (with  
278 low RH) than spring and winter, despite higher mass fraction of non-carbonaceous  
279 aerosol in autumn.

280 In addition, daily  $MAE_{EC,950nm}$  decreased with increasing mass fraction of EC in  
281  $PM_{2.5}$  (Fig. 8b), likely because a low fraction of EC in  $PM_{2.5}$  was due to a high coating  
282 extent of EC by non-carbonaceous aerosols. Such a hypothesis is supported by the fact  
283 that EC was mainly from locally produced vehicle exhaust inside the city while non-  
284 carbonaceous aerosols (mainly secondary inorganic aerosols) were mostly from  
285 regional transport of industrial emission produced outside the city (Tao et al., 2017b).

#### 286 **4. Conclusions**

287 To investigate the seasonal variations of  $MAE_{EC}$  and associated dominant factors,  
288 hourly  $C_{EC}$ ,  $C_{OC}$  and  $b_{ap}$  of  $PM_{2.5}$  were simultaneously measured in urban Guangzhou  
289 in four seasons of 2018-2019. Moderate correlations between  $C_{EC}$  and  $C_{OC}$  were  
290 observed with low OC/EC mass ratios.  $C_{EC}$  also moderately correlated with NOx

291 mixing ratio. These facts demonstrated that carbonaceous aerosols were mainly from  
292 vehicle emissions in this city. The seasonal average AAE values were generally lower  
293 than 1.2 in all the seasons, indicating the dominant contribution of vehicle exhaust to  
294  $b_{ap}$  in the spectrum range of 370–950 nm. In this environment dominated by traffic  
295 emissions, the estimated bulk  $MAE_{EC,550nm}$  was 1.13–1.51 times of the mean value of  
296  $7.5 \text{ m}^2 \text{ g}^{-1}$  commonly used for "pure EC", implying the absorption enhancement of EC  
297 particles due to coating. The enhanced  $MAE_{EC}$  compared to "pure EC" was mainly  
298 related with high non-carbonaceous (mostly SIAs) factions in  $PM_{2.5}$  rather than  
299 photochemically produced SOC, as well high ambient RH. Results revealed the  
300 importance of further reducing the SIAs, particularly nitrate, to improve visibility and  
301 mitigate warming effects induced by EC absorption in the PRD region. Furthermore,  
302 accurately quantifying the value of  $MAE_{EC}$  is largely affected by the measurement  
303 methods for both  $C_{EC}$  and  $b_{ap}$ . Thus, in future, measurements based on more advantage  
304 methods, e.g., photoacoustic soot spectrometer (PASS) for  $C_{EC}$  and single particle soot  
305 photometer (SP2) for  $b_{ap}$ , are needed and suggested to compare with those used in this  
306 study to provide more reliable quantification of  $MAE_{EC}$  in this region.

307 *Data availability. Data used in this study are available from Jun Tao (taojun@jnu.edu.cn).*

308 *Competing interests. The authors declare that they have no conflict of interest.*

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## List of Figures

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Fig. 8. Scatter plots of daily  $b_{ap,950nm}$  versus mass fraction of (a) non-carbonaceous matters and (b) EC in  $PM_{2.5}$  in four seasons.

