

1 **Highly time-resolved characterization of carbonaceous aerosols using a two-wavelength**
2 **Sunset thermal-optical carbon analyzer**

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21

22 **Abstract**

23 Carbonaceous aerosols have great influence on the air quality, human health and climate
24 change. Except for organic carbon (OC) and elemental carbon (EC), brown carbon (BrC) mainly
25 originates from biomass burning, as a group of OC with strong absorption from the visible to near-
26 ultraviolet wavelengths and makes a considerable contribution to global warming. Large amounts
27 of studies have reported long-term observation of OC and EC concentrations throughout the world,
28 but studies of BrC based on long-term observations are rather limited. In this study, we established
29 a two-wavelength method (658 nm and 405 nm) applied in the Sunset thermal-optical carbon
30 analyzer. Based on a one-year observation, we firstly investigated the characteristics,
31 meteorological impact and transport process of OC and EC. Since BrC absorbs light at 405 nm

32 more effectively than 658 nm, we defined the enhanced concentrations ($dEC = EC_{405\text{ nm}} - EC_{658\text{ nm}}$)
33 and gave the possibility to provide an indicator of BrC. The receptor model and MODIS fire
34 information were used to identify the presence of BrC aerosols. Our results showed that the
35 carbonaceous aerosol concentrations were highest in winter and lowest in summer. Traffic
36 emission was an important source of carbonaceous aerosols in Nanjing. Receptor model results
37 showed that strong local emissions were found for OC and EC; however, dEC was significantly
38 affected by regional or long-range transport. The dEC/OC and OC/EC ratios showed similar
39 diurnal patterns and the dEC/OC increased when the OC/EC ratios increased, indicating strong
40 secondary sources or biomass burning contributions to dEC. Two biomass burning events both in
41 summer and winter were analyzed and the results showed that the dEC concentrations were
42 obviously higher in biomass burning days; however, no similar levels of the OC and EC
43 concentrations were found both in biomass burning days and normal days in summer, suggesting
44 that biomass burning emission made a great contribution to dEC and the sources of OC and EC
45 were more complicated. Large number of open fire counts from the northwest and southwest areas
46 of the study site were observed in winter and significantly contributed to OC, EC and dEC. In
47 addition, the near-by Yangtze River Delta (YRD) area was one of the main potential source areas
48 of dEC, suggesting that anthropogenic emissions could also be important sources of dEC. The
49 results proved that dEC can be an indicator of BrC in biomass burning days. Our modified two-
50 wavelength instrument provided more information than the traditional single-wavelength thermal-
51 optical carbon analyzer and gave a new idea about the measurement of BrC; the application of
52 dEC data needs to be further investigated.

531. Introduction

54 Carbonaceous aerosols including organic carbon (OC) and elemental carbon (EC), which
55 have significant influence on the global radiative transfer, human health and atmospheric visibility,
56 have been the focus of research in the atmospheric environment field for many years (Lelieveld et
57 al., 2015; Wu and Yu, 2016; Wang et al., 2018; Zhang et al., 2017; Liu et al., 2019; Zhang et al.,
58 2019). EC mainly originates from fossil fuel and biomass combustion and is estimated to be the
59 second largest warming factor behind CO_2 contributing to climate change (Liu et al., 2015; Zhang
60 and Kang, 2019; Cao and Zhang, 2015). OC originates both from primary emissions and gas-to-
61 particle conversion as secondary organic carbon (SOC) and can scatter the solar radiation which
62 causes negative forcing globally (Zhou et al., 2014; Huang et al., 2014).

63 In the recent decades, brown carbon (BrC), as a kind of light-absorbing organic carbon which
64 can absorb light especially from near-UV to visible wavelength, has caused global concern due to
65 its positive climate effect (Andreae and Gelencsér, 2006; Zhang et al., 2020). BrC is mainly
66 emitted from anthropogenic and biogenic emissions (Zhang et al., 2011). Previous studies have
67 proved that biomass burning and biofuel combustion are the most important sources of primary
68 BrC (Saleh et al., 2014; Wu et al., 2020; Lei et al., 2018). Recent researches reported that in
69 developing countries such as China and India, the contribution of fossil fuel combustion to BrC
70 cannot be ignored (Satish et al., 2017; Yan et al., 2017; Kirillova et al., 2014). Secondary BrC is
71 mainly produced by heterogeneous photo-oxidation reactions or aqueous reactions of
72 anthropogenic and biogenic precursors (Zhang et al., 2020; Li et al., 2020; Zhang et al., 2011).
73 However, due to the lack of understanding of BrC at the molecular level and in situ BrC data, there
74 are still large uncertainties in the estimates of the distribution and the magnitude of the BrC climate
75 effect in both remote sensing and modeling (Arola et al., 2011; Feng et al., 2013).

76 The thermal-optical analysis (TOA) method is one of the most widely used quantitative
77 methods for OC and EC taking use of the difference between the thermo-optical properties of OC
78 and EC (Birch and Cary, 1996; Chow et al., 2004). OC and EC will be volatilized at different
79 heating protocol. The reflectance/transmittance of one laser source (near-infrared wavelength)
80 through the sample filter are continuously monitored and the return of the
81 reflectance/transmittance to its initial value on the thermograph is taken as the split point between
82 OC and EC. This way, the formation of pyrolyzed carbon which can also absorb the light and make
83 the sample darker, is corrected. This method has been widely used in studies employing the NIOSH
84 protocol or IMPROVE_A protocol (Ji et al., 2016; Chow et al., 2007). However, the thermal-
85 optical approach assumed that EC is the only light-absorbing species, the presence of BrC, which
86 is part of OC but also a light-absorbing component, shifts this separation towards EC, resulting in
87 overestimated EC values and underestimated OC values (Chen et al., 2015; Birch and Cary, 1996).

88 Sandradewi et al. (2008) pointed out that light absorption measurements at different wavelength
89 by the aethalometer can be used to quantify the contributions of wood combustion and traffic
90 emissions to aerosols since wood smoke contains organic compounds which enhance the light
91 absorption in the ultraviolet wavelength. But traffic emissions produce more black carbon (BC),
92 which dominates the light absorption in the near-infrared wavelength. They took use of
93 aethalometer data measured at 470 nm and 950 nm to quantify the BC distinction between wood

94 burning and traffic emission. With the similar principle, Wang et al. (2011) used a two-wavelength
95 Aethalometer (370 and 880 nm) to identify the presence of residential wood combustion (RWC)
96 particles which was closely associated with BrC. Organic components of wood smoke particles
97 absorb light at 370 nm more effectively than 880 nm in two-wavelength aethalometer
98 measurements. They believed that the enhanced absorption ($\Delta C = BC_{370nm} - BC_{880nm}$) can serve
99 as an indicator of RWC particles. This method was further used by Wang et al. (2012a; 2012b).
100 Chen et al. (2015) used a modified seven-wavelength thermal-optical transmittance/thermal-
101 optical reflectance (TOT/TOR) instrument (Thermal Spectral Analysis – TSA) allowing the
102 determination of the OC-EC split at different wavelengths and light absorption measurements to
103 be made with wavelength-specific loading corrections, providing additional information including
104 the optical properties of black carbon (BC) and BrC from the IR to UV parts of the solar spectrum
105 and their contributions. Massabò et al. (2016) further corrected the OC/EC split point using the
106 Multi-Wavelength Absorbance Analyzer (MWA) which provides the aerosol absorbance values
107 at five wavelengths from IR to UV together with a Sunset OC/EC analyzer to achieve the BrC
108 concentration. With a set of samples collected during wintertime in the Ligurian Apennines in
109 Italy, clear correlations were found between the BrC and levoglucosan mass concentration. A
110 further step of BrC quantification taking use of TSA was reported by Chow et al. (2018), further
111 proving that the use of seven wavelengths in thermal-optical carbon analysis allows contributions
112 from biomass burning and secondary organic aerosols to be estimated. Their results clearly
113 demonstrated the role of BrC in the thermal-optical analysis. However, these techniques focus on
114 the light absorption measurement of BrC and are still limited reported in previous researches,
115 though they provide quartz-fiber filter samples that are currently being characterized for OC and
116 EC by thermal-optical analysis. These methods mentioned above still cannot achieve the
117 observation of long-term real-time BrC mass concentrations.

