Technical note: Identification of chemical composition and source of fluorescent components in atmospheric water-soluble brown carbon by excitation-emission matrix with parallel factor analysis: Potential limitation and application

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Abstract

Three-dimensional excitation-emission matrix (EEM) fluorescence spectroscopy

is an important method for the identification of occurrences, chemical compositions,

and sources of atmospheric chromophores. However, current knowledge on the

identification and interpretation of fluorescent components is mainly based on

aquatic dissolved organic matter and might not be applicable to atmospheric samples.

Therefore, this study comprehensively investigated EEM data of different types of

strong light-absorbing organic compounds, water-soluble organic matter (WSOM) in

different aerosol samples (combustion source samples and ambient aerosols), soil

dust, and purified fulvic and humic acids supplemented by parallel factor

(PARAFAC) modelling. The results demonstrated that organic compounds with high

aromaticity and strong electron-donating groups generally present strong

fluorescence spectra at longer emission wavelengths, whereas organic compounds

substituted with electron-withdrawing groups have relatively weaker fluorescence

intensity. In particular, aromatic compounds containing nitro groups (i.e.,

nitrophenols), which show strong absorption and are the major component of

atmospheric brown carbon, exhibited no significant fluorescence. EEM-PARAFAC

identified three fluorescent components (i.e., C1, C2, and C3) in ambient WSOM.

Although EEM-PARAFAC derived C1 (235, 270/330 nm) in ambient WSOM is

generally considered as protein-like groups, our findings suggested that it is mainly

composed of aromatic acids, phenolic compounds, and their derivatives, with only

traces of amino acids. C2 is associated with the atmospheric chemical reaction of

biomass burning and/or biogenic organic molecules, with relatively lower degree of oxidation, which are more abundant in Guangzhou WSOM (56%-69%). Whereas, C3 is mainly attributed to highly oxygenated organic molecules derived from soil and atmospheric aging processes and has a relatively higher contribution in Chuzhou WSOM (23%). These findings provide new insights for the analysis of chemical properties and sources of atmospheric fluorophores using the EEM method.

1. Introduction

Water-soluble organic carbon (WSOC) constitutes a substantial fraction (10–80%) of organic aerosols in the atmosphere and is ubiquitous in ambient aerosols, clouds or fog, and rain water (Wozniak et al., 2012; Huang et al., 2022, Zhang et al., 2022a). Recent studies have highlighted that a portion of WSOC, termed brown carbon (BrC), can absorb light in the near-ultraviolet and visible ranges (Laskin et al., 2015, Frka et al., 2022; Ma et al., 2022). Owing to its strong light-absorption capacity, BrC can cause up to 45% solar radiation absorption by atmospheric aerosols and has potential effects on regional and even global climate (Zhang et al., 2013). In addition, BrC also participates in atmospheric photochemical reactions, affects the physicochemical properties of atmospheric aerosols (Laskin et al., 2015; Tang et al., 2020b), and potentially, can be activated to form reactive oxygen species that cause adverse effects on human health (Cao et al., 2021; Zhang et al., 2022b).

Excitation-emission matrix (EEM) fluorescence spectroscopy is a highly sensitive and widely used analytical technique for the identification of chemical

characteristics and sources of chromophores in dissolved organic matter (DOM) in

aquatic environments (Murphy et al., 2010, 2013; Zhang et al., 2014). Recently,

EEM has been further extended and frequently applied for the investigation of

water-soluble organic matter (WSOM), such as light-absorbing organic compounds

in atmospheric aerosols and fine particles from combustion processes (Chen et al.,

2020; Fan et al., 2016; Wu et al., 2020; Yang et al., 2022). For instance, humic-like

substances (HULIS) and protein-like substances (PRLIS) have been identified as

important fluorescent components in combustion-derived particles (Cao et al., 2021;

Tang et al., 2021) and ambient aerosols (Ma et al., 2022; Wu et al., 2020; Yang et al.,

2022). Chen et al. (2016) used EEM coupled with parallel factor analysis

(PARAFAC) and high-resolution mass spectrometry to identify chromophores in

ambient aerosols and proposed that fluorescent components with longer excitation

(Ex)/emission (Em) wavelengths comprise more highly oxygenated groups (Chen et

al., 2016a). In addition, further application of the EEM method has also revealed that

the concentration and types of fluorophores obviously vary during atmospheric

processes, such as photolytic aging of biomass burning (BB)-derived chromophores

(Aftab et al., 2018; Tang et al., 2020b). Therefore, the EEM method has significant

potential for the characterization (types, sources, and evolution) of atmospheric BrC.