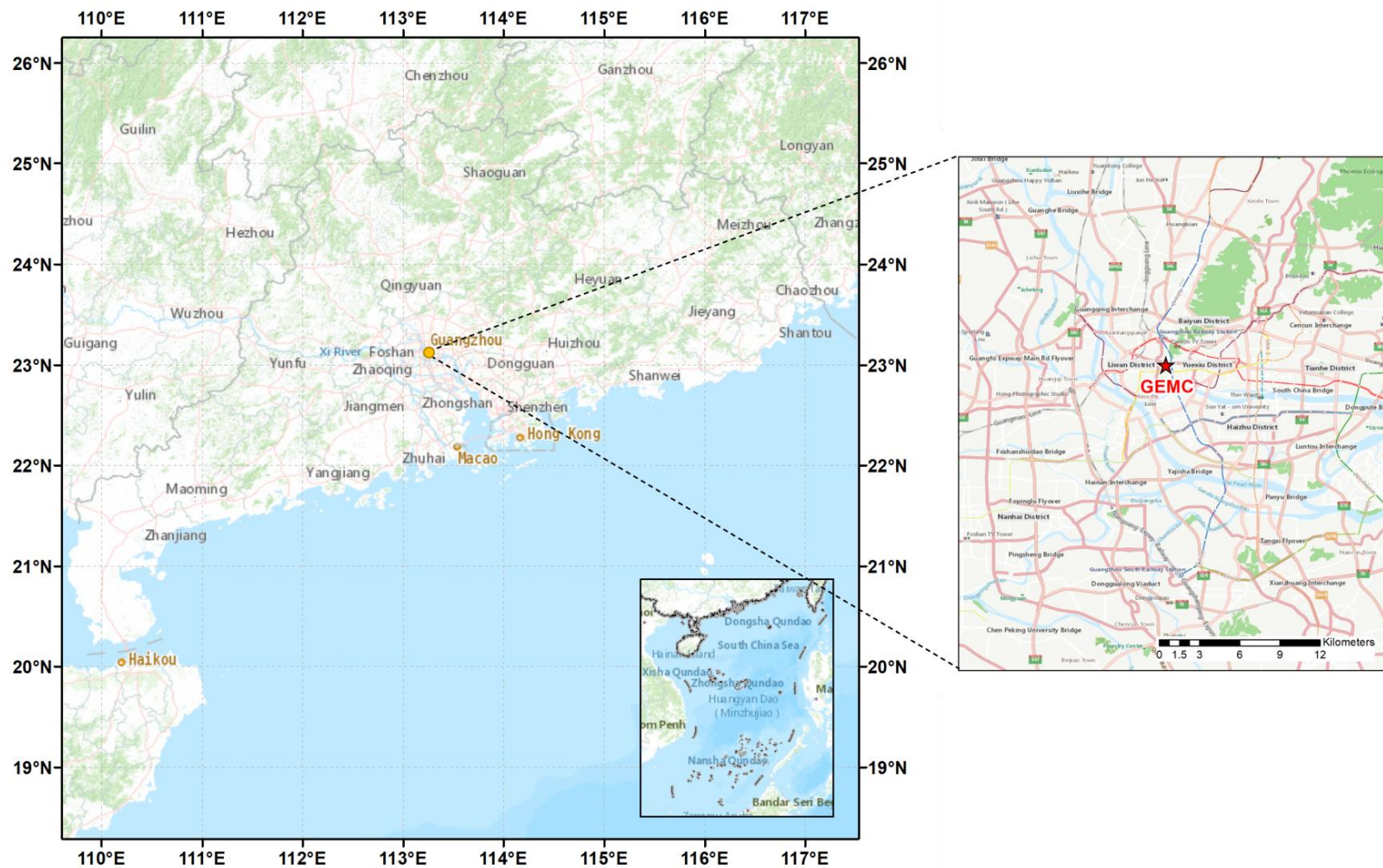


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