118 Since the establishment of the TOT method by the Sunset Laboratory, the Sunset OC/EC
119 instrument, as part of the Chemical Speciation Network (CSN), with over 100 monitors across the
120 United States over 15 years, offering long-term measurement of OC and EC concentrations, has
121 been widely used in the United States and throughout the world providing important in-situ data
122 of OC and EC (U.S.EPA, 2019; Birch and Cary, 1996). This instrument had been designed with a
123 tuned diode laser (red 660 nm) to correct the formation of pyrolyzed carbon. In this study, we
124 modified the Sunset instrument to a two-wavelength (658 nm and 405 nm) Sunset carbon analyzer

125 by adding one more violet diode laser at $\lambda=405$ nm. The violet diode laser together with the red
126 diode laser focus through the sample chamber, then the laser beam passes through the filter to
127 correct for the pyrolysis-induced error. Previous work reported by Chen et al. (2015) as mentioned
128 above was integrating the optical instrument like the aethalometer to the traditional OC/EC
129 analyzer; in this way, they provided the light absorption contributions of BC and BrC. The
130 enhanced carbon analyzer provided new insight into more accurate OC and EC measurements.
131 Their work was conducted in offline mode; based on their work, our instrument can get the real-
132 time OC and EC mass concentrations both at 658 nm and 405 nm. BrC particles absorb light at
133 405 nm more effectively than 658 nm in the two-wavelength Sunset carbon measurements. We
134 define $dEC=EC_{405\text{ nm}}-EC_{658\text{ nm}}$ and hope it can be an indicator of BrC aerosols so that we can divide
135 real-time BrC mass concentration measurement from the two-wavelength measurement.

136 Nanjing, as one of the largest cities in the Yangzi River Delta region, represents a heavy industry
137 area with a dense population. In addition, due to its topography, Nanjing is very sensitive to
138 regional transport of air masses from its surrounding areas. OC, EC and dEC were measured from
139 June 2015 to July 2016 at Nanjing University of Information Science and Technology (NUIST).
140 Based on the abundant data, together with MODIS fire information, we can analyze the temporal
141 variation, transport processes and sources of carbonaceous aerosols in North Nanjing and evaluate
142 the biomass burning impact on dEC, which can be the scientific basis of pollution control policy.

1432. **Methods**

144 **2.1 Study site**

145 In this study, the sampling site is located at Nanjing University of Information Science and
146 Technology (NUIST) in the North Suburb of Nanjing (32°207'N, 118°717'E). The study site
147 is surrounded by housing and industrial areas. Many chemical enterprises, for example, Yangzi
148 Petrochemical, Nanjing Chemical Industry and Nanjing Iron and Steel Group are located at the
149 northeast of the study region, which produces exhaust with large amounts of aerosol particles. The
150 study site is adjacent to a heavily trafficked road (Ningliu Road) located near the site,
151 approximately 600 m to the east. Therefore, this region has intense human activities, industrial
152 emissions and heavy traffic flow.

153 **2.2 Two-wavelength TOT measurement**

154 Hourly concentrations of OC and EC in PM_{2.5} were sampled and measured by a semi-
155 continuous carbon analyzer (Model-4, Sunset Lab, USA). Air samples were collected continuously

156 with a sample flow of ~8 L/min through a PM_{2.5} cyclone. The collection time was set at 45 min
157 for each cycle. The airstream passed through a parallel plate organic denuder to reduce the effect
158 of volatile organic compounds and finally deposited on a quartz filter with a diameter of ~17mm.

159 After a sample was collected, OC and EC were determined using the TOT method by applying
160 a slightly modified NIOSH 5040 protocol. The details of the heating setup are shown in Table S1.
161 Figure 1 shows the structure and operational principle of the instrument. Briefly, it consists of two-
162 stages: the oven is first purged with helium and the oven temperature increased in a stepped ramp
163 to 840°C, OC is volatilized in this stage. Then the oven temperature is kept at 840°C for a while
164 and goes down to 550°C. In the second stage, EC is volatilized in a second temperature ramp to
165 850°C while purging the oven with a mixture containing 2% oxygen and 98% helium. The
166 pyrolysis products are converted to carbon dioxide (CO₂) which is quantified using a self-
167 contained nondispersive infrared (NDIR) system.

168 Also, in this study, we used a two-diode lasers (658 nm and 405 nm) equipped Sunset analyzer;
169 thus mass concentrations of OC and EC at different wavelengths can be measured with the 2-lasers
170 system. The split point between OC and EC is detected automatically by the RTCalc731 software
171 provided by Sunset Lab. The principle is the same as for the traditional Sunset carbon analyzer
172 (Birch and Cary, 1996). An example thermogram of sample analysis using the two-wavelength
173 Sunset semi-continuous carbon analyzer is shown in Fig. 2. During the sample analysis, the laser
174 beam at 658 nm and 405 nm are both sent through the filter and the transmitted light signal is
175 monitored to correct the undesired formation of pyrolyzed carbon (PyrC) and then to determine
176 the split point of OC and EC at both wavelengths. BrC aerosols absorb light at 405 nm more
177 significantly than 658 nm in the 2-lasers system. Due to the strong absorption of BrC at the near-
178 ultraviolet wavelength, the enhanced absorption at 405 nm can serve as an indicator of BrC
179 aerosols (Liu et al., 2015). We define dEC data as the difference of EC concentrations at two
180 wavelengths ($dEC = EC_{405nm} - EC_{658nm}$) to identify the presence of BrC aerosols. Our study provides
181 a one-year measurement of dEC mass concentrations. Besides, OC and EC represent the OC and
182 EC concentrations at 658 nm in this paper without a special explanation.

183 At the end of each analysis, a fixed volume of an internal standard containing 5% methane
184 and 95% Helium is injected and thus a known carbon mass can be derived. The external sucrose
185 standard (4.207 $\mu\text{g } \mu\text{L}^{-1}$) calibration was conducted every week to insure repeatable quantification.
186 Calibration with an instrument blank was conducted every day. Both detection limit for OC and

187 EC of the instrument was $0.5 \mu\text{g m}^{-3}$. We also did the measurements of OC and EC in PM_{2.5} filter
 188 samples using the same method followed by the NIOSH protocol. All data were corrected to blank
 189 measurement before comparison. Figure S1 shows the correlations between the real-time OC, EC
 190 concentrations and sampling OC, EC concentrations at the same time. The results showed that the
 191 online and offline data during the corresponding periods had good correlations with R² of 0.8 for
 192 OC, R² of 0.4 for EC and R² of 0.8 for TC. In order to evaluate the impact of PyrC, we calculated
 193 the PyrC at 658 nm fraction of dEC and the average PyrC/dEC was 4.4%, indicating the little
 194 influence of PyrC.

195 **2.3 Test of the new dEC data**

196 To evaluate the new dEC data, parallel BC concentrations were measured with a seven-
 197 wavelength Aethalometer with dEC concentrations in December, 2019. Radiation attenuation of
 198 an aerosol deposition on a filter (ATN_{λ}) is determined by the Beer-Lambert law:

$$199 \quad ATN_{\lambda} = \ln \frac{I_{0,\lambda}}{I_{\lambda}} \quad (1)$$

200 Where $I_{0,\lambda}$ and I_{λ} are the measured wavelength-specific laser reflectance signals. ATN_{λ} is used to
 201 calculate the attenuation coefficient with Eq. (2):

$$202 \quad b_{ATN} = \frac{A}{V} \quad (2)$$

203 Where A is the filter area and V is the sampled air volume. Then a simplified two-component
 204 model is used to calculate the contribution of light attenuation to both BC and BrC (Chow et al.,
 205 2018; Chen et al., 2015; Sandradewi et al., 2008; Hareley et al., 2008):

$$206 \quad b_{ATN}(\lambda) = q_{BC} \times \lambda^{-AAE_{BC}} + q_{BrC} \times \lambda^{-AAE_{BrC}} \quad (3)$$

207 Where q_{BC} and q_{BrC} are fitting coefficients, AAE is the absorption Ångström exponent which
 208 represents the wavelength-dependent characteristics of light absorption capability of aerosols. The
 209 AAE of BC was assumed to be 1. Fitting coefficients in Eq. (3) were obtained for potential AAE_{BrC}
 210 between 1 and 8 by least squares linear regression and the AAE_{BrC} leading to the overall best fit in
 211 terms of r^2 is selected as the effective AAE_{BrC} . Using these fitting coefficients, the b_{ATN} due to BC
 212 and BrC are calculated at each wavelength. Figure S2 shows that the fitted b_{ATN} at 405 nm are
 213 within $\pm 5\%$ of the measured values for $b_{ATN} > 0.01$. Figure 3 shows the relationship between the
 214 b_{ATN} due to BrC at 405 nm and the dEC. Good correlation between them is found with R square
 215 of 0.64, indicating that dEC was associated with BrC.

216 **2.4 Sampling**

217 2.4.1 Real-time PM_{2.5} observation

218 The real-time PM_{2.5} concentrations were measured through the Tapered Element Oscillating
219 Microbalance (TEOM) method (TEOM1405-DF, Thermo Scientific, America) from August, 2015
220 to July, 2016. The resolution of the measured data was 6 min. The instrumental operation
221 maintenance, data assurance and quality control were performed according to the Chinese Ministry
222 of Environmental Protection Standards for PM₁₀ and PM_{2.5} which was named “HJ 653-2013”
223 (Zhang and Cao, 2015b).