However, application of the EEM method for the identification of atmospheric

BrC has some limitations. It is well known that the present identification,

classification, and interpretation of fluorescent components in atmospheric WSOM

are mainly based on the fluorescence peak position of DOM in aquatic environments

(Coble, 1996; Wünsch et al., 2019). Nonetheless, the chemical and molecular composition and source of WSOM in atmospheric aerosols significantly vary from those of DOM in aquatic environments (Graber and Rudich, 2006; Laskin et al., 2015); hence, the current fluorescence criterion derived from aquatic environments could lead to some inaccurate description of the fluorescent components in atmospheric WSOM. For instance, the EEM region at Ex/Em = 235(270)/330 nm is assigned to PRLIS and/or tryptophan-like substances in aquatic environments (Coble, 1996), but is also associated with non-nitrogen species such as polyphenols in atmospheric WSOM (Chen et al., 2016b). The EEM region at peak M (290–315/370–420 nm) is considered as a typical signal of marine-derived HULIS (Coble, 2007; Zhao et al., 2019), but the source of this peak should be cautiously investigated when interpreting BrC in continental aerosols. In addition, the intensities of fluorescent species are not always linearly correlated with their concentrations, which can be affected by the aromatic ring system and the number and types of functional groups, thereby leading to greater uncertainty in intensity measurements (Andrade-Eiroa et al., 2013; Chen et al., 2020; Wang et al., 2020). Atmospheric BrC is composed of complex organic molecules with different light absorption properties (Lin et al., 2020; Huang et al., 2021; Jiang et al., 2022), and only a subset of BrC molecules that contain functional groups are capable of fluorescence emission upon relaxation from an excited state (Andrade-Eiroa et al., 2013). Hence, interpretation of fluorescence data may only correspond to fluorescent chromophores and may not be representative of BrC as a whole (Chen et al., 2020;

107 Wang et al., 2020). All these factors limit further application of the EEM method for

108 the analysis of atmospheric BrC. Therefore, it is essential to investigate the

109 light-absorbing species that can be detected by EEM and obtain important

110 information for identifying the chemical compositions and possible sources of these

111 species.

112 Accordingly, in the present study, the EEM profiles of a series of BrC model

113 compounds and WSOM isolated from primary combustion samples, soils, and

114 atmospheric aerosols were investigated. The chemical characteristics and sources of

115 the main fluorophores were interpreted according to the fluorescence peaks location

116 and intensity, and the chemical structures of the model compounds and source

117 samples were analyzed. Then, atmospheric aerosols in Guangzhou (GZ) and

118 Chuzhou (CZ) cities were collected and fluorescent chromophores within the

119 water-soluble fraction were identified to estimate the application of the

120 EEM-PARAFAC method in characterizing atmospheric BrC. The results obtained

121 help to broaden the application of the EEM-PARAFAC method to study atmospheric

122 BrC.

123

124 **2. Materials and methods**

125 2.1. Materials

126 For accurate identification of the chemical composition and structures of

127 fluorophores in atmospheric BrC and for assessment of application of the EEM

128 method to examine atmospheric BrC, a total of 136 samples were investigated in this

study. The samples comprised: (1) 35 BrC model compounds, including phenolic

compounds, aromatic acids, nitroaromatic compounds (NACs), PRLIS,

N-heterocyclic compounds, and polycyclic aromatic hydrocarbons (PAHs) and their

derivatives (detailed information in Text S1.1 and Table S1 of supporting

information (SI)). These compounds are usually detected in ambient samples and

have been considered typical BrC model compounds (Frka et al., 2022, Lin et al.,

2016; 2017; Wang et al., 2017; Huang et al., 2021); (2) 13 primary combustion

source samples collected from BB, coal combustion (CC), and vehicle emission

(VE); (3) five soil samples obtained from the rural area of Guangdong Province,

China, with different vegetation, which is also an important source of atmospheric