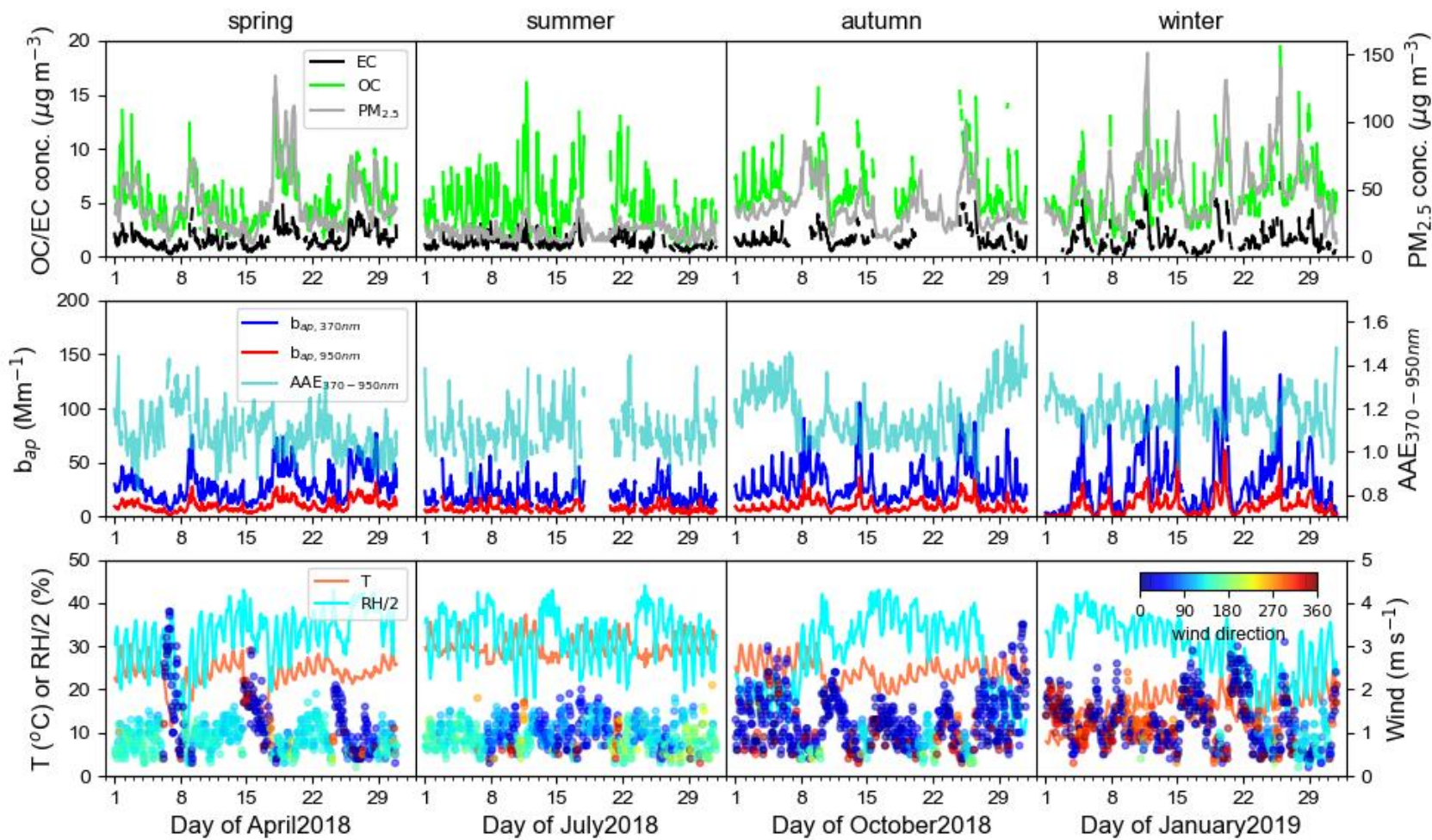
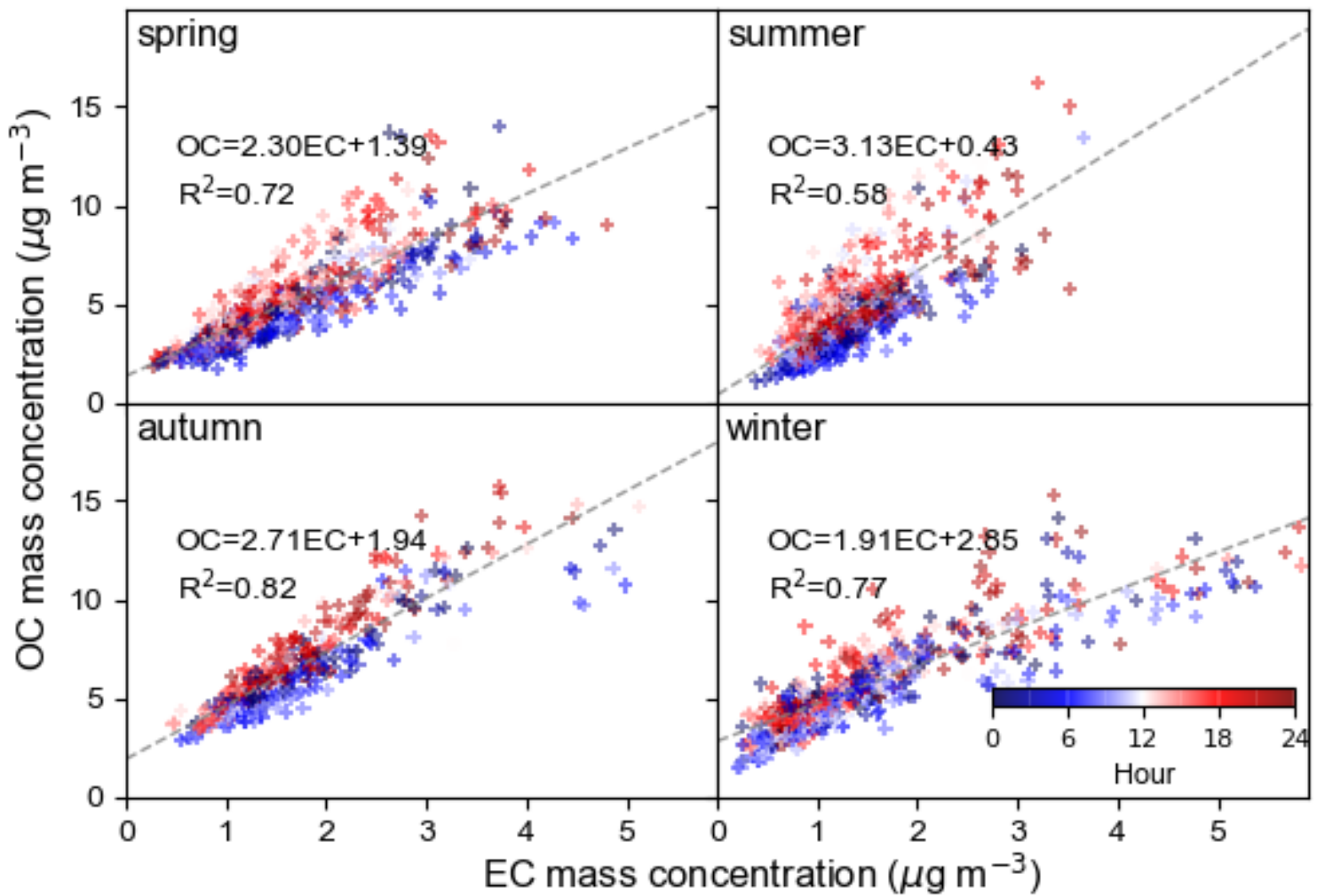