224 2.4.2 Sample collections

225 PM_{2.5} in the atmosphere was collected on 8*10 inch prebaked quartz fiber filters (QFF, PALL,
226 America) by a high volume air sampler (KC-1000, Qingdao, China) at a flow rate of 999 L min⁻¹
227 in four months: 4 June to 18 June, 6 October to 2 November and 10 December to 31 December in
228 2015, 10 May to 31 May in 2016. Sampling started and ended at around 8:00 and 20:00 every day;
229 each sample was collected for 12 hours. A total of 148 samples were collected including four field
230 banks in the four seasons using 10 min exposure to ambient air without active sampling.

231 All QFFs were pre-baked at 450 °C for 6 h before sampling to remove residual carbon. Before
232 and after sampling, all QFFs were weighed with an electronic balance (Sartorius, 0.1 mg,
233 Germany). After weighting, the filters were wrapped in aluminum foils, packed in air-tight
234 polyethylene bags and stored at -20°C until further analysis. All procedures during handling of
235 filters were strictly quality controlled to avoid any possible contamination.

236 **2.5 Identification of potential regional sources**

237 The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSLPIT4.8) model, provided
238 by the National Oceanic and Atmospheric Administration (NOAA), was used to investigate the air
239 mass origins of carbonaceous aerosols. The 48-hour back trajectories at Nanjing (32.2°N, 118.7°E)
240 were calculated every hour (Draxler and Hess, 1998; Rolph et al., 2017; Cohen et al., 2015). In
241 order to evaluate the behavior of the air mass circulation in the planetary boundary layer (PBL),
242 the trajectories at 500 m corresponding to the upper-middle height of the PBL were calculated,
243 representing well-mixed convective boundary layer for regional transport investigation (Xu and
244 Akhtar, 2010). The National Center for Environmental Prediction Global Data Assimilation
245 System (NCEP GDAS) data obtained from NOAA with a spatial resolution of 1° × 1° and 24 levels
246 of the vertical resolution were used as meteorological data input to the model. The Potential Source
247 Contribution Function (PSCF) model was usually applied to localize the potential sources of

248 pollutants. The details about the setup of the model can be found in Bao et al. (2017).

249 **3. Results and discussion**

250 **3.1 Characteristics of carbonaceous aerosols**

251 3.1.1 Concentrations of carbonaceous aerosols

252 The statistics for the PM_{2.5}, OC, EC and dEC mass concentrations at the NUIST site are
253 summarized in Table 1. The hourly OC concentrations ranged from 0.5 to 45.8 $\mu\text{g m}^{-3}$ (average of
254 $8.9 \pm 5.5 \mu\text{g m}^{-3}$), and the EC concentrations ranged from 0.0 to 17.6 $\mu\text{g m}^{-3}$ (average of 3.1 ± 2.0
255 $\mu\text{g m}^{-3}$). The results are comparable to those reported by Chen et al. (2017) in the Xianlin Campus
256 of Nanjing University ($5.7 \mu\text{g m}^{-3}$ for OC and $3.2 \mu\text{g m}^{-3}$ for EC), which site was located in the
257 southeast suburb of Nanjing and close to the G25 highway and were also affected by traffic sources.
258 The higher OC concentrations in this study are probably due to the around chemical enterprise
259 emissions. The average contributions of OC and EC to the total measured PM_{2.5} mass was 12.8%
260 and 4.3%, respectively, suggesting that carbonaceous fraction made an important contribution to
261 fine particulate matter. The average dEC mass concentration was $0.8 \mu\text{g m}^{-3}$ contributing 10.0% to
262 OC, 22.3% to EC and 1.3% to the PM_{2.5} concentrations with maximum concentration of $8.1 \mu\text{g m}^{-3}$
263 contributing 48.2% to OC, 97.8% to EC and 17.6% to total PM_{2.5} concentrations. This
264 information can be further applied in the PMF analysis to evaluate the sources of the carbonaceous
265 aerosols (Zhu et al., 2014; Sahu et al., 2011; Yan et al., 2019).

266 Compared with carbonaceous aerosol levels in other cities (Table S2), the OC and EC
267 concentrations in Nanjing were generally lower than those observed in urban sites such as Beijing
268 and Shanghai and inland cities like Chengdu and Chongqing which are affected by the basin terrain
269 characteristics with static wind and unfavorable diffusion conditions, but higher than those
270 observed in the southern coastal cities such as Guangzhou, which is a megacity in China. It could
271 be explained since the site in Guangzhou was a rural site. In general, the level of carbonaceous
272 aerosol concentrations in China is higher than that in developed countries in the United States and
273 Europe and lower than that in developing countries like India, though the sampling period in India
274 was from late autumn to winter and the much higher concentrations in India indicated the heavy
275 pollution level. The average OC/EC ratio in this study was 3.6, which is lower than most of those
276 reported in other studies, indicating the important impact of vehicle emissions at our study site.

277 Figure 4 shows the mass fractions of hourly carbonaceous aerosols and OC/EC ratios at
278 different PM_{2.5} concentration intervals during the study period. During that period, 84.2% of the

279 PM_{2.5} samples exceeded the daily averaged Chinese national ambient air quality standard (NAAQS)
280 of 35.0 $\mu\text{g m}^{-3}$ for the first grade and 40.1% of the total samples exceeded the NAAQS of 75.0 μg
281 m^{-3} for the second grade, reflecting heavy aerosol pollution in the study area. Generally, the
282 fractions of carbonaceous components decreased with increasing PM_{2.5} pollution level. A larger
283 mass fraction (about 32.3%) of carbonaceous aerosols in PM_{2.5} was found for relatively lower
284 PM_{2.5} levels (0–20 $\mu\text{g m}^{-3}$) compared to high PM_{2.5} levels (300–500 $\mu\text{g m}^{-3}$) with a carbonaceous
285 aerosol mass fraction of 5.2%. The results indicate that other components like secondary inorganic
286 aerosol (SIA) contribute more significantly to heavy haze events in Nanjing, which was also found
287 in other cities in the Yangtze River Delta area (Yang et al., 2011; Zhang and Zhang, 2019). The
288 contribution of dEC to OC decreased with the increase of PM_{2.5} concentrations between 0–200 μg
289 m^{-3} , and then increased with the increase of PM_{2.5} concentrations between 200–500 $\mu\text{g m}^{-3}$. The
290 dEC contributed most significantly to OC of 14.3% for PM_{2.5} concentrations below 20 $\mu\text{g m}^{-3}$. A
291 similar trend was found for the OC/EC ratios which showed a sharp increase along with enhanced
292 PM_{2.5} level above 150 $\mu\text{g m}^{-3}$. Previous studies have reported that high OC/EC ratios were related
293 to SOC formation or biomass burning emissions whereas low OC/EC ratios were related to vehicle
294 exhaust (Wang et al., 2015). We divided the dEC/OC at different intervals of OC/EC ratios and
295 found that the dEC/OC increased when the OC/EC ratios increased in the four seasons, indicating
296 strong secondary sources or biomass burning contributions to dEC during heavy pollution periods
297 (Fig. S3).

298 3.1.2 Seasonal variations of carbonaceous aerosols

299 As shown in Fig. 5, the OC, EC, dEC concentrations and dEC/OC ratios showed similar
300 variations with highest in winter and lowest in summer. The average OC and EC concentration in
301 winter was ~1.4 times and 1.5 times higher than that in summer and the average dEC
302 concentrations and dEC/OC in winter were approximately 1.4 and 1.6 times higher than those in
303 summer (Table 1). High dEC/OC was found in January and February in winter, indicating strong
304 influence of anthropogenic sources on dEC, such as coal combustion. In addition, we found strong
305 biomass burning activities in February, which significantly contributed to the high concentrations
306 of dEC in February; more details can be found in section 3.3. The seasonality of carbonaceous
307 species in PM_{2.5} was strongly influenced by seasonal variations in emission intensities and
308 meteorological parameters. Table S3 summarizes the meteorological parameters in the four
309 seasons during the study period. The high carbonaceous aerosol concentrations in winter were

310 mainly a result of relatively stable atmospheric conditions with low temperature, relative humidity
311 and boundary layer on one hand, and on the other hand, increasing emissions from fossil-fuel
312 combustion for heating from the chemical enterprises nearby. In summer, the higher boundary
313 layer resulted in the dispersion of aerosols in the atmosphere, and the higher temperature promoted
314 the partitioning of semi-volatile organic compounds (SVOCs) into the gaseous phase (Yang et al.,
315 2011). In addition, large precipitation in summer (586 mm in total) favored the wet scavenging
316 processes of aerosols.