BrC and has been widely identified in previous studies (Chen et al., 2020; Vasilatou

et al., 2017); (4) six purified fulvic and humic acids (FAs and HAs, respectively)

kindly provided by Professor Weilin Huang (Rutgers, The State University of New

Jersey, NJ, USA); and (5) 34 diurnal fine particulate matter ($PM_{2.5}$) samples

collected from 6 to 22 April, 2021 at GZ and CZ, respectively. In addition, 43 annual

$PM_{2.5}$ samples were collected from February 2018 to January 2019 at the GZ site and

classified as wet and dry season atmospheric $PM_{2.5}$ samples (for detailed information,

see Text S1 of SI). Field blank samples were collected without instrument power on

during each sampling period.

2.2. Standard solution and aqueous extraction of ambient samples

Solutions of model organic compounds were prepared by dissolving a certain

151 amount of dried solid or liquid samples in Milli-Q water or methanol. The ambient

152 aerosol and soil samples were ultrasonically extracted with ultrapure water three

153 times, and the supernatants were filtered using a 0.22-μm PTFE syringe filter to

154 isolate the WSOM. The specific separation and purification methods have been

155 published in previous studies (Chen et al., 2020; Fu et al., 2015; Wang et al., 2020;

156 Yan and Kim, 2017) and are presented in the SI (Test S2).

157

2.3. EEM-PARAFAC analysis

159 The EEM fluorescence spectra of the aqueous extraction of the samples in 1-cm

160 quartz cuvettes were recorded using a three-dimensional fluorescence

161 spectrophotometer (Aqualog; HORIBA Scientific, USA) at room temperature. The

162 scanning ranges for Ex and Em were 200–500 and 250–550 nm, respectively. The

163 wavelength increment of the Ex and Em scans was 5 nm, the integration time was

164 0.5 s, and Milli-Q water (18.2 MΩ cm) used as blank reference. The absorbance

165 measurements were used to correct the EEM for inner filter effects (IFEs) as

166 described previously (Fu et al., 2015) if the absorbance was > 0.05 at 250 nm

167 (Murphy et al., 2013; Tang et al., 2020a). Background samples were also analyzed

168 and the background values were subtracted from the values obtained for all the

169 samples. To avoid concentration effects, the fluorescence spectra were normalized by

170 the water Raman area to produce Raman unit (R.U.) and further by the organic

171 carbon concentration of the samples to the normalized fluorescence intensities

172 (R.U./(mg C/L)) (Yang et al., 2022) are shown in Table S2.

173   The PARAFAC modelling procedure was conducted for 77 atmospheric WSOM

174   samples in MATLAB 2014b (Mathwork.Inc, USA) using the drEEM toolkit

175   (Murphy et al., 2018; Wünsch et al., 2019). PARAFAC was computed using two to

176   nine component models, with non-negativity constraints and residual analysis, and

177   split-half analysis was employed to validate the number of fluorescent components.

178   Based on the results of the split-half and core consistency analyses, three-component

179   models were chosen for further investigation. The relative contribution of individual

180   chromophores was estimated by calculating the maximum fluorescence intensities

181   (F_{max}: maximum fluorescence intensity of the identified fluorescent components;

182   relative content (%) = $F_{max}/\Sigma F_{max}$) (Chen et al., 2020; Fan et al., 2020).

183

184   **3. Results and discussion**

185   **3.1. Fluorescence properties of BrC model compounds**

186   To identify whether the light-absorbing species possess fluorescence, a series of

187   BrC model compounds were tested by the EEM method, and the fluorescence

188   profiles are shown in Fig. S1. The results revealed that the location and intensity of

189   the fluorescence peaks of different compounds were different, which varied with the

190   distinct functional groups and aromatic conjugate system.