Fig.2

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**Fig.3**

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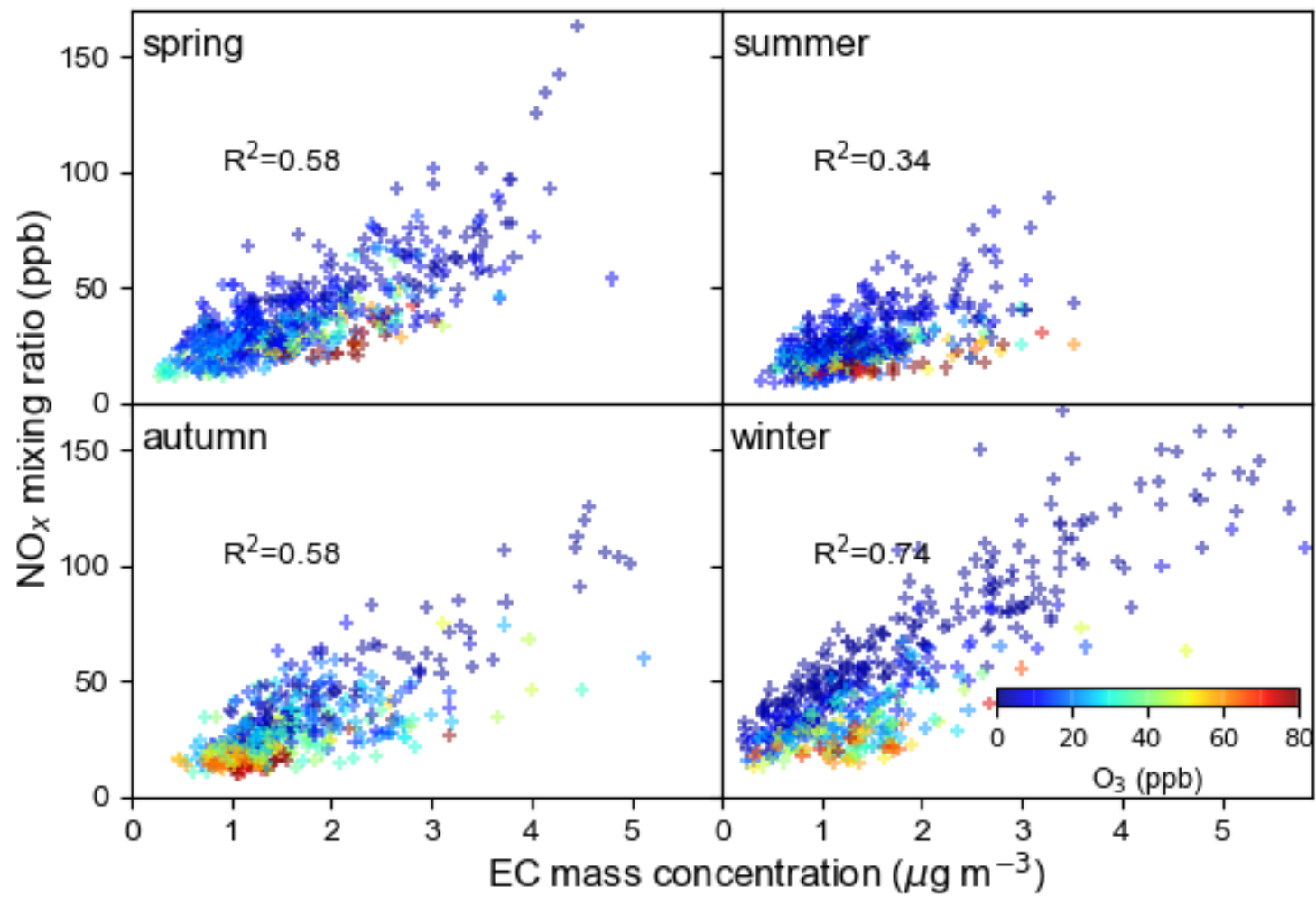