317 The average OC/EC ratios in spring, summer, autumn and winter were 3.9, 4.0, 2.8 and 3.4,
318 respectively (Table 1). The OC/EC ratio could give some information about primary and secondary
319 organic carbon (Turpin and Huntzicker, 1995; Lim and Turpin, 2002). In summer, strong
320 convective activities in the atmospheric boundary layer and solar radiation, high temperature and
321 plenty of moisture in the atmosphere were favorable for the formation of SOC. On the other hand,
322 the high OC/EC ratios in June in this study were also strongly related to biomass burning which
323 will be discussed in 3.3 sections. The lower ratios of OC to EC in autumn and winter indicate
324 strong primary sources in these two seasons. It should be noted that the OC/EC ratios were a rough
325 indicator to estimate the primary and secondary organic carbon; further analysis of the formation
326 of SOC needs to be conducted in the future (Pio et al., 2011; Wu and Yu, 2016).

327 3.1.3 Diurnal variation of carbonaceous aerosols

328 The diurnal pattern of carbonaceous aerosols can be affected by both meteorological
329 parameters and sources (Ji et al., 2016). Figure 6 depicts the diurnal variation of OC, EC, dEC,
330 dEC/OC and OC/EC ratios during the study period. Clear diurnal variations were observed in OC
331 and EC. Both the OC and EC concentrations kept high levels at night and low levels in the daytime,
332 indicating the strong influence of the atmospheric boundary layer on air quality in northern
333 Nanjing. The peak occurred in the morning both for OC and EC, indicating the significant impact
334 of traffic sources on the OC and EC concentrations. The dEC/OC and OC/EC ratios showed similar
335 trends in the daytime with gradually increase from morning till afternoon, indicating the
336 importance of the contribution of secondary sources to dEC. Similar though not so obvious diurnal
337 variations were found in dEC. It should be noted that the vehicle emissions and the boundary layer
338 height had no significant effect on the diurnal variation of dEC/OC, suggesting there were no
339 significant local sources of dEC. There was a small peak in dEC/OC at 3:00 am, which might be
340 related to the aqueous secondary organic aerosol formation during nighttime (Sullivan et al., 2016).

341 The relative humidity (RH) and Temperature (T) dependent distributions of OC, EC mass
342 concentrations and dEC/OC and OC/EC throughout the study period are shown in Fig. 7. High
343 dEC/OC (>30 %) can be found in three areas, first shown in the right area with relatively high T
344 at 25-40 °C and RH at 40-60 %, which were usually found in the summer afternoon which was
345 closely related to the strong formation of SOC. This distribution was also seen in OC/EC. The
346 second area is in the upper region with RH over 80 % and T at 10-20 °C and the third area appears
347 for RH below 30 % and T at about 10 °C, corresponding to nighttime and winter afternoon. In
348 general, dEC had no strong dependence on the RH and T distribution, indicating the complex
349 formation mechanism of dEC. OC and EC show similar distributions with the highest mass loading
350 (OC: > 20 $\mu\text{g m}^{-3}$; EC: > 8 $\mu\text{g m}^{-3}$) at relatively high RH at 60-80 % which usually occurred at
351 night with relatively low boundary layer height, leading to the accumulation of aerosols. However,
352 the corresponding OC/EC ratios were low, suggesting the importance of primary sources to OC
353 and EC in northern Nanjing, which will be verified in the wind rose of OC and EC (Fig. 8).

354 **3.2 Air mass transport**

355 3.2.1 Windrose of carbonaceous aerosols

356 To investigate the influence of air mass transport to the study site, the wind rose of OC, EC and
357 dEC/OC using hourly data in the four seasons is shown in Fig. 8 (Carslaw and Ropkins, 2012).
358 Two points should be noted. First, high OC and EC mass concentrations were found near the field
359 site (indicated by wind speed (WS) < 1 m s^{-1}), suggesting that local and primary emissions (e.g.,
360 industrial and vehicle emissions) were stable and important sources contributing to atmospheric
361 OC and EC mass concentrations in northern Nanjing. The OC mass concentrations from the
362 southwest increased with the increase of WS in summer, indicating that the sources of OC are
363 complicated in summer including secondary reaction during long-range or regional transport.
364 Second, compared with OC and EC, dEC showed no significant local sources. The dEC/OC
365 increased with increasing WS and the highest dEC/OC were found for WS over 3 m s^{-1} . Long-
366 range or regional transport were highly likely the main sources contributing to the dEC mass
367 concentrations.

368 3.2.2 The potential source areas of carbonaceous aerosols

369 The possible source contributions were evaluated using the PSCF model and the PSCF maps
370 are shown in Fig. 9 (Petit et al., 2017). The areas with high PSCF values were highly likely the
371 potential pollution source areas. As shown in Fig. 9, the PSCF results further proved the strong

372 regional transport contribution to dEC and local contributions to OC and EC. In spring, the
373 potential source areas of OC and EC were mainly from the southwest of Nanjing; however, the
374 potential source areas of dEC were from the east of Nanjing, indicating obvious different sources
375 between OC, EC and dEC. In summer, local areas were the main source areas of EC and the near-
376 by Yangtze River Delta City Group from the southeast of Nanjing including developed cities like
377 Shanghai were the main sources areas of OC and dEC. The anthropogenic emissions from these
378 areas might be important sources of OC and dEC. Besides, both the potential sources areas of dEC
379 and EC were in the northwest of Nanjing in summer, suggesting strong primary sources of dEC
380 from this area which were very likely associated with biomass burning, more details are given in
381 section 3.3. In autumn, local sources from the study site were strongest for OC and EC. However,
382 dEC mainly originated from regional transport from the northwest and southeast areas of Nanjing.
383 Biomass burning has been proved to be an important source of air pollutants in the Yangtze River
384 Delta (YRD) area, especially in the wheat harvest seasons (e.g., June and October) (Cheng et al.,
385 2014; Zhang and Cao, 2015a). In addition, the YRD area is the most economically developed
386 region in China and has lots of industrial cities, which means that industrial emissions and
387 anthropogenic sources contributed to high carbonaceous aerosol pollution levels. In winter, dEC
388 was mainly from long-range transport from northern cities and regional transport from the
389 southwest areas of Nanjing while both long-range transport and local sources were found in OC
390 and EC concentrations.

391 **3.3 The characteristics of carbonaceous aerosols during biomass burning periods**

392 The biomass burning emission has been proved to be an important source of BrC on a global
393 scale; it is consistently observed in large-scale forest fire events (Laskin et al., 2015). Based on the
394 Fire Information for Resource Management System (FIRMS) derived from the Moderate
395 Resolution Imaging Spectroradiometer (MODIS), we found that the fire points amounted to 2028,
396 1773 and 967 on 11 Jun 2015, 7 February 2016 and 2 March 2016, respectively, in the areas around
397 our study site, suggesting there were strong biomass burning events on these days (Fig. S4). To
398 further investigate the biomass burning impact on dEC, we analyzed the temporal trends of
399 carbonaceous aerosols from 4 June 2015 to 19 June 2015 and 7 February 2016 to 3 March 2016,
400 respectively. Combining the observed aerosol concentrations and fire information, we divided the
401 periods into normal days and biomass burning days. It should be noted that the biomass burning
402 days are not determined based only on fire points. We also considered the 48-h backward

403 trajectories and open biomass burning areas. For example, we found lots of fire points from 11
404 June 2015 to 12 June 2015 and from 7 February 2016 to 10 February 2016, respectively, and the
405 48-h back trajectories passed over these biomass burning areas (Fig. S5b, c). However, although
406 there were large amounts of fire points in the northwest of Nanjing from 8 June 2015 to 9 June
407 2015, the backward trajectories showed that the air masses during the periods came from the
408 southeast areas where no open fire points were found (Fig. S5a). In contrast, there were only a few
409 fire points found near the study site from 26 February 2016 to 27 February 2016, the 48-h backward
410 trajectories showed the air masses came exactly from the area (Fig. S5d).

411 As shown in Fig. 10 and Fig. 11, we found that dEC concentrations, dEC/OC and OC/EC
412 ratios showed peaks during each biomass burning period which were not that obvious in OC and
413 EC concentrations, suggesting the unique biomass burning impact on dEC and the sources of OC
414 and EC were more complicated. It should be noted that there were peaks of dEC on 9 June 2015
415 and 13 February 2016, which were not biomass burning days, suggesting that biomass burning
416 was not the only source of dEC. As mentioned in sections 3.1 and 3.2, anthropogenic emissions
417 could be the sources of dEC and the secondary sources cannot be ignored, either. Summarized in
418 Table 2 are the average and standard deviation values of OC, EC, OC/EC, dEC and dEC/OC during
419 biomass burning and normal days. The OC/EC, dEC concentrations and dEC/OC were obviously
420 higher in biomass burning days than in normal days, but similar levels of the OC and EC
421 concentrations were found both in biomass burning days and normal days in summer, suggesting
422 the great contribution of biomass burning emissions to dEC and there were other sources of OC
423 and EC in summer. All the carbonaceous aerosols were higher in biomass burning days in winter;
424 in addition, the locations of open fire counts were mainly in the northwest and southwest area of
425 the study site (Fig. S5c, d), which were the potential source areas of OC, EC and dEC in winter as
426 discussed in section 3.2.2, indicating strong contributions of biomass burning emissions to all the
427 carbonaceous aerosols in winter.