191   Although phenolic compounds are important light-absorbing species in

192   atmospheric BrC (Smith et al., 2016; Yu et al., 2014, 2016), not all of them exhibit

193   strong fluorescence. As shown in Fig. S1a, a strong fluorescence peak in the EEM

194   spectrum of phenol was observed at Ex/Em = 270/295 nm. When the phenol

195   compounds were substituted with electron-donating groups (e.g., hydroxyl), all of

196   the stronger fluorescence peaks were obviously red-shifted to 310–320 nm (e.g.,

197   catechol, hydroquinone, and 2-methoxyphenol). However, phenolic compounds

198   substituted with electron-withdrawing groups (e.g., carboxyl and aldehyde)

199   displayed weaker or even no fluorescence (Fig. S1a). These differences could be due

200   to the ability of the electron-donating groups to form a larger conjugate system

201   coupled with the benzene ring and decrease the $\pi \rightarrow \pi^*$ transition energy, thus leading

202   to an increase in the Em wavelength (i.e., red shift) and variation in fluorescence

203   intensity (Chen et al., 2002; Andrade-Eiroa et al., 2013). In contrast, the

204   electron-withdrawing group can reduce the conjugated structure formed by the

205   benzene   ring   and   hydroxyl   group,   reducing   the   fluorescence   intensity

206   (Andrade-Eiroa et al., 2010; Andrade-Eiroa et al., 2013).

207   Aromatic acid and its derivatives are also important light-absorbing organic

208   compounds in atmospheric BrC. Owing to the negative effects of the carboxyl group,

209   a weak fluorescence peak (275/315 nm) was identified for benzoic acid, and no

210   fluorescence was detected for benzene polycarboxylic acids, such as phthalic acid,

211   terephthalic acid, and trimesic acid (Fig. S1b). However, when benzoic acid was

212   substituted with electron-donating groups (e.g., hydroxyl, methoxy), higher intensity

213   fluorescence peaks were observed. Two strong fluorescence peaks at 230/405 and

214   290/405 nm were identified for 2-hydroxybenzoic acid substituted with only one

215   hydroxyl group. These peaks could have been the result of the ortho structure of the

216   hydroxy and carboxyl groups, which is favorable for the formation of intramolecular

217 hydrogen bonds and generates a double-ring conjugate structure, reducing the

218 transition energy and thereby presenting strong UV absorption and fluorescence

219 (Andrade-Eiroa et al., 2013).

220   N-containing compounds, especially NACs, have strong light absorption, and

221 have been reported to be the major components of atmospheric BrC, accounting for

222 more than 60% of the total light absorption intensity at 300–500 nm (Huang et al.,

223 2021; Lin et al., 2016; Lin et al., 2017; Wang et al., 2017; Frka et al, 2022). However,

224 most of the NACs did not exhibit any fluorescence (Fig. S1c), similar to that

225 reported in a previous study by Chen et al. (2020), which could be due to the

226 significant reduction in the electron density of the benzene ring by the nitro ($-NO_2$)

227 group—strong electron-withdrawing group—thereby weakening the fluorescence.

228   Tryptophan and tyrosine are the two most studied PRLIS species, and their

229 EEM spectra are generally used as standards for comparison with fluorophores in

230 atmospheric WSOM (Matos et al., 2015; Qin et al., 2018). As shown in Fig. S1d, the

231 Ex/Em peaks at 275/300 and 275/350 nm corresponded to tyrosine and tryptophan,

232 respectively. The maximum Em wavelength of phenylalanine was more inclined to

233 short wavelength (280 nm) and with much weaker fluorescence intensity. Moreover,

234 the fluorescence peaks of PRLIS obviously overlapped with those of phenols and

235 aromatic acids (Fig. S1a, b). It must be noted that the concentrations of phenols and

236 aromatic acids were significantly higher than those of tryptophan and tyrosine in the

237 atmospheric samples (Table S2); therefore, the aerosol BrC fluorophores in these

238 regions are more likely to have originated from phenols and aromatic acids rather

239 than PRLIS.

240 N-heterocyclic compounds such as pyrrole, pyridine, and imidazole are

241 commonly identified in atmospheric samples (Dou et al., 2015; Jiang et al., 2019;

242 Kosyakov et al., 2020). However, no fluorescence was observed for these three

243 species in the present study, indicating that the absorbed energy may have been

244 consumed by relaxation or vibration (Fig. S1e). Nevertheless,

245 imidazole-2-formaldehyde produced two strong fluorescence peaks at 290/440 and

246 350/440 nm, formed from the oxidation of imidazole, suggesting that some

247 N-heterocyclic compounds from secondary reactions may exhibit strong

248 fluorescence at higher wavelength in atmospheric BrC (Ackendorf et al., 2017).