Fig.4

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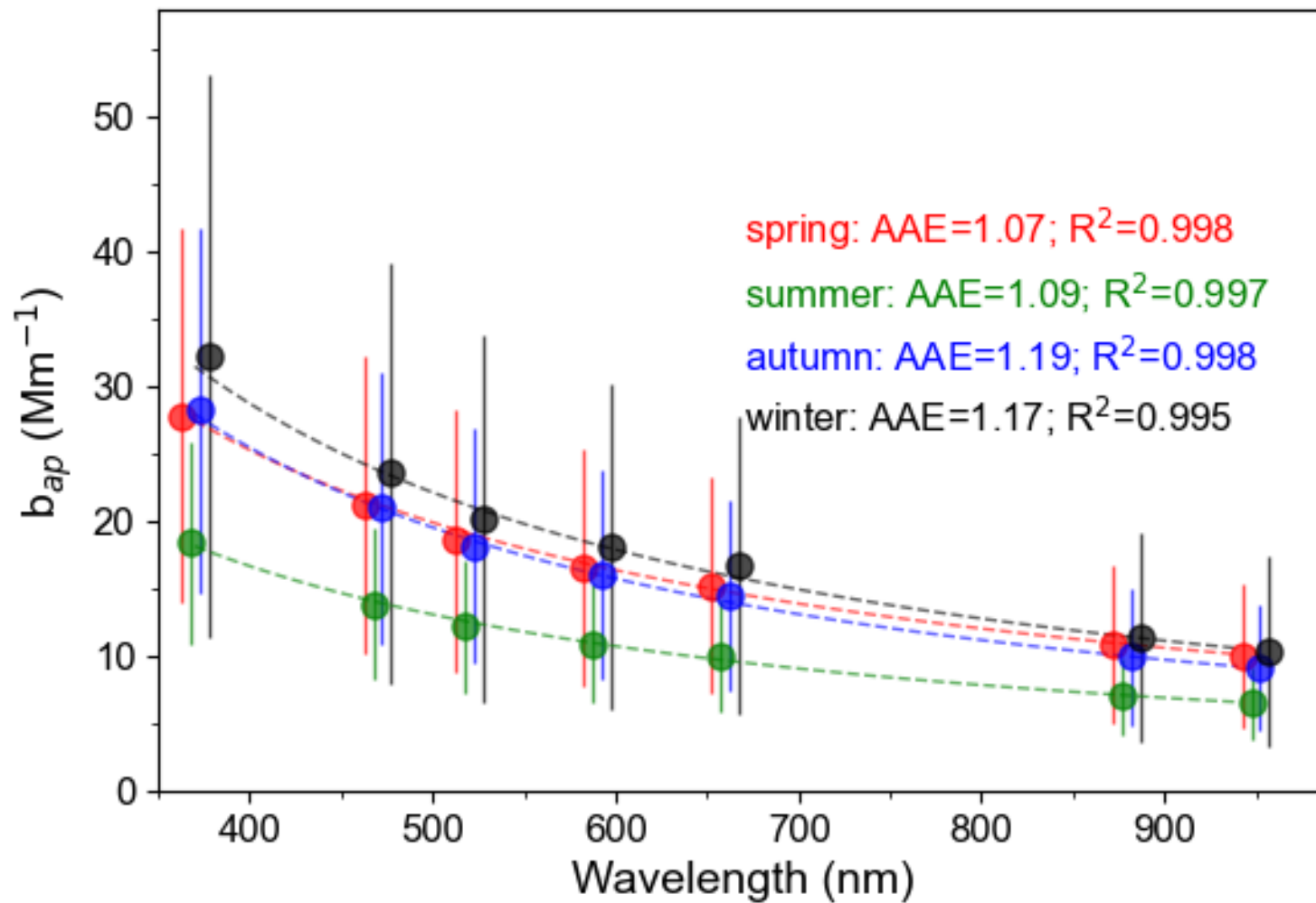