428 **4. Conclusions**

429 In this study, the characteristics and sources of carbonaceous aerosols in North Nanjing were
430 investigated and we introduced a two-wavelength method by modifying the Sunset carbon analyzer.
431 We incorporated a new diode laser at $\lambda=405$ nm in the instrument, making it possible to detect the
432 laser beam passing through the filter at both wavelength $\lambda=658$ nm and $\lambda=405$ nm, so that we can
433 obtain the dEC concentrations. Our study illustrated the feasibility of using dEC to characterize

434 the BrC aerosols, providing a new idea about the measurement of BrC. The results showed that
435 high (low) OC, EC and dEC concentrations were found in winter (summer), indicating the
436 significant impact of the increase of various emission sources in winter and wet scavenging by rain
437 in summer. Similar diurnal cycles for OC and EC concentrations were found with high at night
438 and low in daytime, strongly affected by the boundary layer. Traffic emissions were found to have
439 a significant influence on the concentrations of OC and EC. Similar trends were found in the
440 diurnal cycle of dEC/OC and OC/EC and the dEC/OC increased when the OC/EC ratio increased,
441 indicating strong secondary sources or biomass burning impact on dEC. The wind rose and
442 receptor model results showed that strong local emissions were found for OC and EC; however,
443 dEC was significantly affected by regional or long-range transport. The near-by YRD area was one
444 of the main potential source areas of dEC, suggesting that anthropogenic emissions could be the
445 sources of dEC. Together with the back trajectories analysis and MODIS fire information, we
446 analyzed two biomass burning events both in summer and winter. The results showed that the
447 sources of OC and EC were more complicated than those of dEC in summer. Biomass burning
448 emission made a great contribution to dEC concentrations in summer. A large number of open fire
449 counts from the northwest and southwest areas of the study site was observed; these fires
450 significantly contributed to the carbonaceous aerosol pollution.

451 Our modified two-wavelength instrument provided more information than the traditional
452 single-wavelength thermal-optical carbon analyzer. The results proved that dEC can be an
453 indicator of BrC in biomass burning days. It should be noted that the sources of dEC were
454 complicated and the anthropogenic emissions and secondary formations of dEC aerosols could not
455 be ignored; further chemical analysis needs to be conducted in the future. The evaluation of SOC
456 formation and the relationship between dEC and SOC can be conducted. In addition, more
457 chemical analysis such as the analysis for ions, organic matter or sugars in PM_{2.5} can be made;
458 thus we can get some information of the tracers of different sources and more accurate and
459 quantitative source apportionment can be done (Bhattaraia et al., 2019; Wu et al., 2018; 2019). We
460 also hope that the dEC data can be further applied in more research.

461

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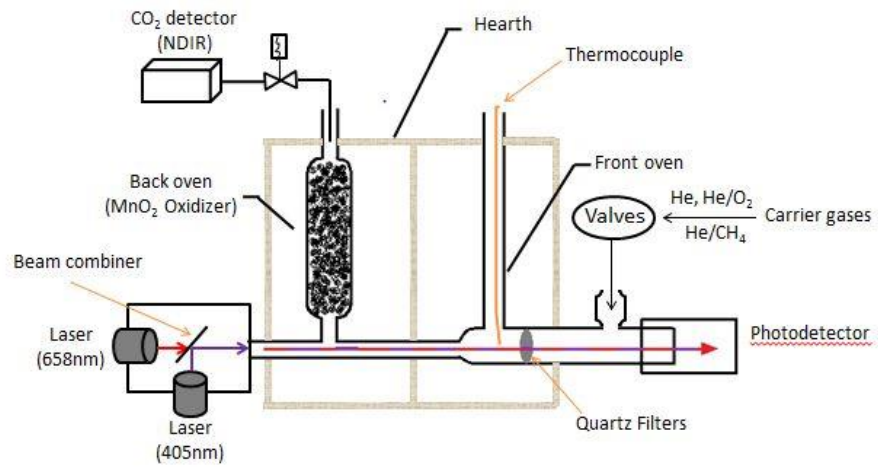
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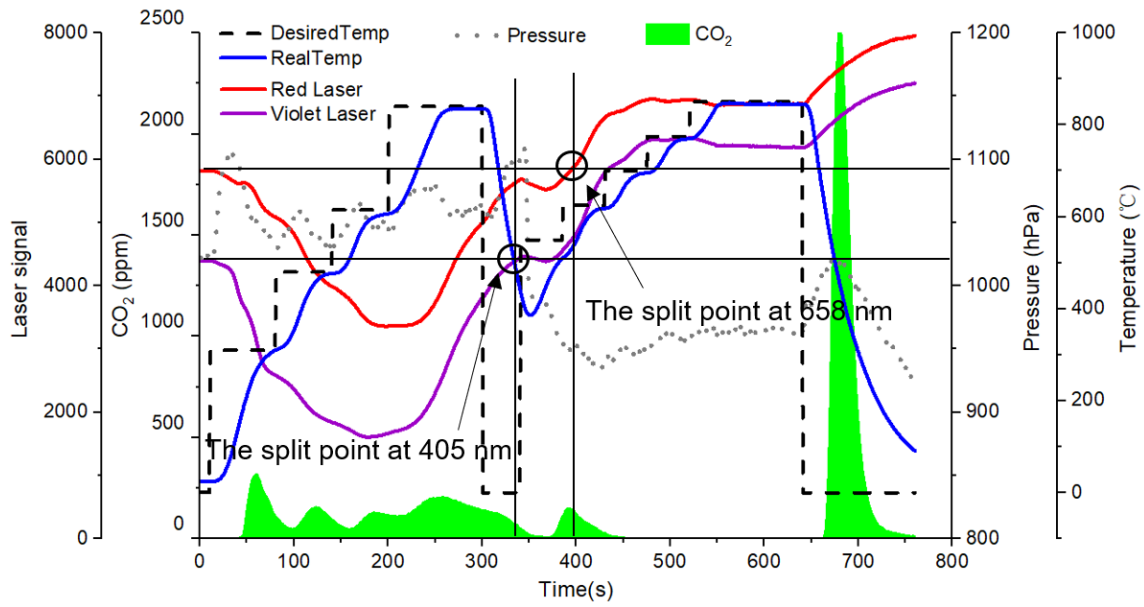
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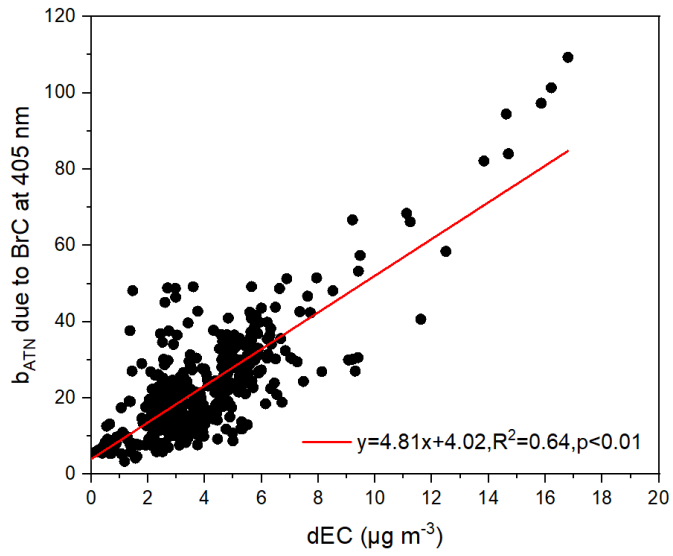
674 **Figure 1.** Principle and structure of the Sunset semi-continuous carbon analyzer.

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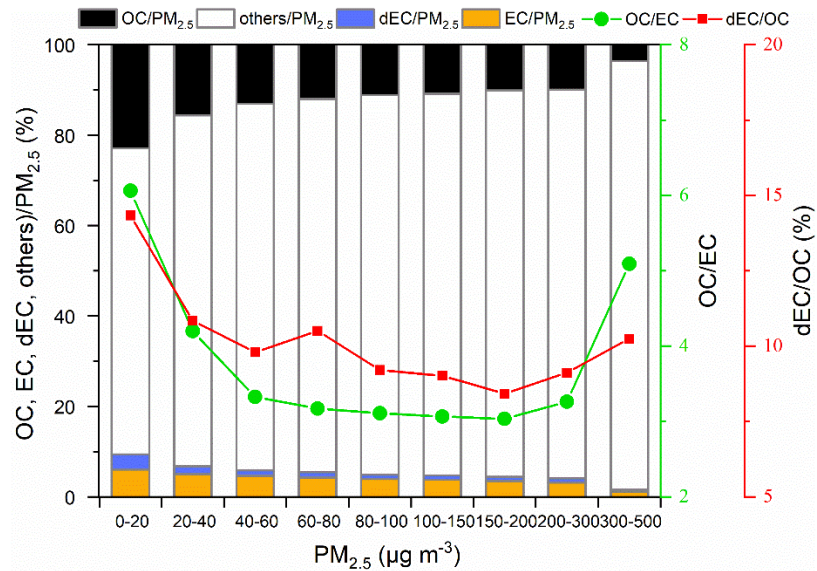
676

677 **Figure 2.** Example thermogram of sample analysis using the two-wavelength Sunset semi-
 678 continuous carbon analyzer.