249 PAHs and their derivatives are mainly formed from incomplete combustion

250 processes and are important components of BrC (Chen et al., 2020; Lin et al., 2017;

251 Mahamuni et al., 2020). As shown in Fig. S1f, all PAHs exhibited strong

252 fluorescence emission, with its peak location associated with the conjugated

253 aromatic system. Naphthalene presented a fluorescence band located at the

254 maximum Em wavelength of approximately 325 nm. As expected, with the

255 increasing size of the π-bond system and degree of conjugation, the fluorescence

256 band moved toward the longer wavelength range, and a new Em band was observed

257 at 360–390 nm for 3–4-ring phenanthrene and pyrene, and at 400–500 nm for ≥

258 5-ring PAHs (Mahamuni et al., 2020). The fluorescence spectra of high-ring PAHs

259 were more complex because of more types of double bonds. As shown in Fig. S1f,

260 the intensity and location of the fluorescence peaks were also significantly changed

261 when different types of groups were substituted with PAHs. For example, 1-naphthol

262 exhibited a stronger EEM peak at a relatively longer wavelength (230, 290/460 nm)

263 owing to its highly conjugated structure, when compared with naphthalene. This

264 EEM spectrum was located in the EEM region of FAs, implying that FAs are

265 composed of aromatic units and O-containing groups. In contrast, relatively weaker

266 fluorescence was observed for 9-fluorenone, anthraquinone, and

267 2-naphthalenecarboxylic acid, and no EEM signals were observed for

268 2-nitronaphthol (Fig. S1c), which was substituted with a strong

269 electron-withdrawing group ($-NO_2$).

270

271 **3.2. Fluorescence properties of BrC from different sources**

272 As shown in Fig. S4a and S4b, BB and CC WSOM exhibited similar

273 fluorescence spectra (Tang et al., 2020a; Chen et al., 2020; Yang et al., 2022), with

274 two types of fluorescence peaks at Ex/Em ≈ (230–240)/(340–400) nm (peak A) and

275 Ex/Em ≈ (260–280)/(330–360) nm (peak B), respectively. The two fluorescence

276 peaks were similar to those previously reported for BB WSOM and HULIS (Fan et

277 al., 2020; Tang et al., 2020a; Yang et al., 2022). In general, peak A mainly

278 corresponds to the protein-like UV region, with a minor contribution from fulvic-like

279 substances, whereas peak B could be attributed to tryptophan-like fluorophores.

280 However, based on the results of the present study, these two peaks could be mainly

281 attributed to aromatic species such as aromatic acids, phenolic compounds, and

282 minor quantities of PAHs (e.g., naphthalene) (Fig. 1). The fluorescence spectra of

283 WSOM from two types of vehicles (diesel and gasoline) also presented two

284 fluorophores. A relatively strong fluorescence peak was observed at the low Ex

285 wavelength (Ex/Em ≈ 230/350 nm) and a relatively weaker peak was detected at the

286 high Ex wavelength (Ex/Em ≈ 270/350 nm) (Fig. S4c). These results are consistent

287 with those reported in previous studies on VE (Chen et al., 2020; Tang et al., 2020a;

288 Yang et al., 2022) and similar to the EEM fluorescence spectra of BB and CC

289 WSOM (Chen et al., 2020; Fan et al., 2020; Cao et al., 2021; Yang et al., 2022).

290 However, the fluorescence ranges of vehicle WSOM were obviously narrower,

291 suggesting that BB and CC WSOM fluorescent components are more complex.

292 Soil-derived DOM is also a primary source of atmospheric WSOM. As shown

293 in Fig. S5a, two main fluorescence peaks located at Ex/Em = 230/430 and 320/430

294 nm, were detected in the fluorescence spectra of soil DOM, which are similar to

295 those reported in previous studies (Ge et al., 2021; Liu et al., 2009) and particularly

296 close to the position of FAs (Fig. S5b).