Fig.5

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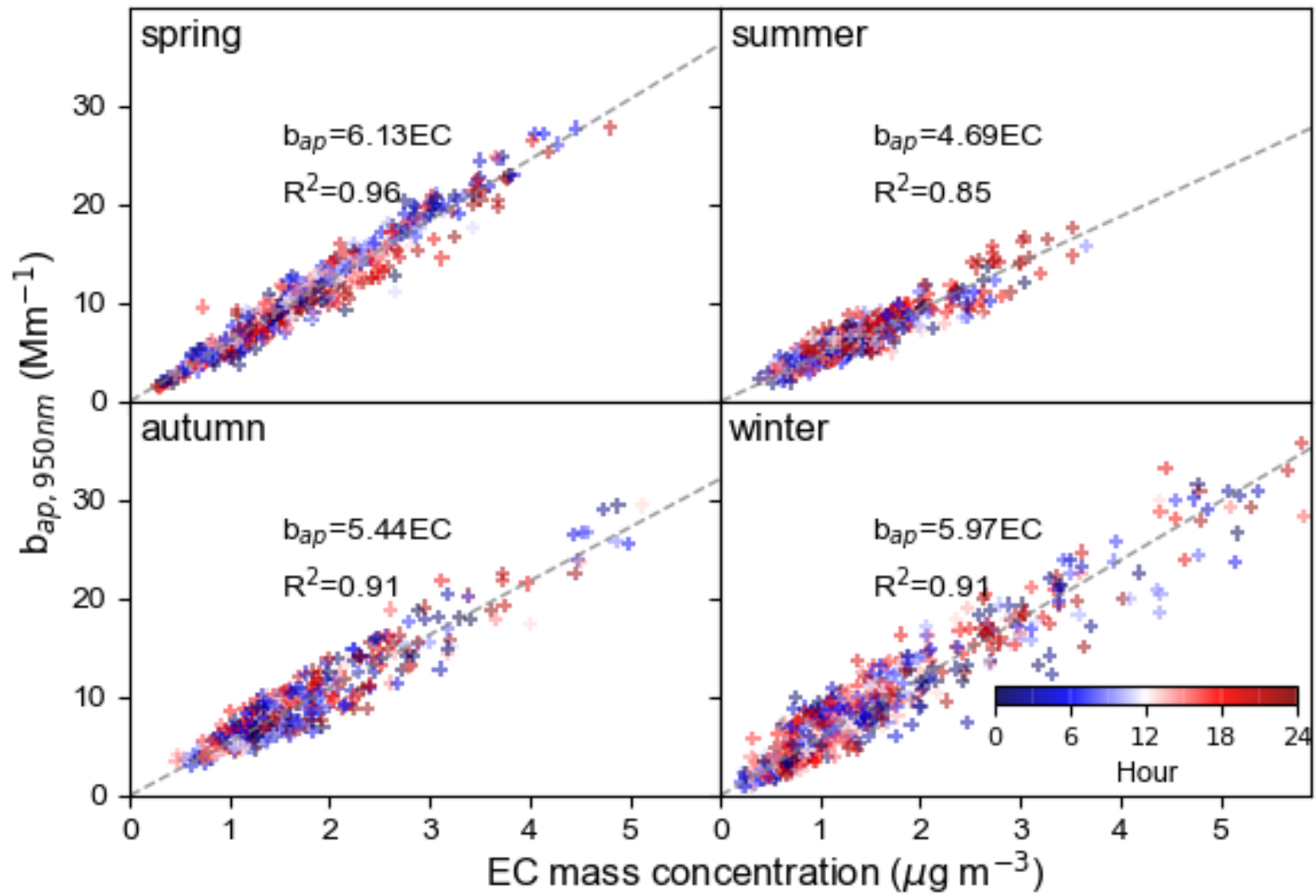