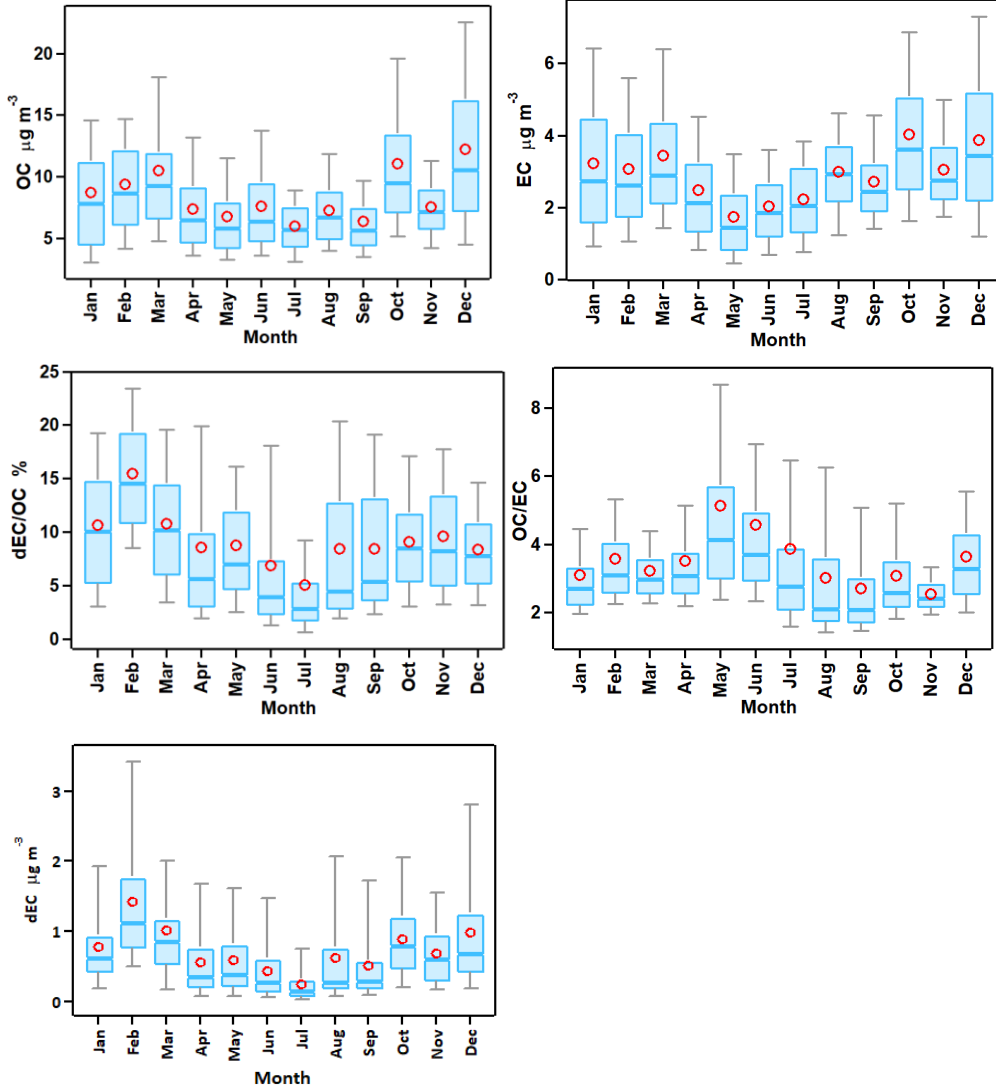


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680 **Figure 3.** Relationship between the b_{ATN} due to BrC at 405 nm and the dEC concentrations.



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 682 **Figure 4.** Carbonaceous species fractions of PM_{2.5} and OC/EC ratios at different PM_{2.5}
 683 concentration intervals at NUIST from June 2015 to August 2016.



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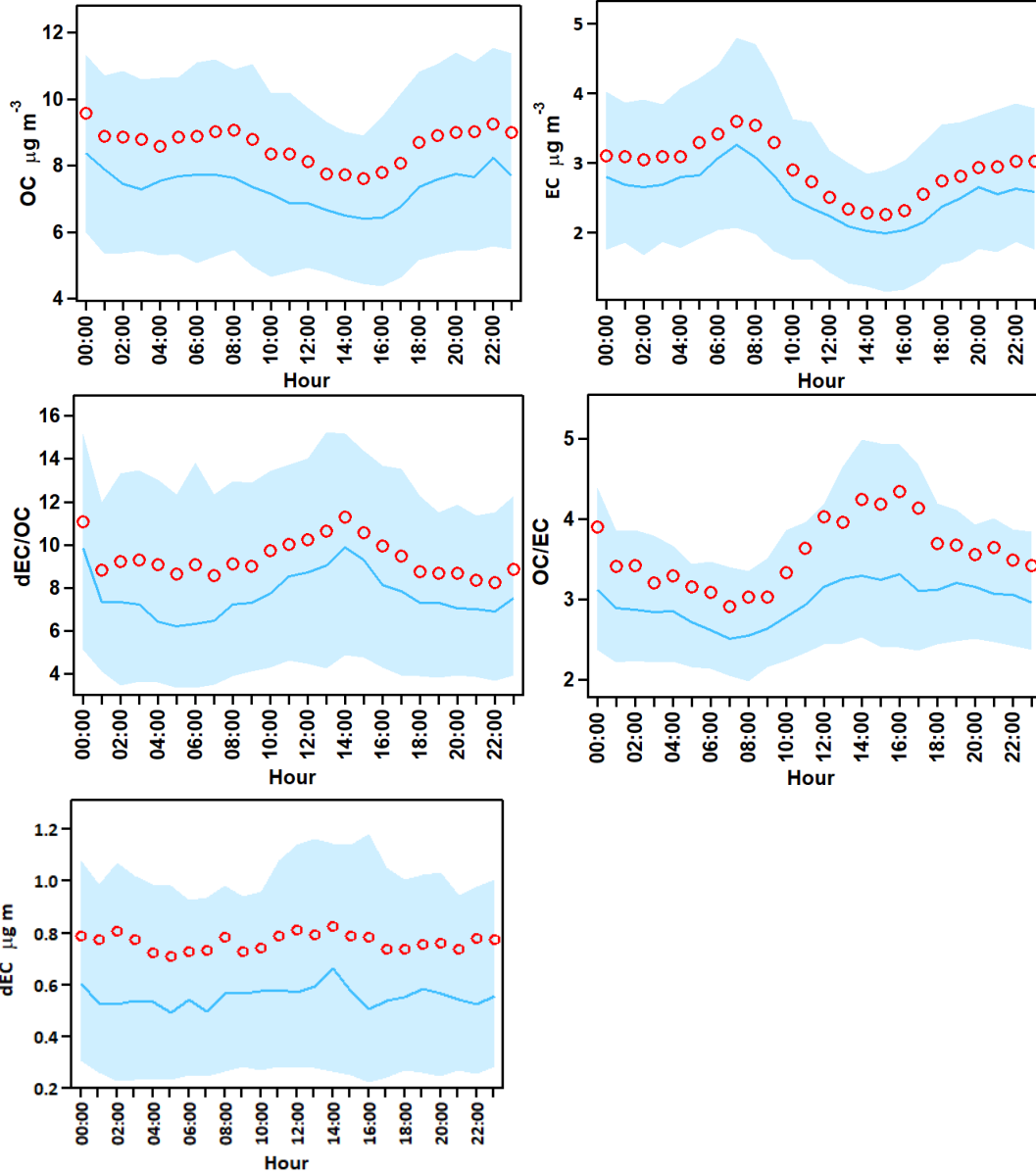
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Figure 5. Monthly variations of OC, EC, dEC, dEC/OC and OC/EC ratios at NUIST from June 2015 to August 2016. The boundary of the box indicates the 25% and 75% percentile, respectively. The lower and upper whiskers indicate the 10% and 90% percentile, respectively. The red circle within the box marks the average while the line within the box marks the median.