Fig.6

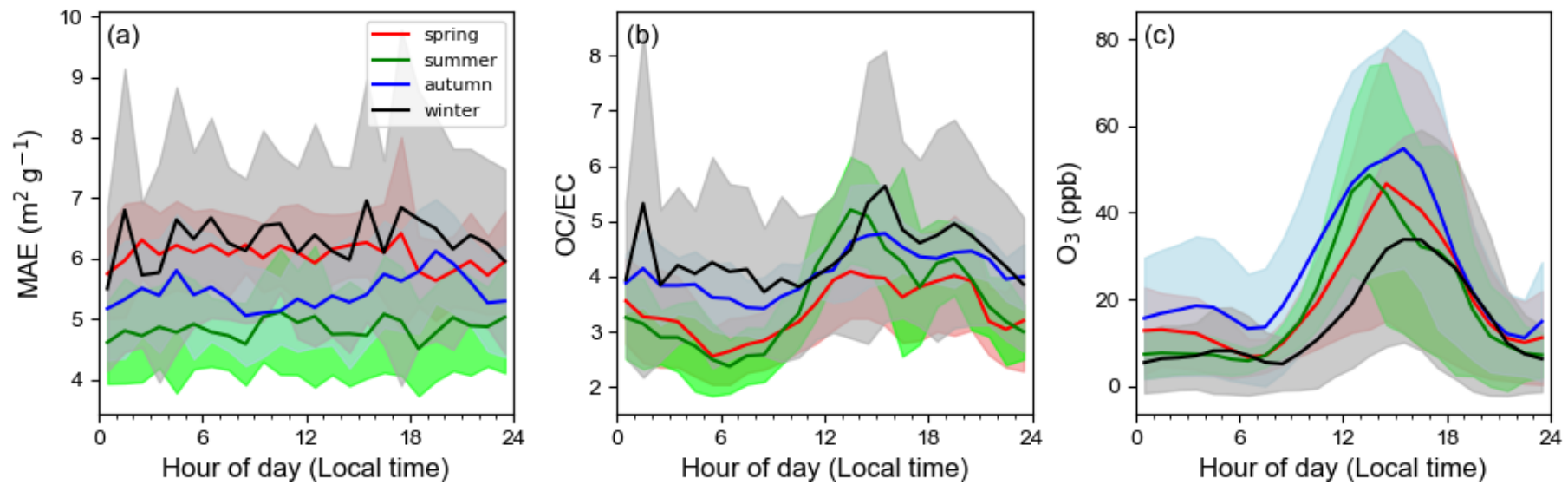


Fig.7

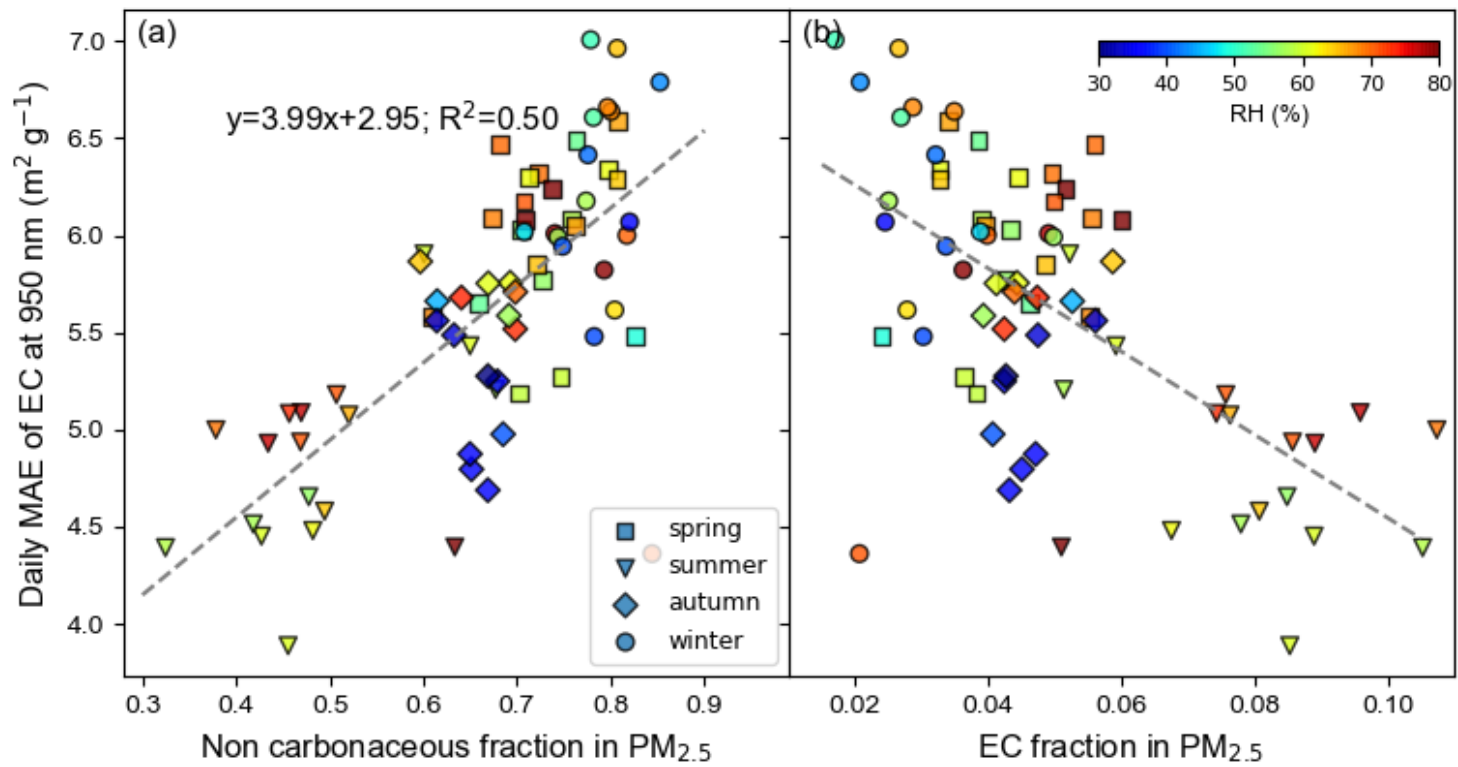


Fig.8

Supplemental files for

## Seasonal variations of mass absorption efficiency of elemental carbon in PM<sub>2.5</sub> in urban Guangzhou of south China

by Chenglei Pei et al.

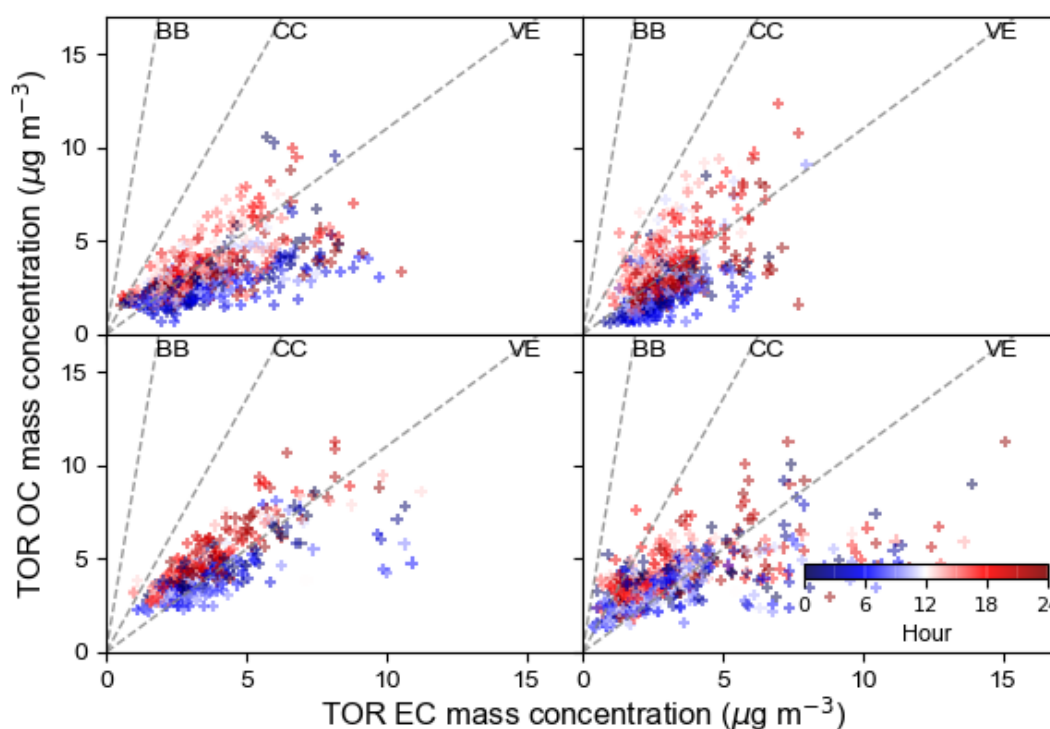


Fig. S1 Scatter plots of hourly mass concentration of OC versus EC under the IMPROVE-TOR protocol in four seasons. The TOR EC mass concentrations were calculated from the measured EC mass concentrations using the NIOSH-TOT protocol by considering a conversion factor of 2.2 proposed by Wu et al. (2016). The TOR OC mass concentrations were then calculated by subtracting the TOR EC mass concentrations from the total carbon mass concentrations, which are the sum of measured OC and EC concentrations. Dashed lines represent the typical TOR OC/EC mass ratios for biomass burning (BB, 9), coal combustion (CC, 2.7) and vehicle exhaust (VE, 1.1), respectively, proposed by Waston et al. (2001).

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