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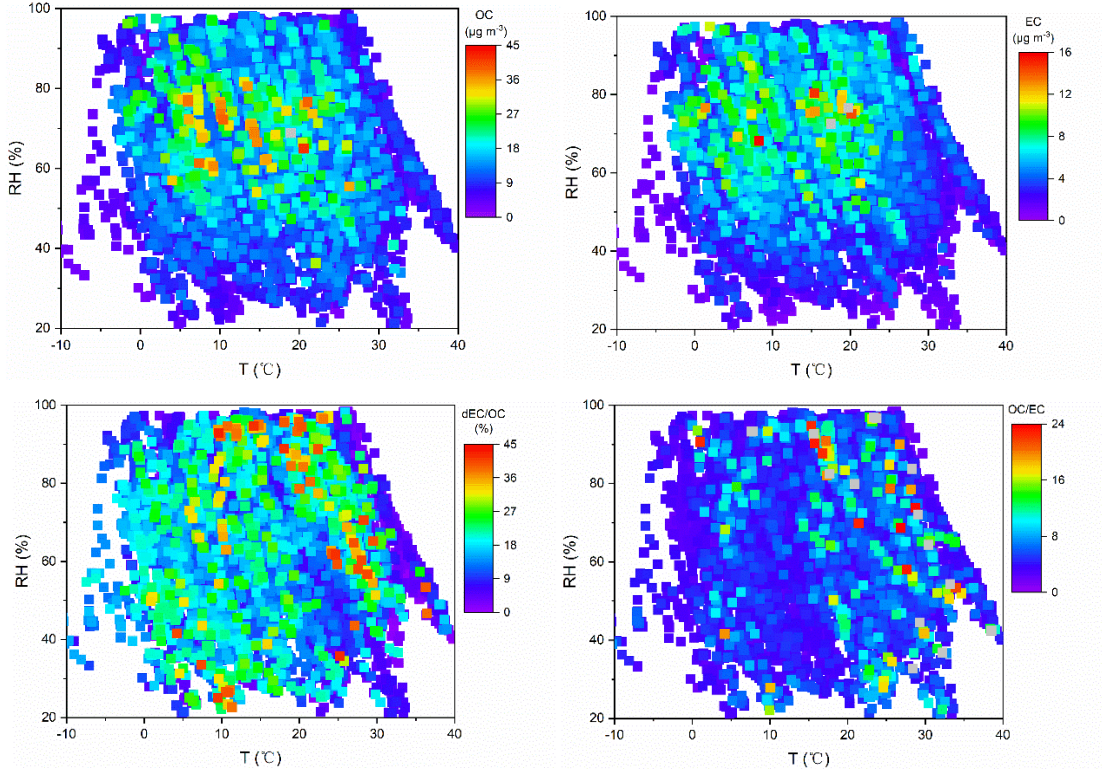
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Figure 6. Diurnal variations of OC, EC, dEC concentrations, dEC/OC and OC/EC ratios during the study period. The boundary of the shaded area indicates the 25% and 75% percentile, respectively. The red circle marks the average while the blue line marks the median.

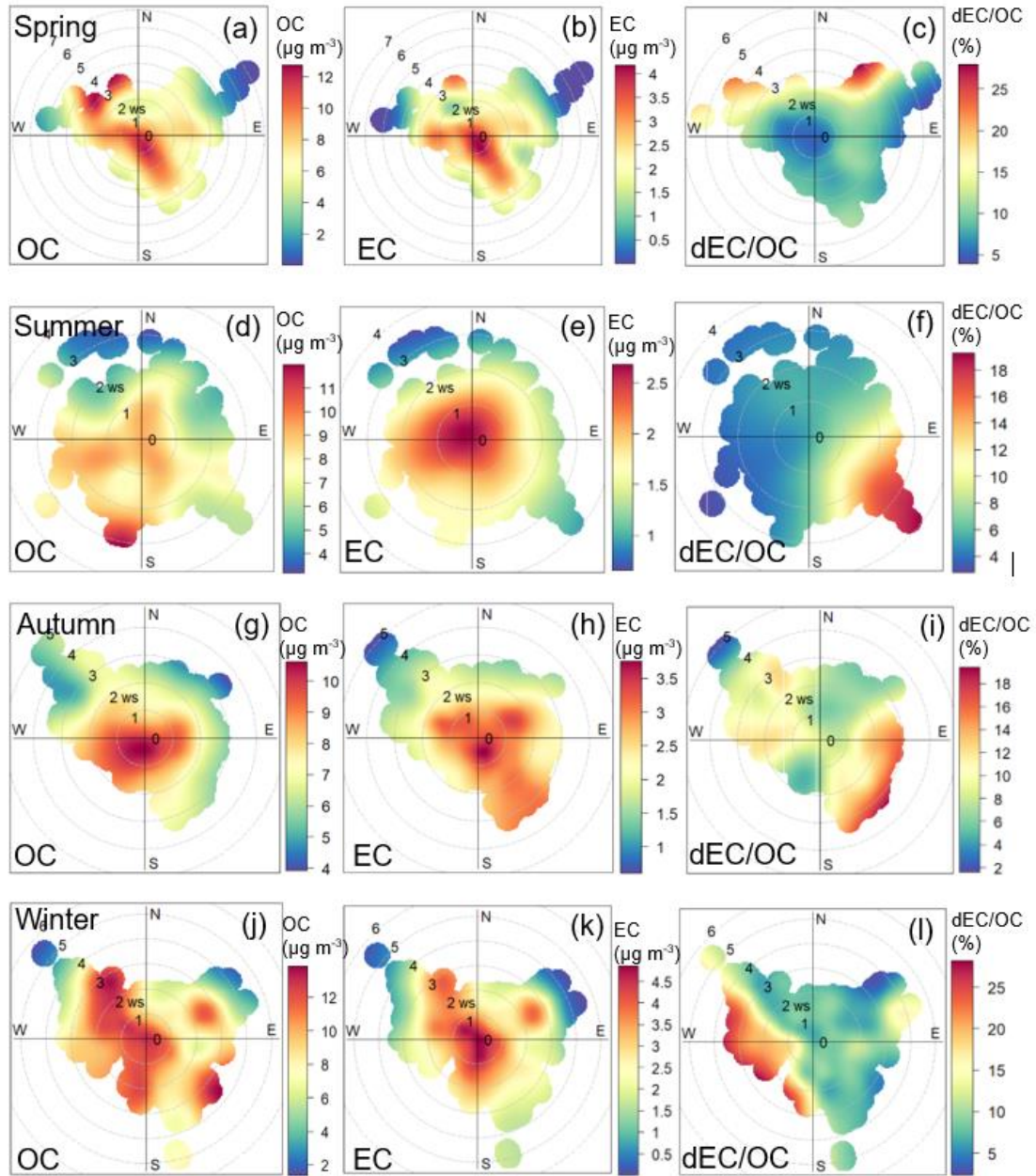


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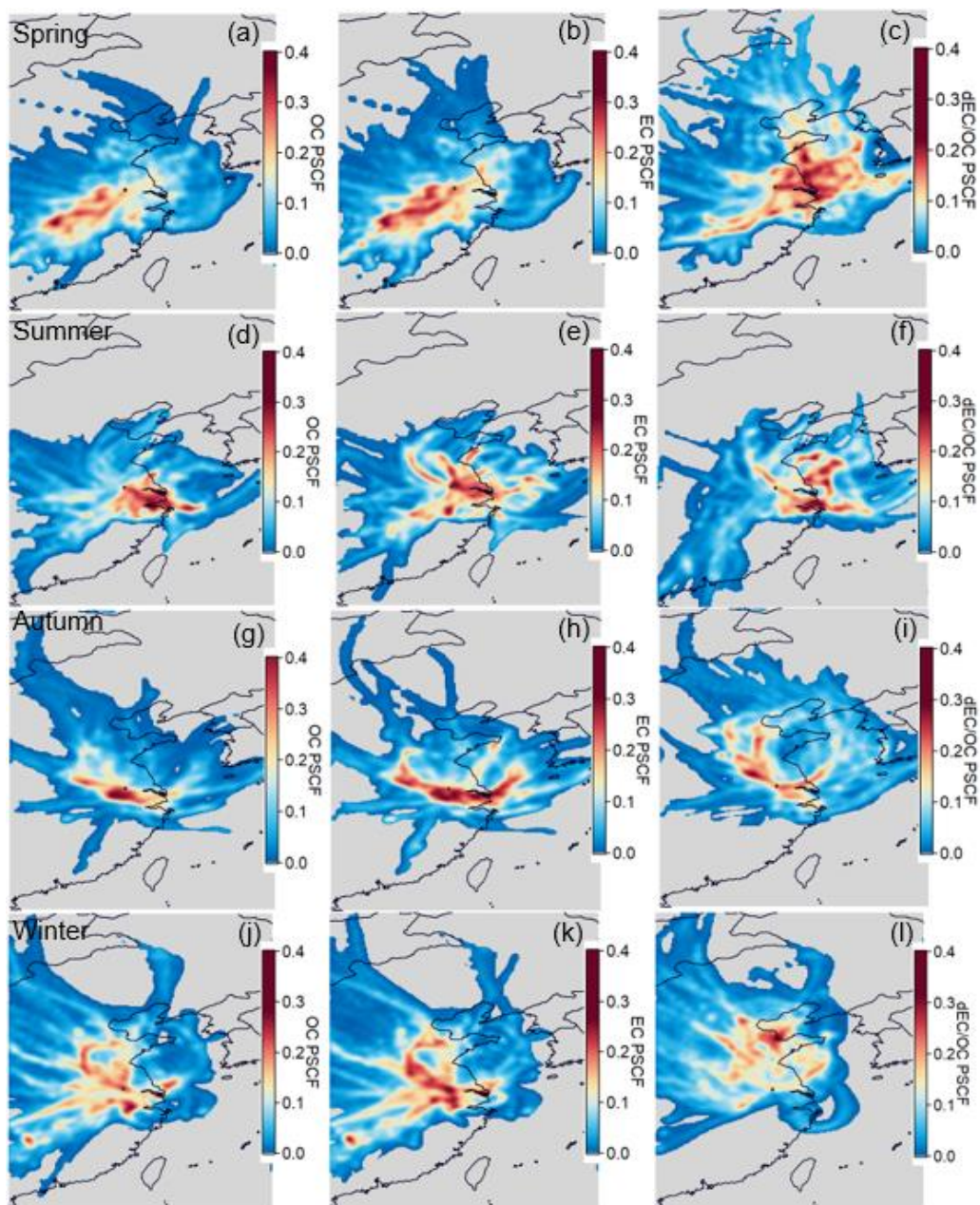
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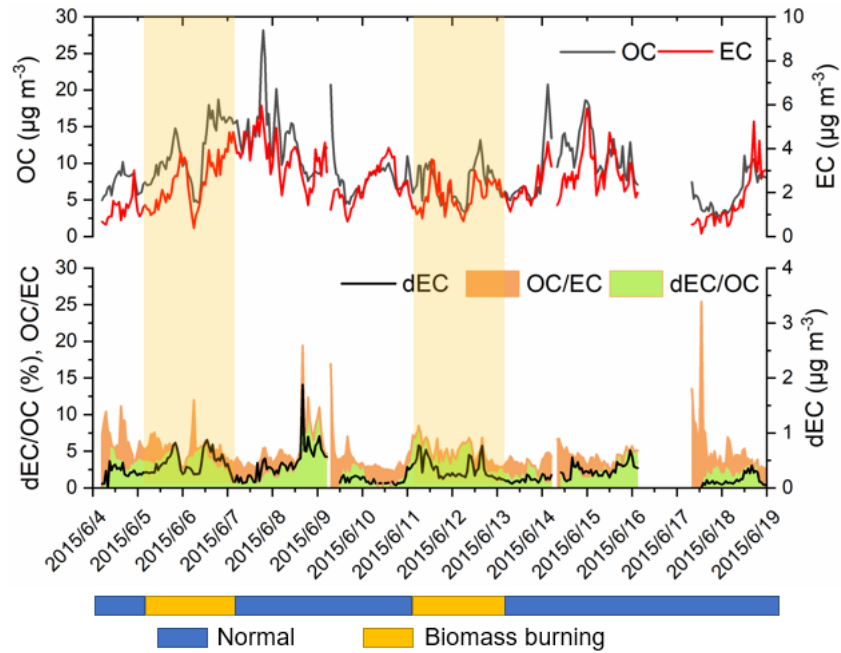
Figure 7. RH/T dependence of OC, EC, dEC/OC and OC/EC ratios during the study period.



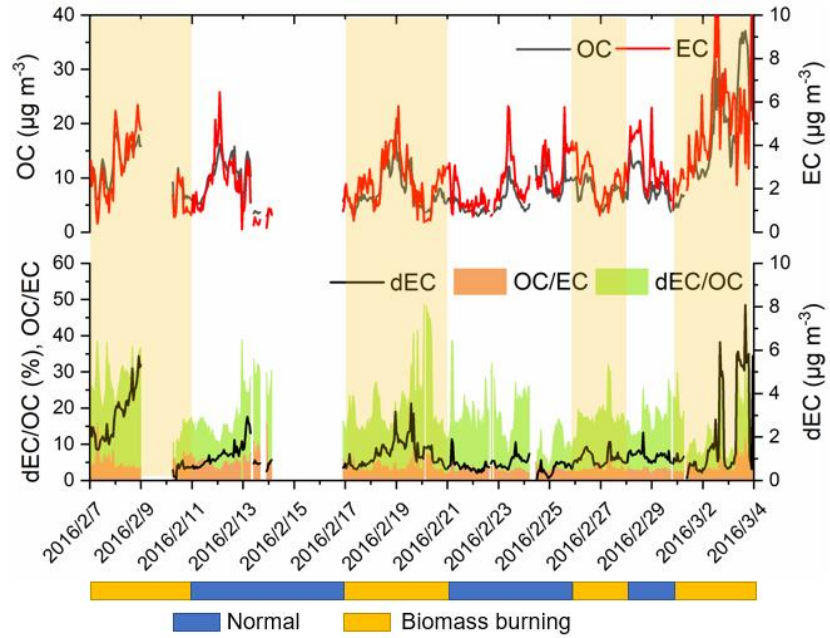
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 701 **Figure 8.** Wind rose of OC, EC and dEC/OC in spring ((a), (b), (c)), summer ((d), (e), (f)), autumn
 702 ((g), (h), (i)) and winter ((j), (k), (l)).



703
 704 **Figure 9.** PSCF map for OC, EC and dEC/OC in spring ((a), (b), (c)), summer ((d), (e), (f)), autumn
 705 (g), (h), (i)) and winter ((j), (k), (l)).



706
 707 **Figure 10.** Time series of OC, EC, dEC/OC, dEC and OC/ EC from 4 June 2015 to 19 June 2015.
 708 The period was divided into normal days (blue bars) and biomass burning days (yellow bars). The
 709 yellow shadow represents the biomass burning periods.



710
 711 **Figure 11.** Time series of OC, EC, dEC/OC, dEC and OC/ EC from 7 February 2016 to 3 March
 712 2016. The period was divided into normal days (blue bars) and biomass burning days (yellow bars).
 713 The yellow shadow represents the biomass burning periods.

714 **Table 1.** Statistical summary on the PM_{2.5} and carbon species concentrations.

N=5113	Annual					Spring	Summer	Autumn	winter
	Average	Standard Deviation	Median	Min	Max	Average	Average	Average	Average
PM _{2.5} (µg m ⁻³)	77.2	48.6	65.0	2.5	458.1	72.1	47.9	70.5	91.8
OC (µg m ⁻³)	8.9	5.5	7.5	0.5	45.8	8.4	7.2	8.4	10.2
EC (µg m ⁻³)	3.1	2.0	2.6	0.0	17.6	2.6	2.3	3.3	3.4
OC/EC	3.5	2.4	2.9	1.0	29.3	3.9	4.0	2.8	3.4
dEC (µg m ⁻³)	0.8	0.8	0.6	0.0	8.1	0.8	0.5	0.7	1.1
dEC/OC (%)	10.0	7.2	8.6	0.0	48.2	9.5	6.9	9.0	11.3
dEC/EC (%)	22.3	16.7	18.5	0.1	97.8	24.5	18.2	18.7	25.9
OC/PM _{2.5} (%)	12.8	5.6	11.6	0.7	66.2	13.2	14.4	14.1	11.1
EC/PM _{2.5} (%)	4.3	2.3	3.9	0.0	33.2	3.9	4.7	5.8	3.7
dEC/PM _{2.5} (%)	1.3	1.2	0.9	0.0	17.6	1.4	1.3	1.2	1.3

715

716 **Table 2.** Statistics of OC, EC, OC/EC, dEC and dEC/OC during biomass burning days and normal
 717 days. The values represent average±standard deviation.

		OC ($\mu\text{g m}^{-3}$)	EC ($\mu\text{g m}^{-3}$)	OC/EC	dEC ($\mu\text{g m}^{-3}$)	dEC/OC (%)
June 4 th to	Normal days	9.5±4.5	2.6±1.3	4.3±2.3	0.2±0.1	2.5±1.3
19 th	Biomass burning days	9.0±3.6	2.0±0.9	4.8±1.6	0.4±0.2	4.6±1.4
February	Normal days	7.5±3.3	2.5±1.2	3.3±1.3	0.8±0.3	12.7±5.6
7 th to	Biomass burning days	11.2±7.2	3.1±1.9	4.0±1.8	1.7±1.4	15.4±7.8
March 3 rd						

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