297 Secondary chemical formation is another important source of atmospheric

298 WSOM. For example, the aqueous-phase reactions of aldehydes with ammonium

299 sulfate (AS) can produce highly fluorescent species (Hawkins et al., 2016). The

300 Glyoxal-AS and glyoxal/glycine reaction products fluoresces at 340/450 nm,

301 whereas formaldehyde-AS reaction product fluoresce at 250/430 nm. Secondary

302 organic aerosols (SOAs) produced in the limonene/O_3 system have been reported to

303 strongly fluoresce in the presence of NH_3 (Bones et al., 2010). In addition, aging of

304 primary organic compounds has also been found to change the fluorescence spectra

305 (Lee et al., 2013; Li et al., 2021; Powelson et al., 2014). For instance, aging of

306 syringic acid with OH radicals caused the initial fluorescence band to move toward

307 the long wavelength range, producing a new band at a broad Em band at 400–600

308 nm. Similarly, the fluorescence peaks red-shifted (e.g., from 260–270/360 nm to

309 280–290/390–400 nm) during the O_3 aging process (Fan et al., 2020), suggesting the

310 degradation of the initial compound and formation of new secondary organic

311 compounds generally located at longer wavelengths, possibly with a high degree of

312 aromaticity or highly oxidized functional groups (Chen et al., 2016a; Vidović et al.,

313 2019, 2020; Powelson et al., 2014; Vione et al., 2019; Yu et al., 2016).

314

315 **3.3. Identification of chemical species and potential sources of fluorescent**

316 **components in ambient aerosols**

317 The typical EEM spectra of atmospheric water-soluble light-absorbing

318 compounds are shown in Fig. 2. Three fluorescence peaks were identified in the

319 aerosol WSOM samples: a stronger fluorescence peak at Ex/Em = 230–250/360–420

320 nm, and two relatively weaker fluorescence peaks at Ex/Em = 270–290/340–370 nm

321 and 300–320/360–420 nm. Similar fluorescence bands have been previously

322 identified in the EEM fluorescence spectra of WSOM from $PM_{2.5}$ in the cold and

323 warm seasons in Aveiro, Portugal (Matos et al., 2015), the High Arctic atmosphere

324 (Fu et al., 2015), Godavari, Nepal (Wu et al., 2019), Lanzhou and Xi'an,

325 northwestern China (Qin et al., 2018; Chen et al., 2020), Chongqing, southwestern

326 China (Wang et al., 2020), and Harbin, northeastern China (Ma et al., 2022).

327 Although the fluorescence intensities varied with different sites and seasons, the

328 shapes of the EEM spectra of WSOM were very similar, making it difficult to

329 directly distinguish the different samples solely based on the characteristics of the

330 EEM profiles. Therefore, a more powerful protocol named the PARAFAC method

331 was employed to identify the individual fluorophores in ambient WSOM.

332

3.3.1. Identification and quantification of fluorescent components by the PARAFAC method

335 As shown in Fig. 3, three fluorescent components (C1, C2, and C3) were

336 identified in the atmospheric samples; C1 occurred at a relatively lower Em

337 wavelength, exhibiting two fluorescence peaks at Ex/Em = 235(270)/330 nm, C2

338 presented fluorescence peaks at around Ex/Em = 235(320)/390 nm, and C3 had a

339 longer Em wavelength than C1 and C2, which was located at Ex/Em = about

340 250(355)/455 nm. In general, these fluorescent components have been interpreted

341 based on knowledge of the fluorescence characteristics of aquatic DOM.

342 Accordingly, C1 is considered to belong to the typical PRLIS (Coble, 1996; Wünsch

343 et al., 2019), C2 is associated with fulvic-like substances or less-oxygenated HULIS

344 (Liu et al., 2009; Zhang et al., 2014), and C3 is usually considered to correspond to

345 terrestrial HULIS that are highly oxygenated organic matter (Table S3) (Liu et al.,

346 2009; Wünsch et al., 2019; Zhou et al., 2017). However, it must be noted that the

347 sources and transformation process are significantly different for WSOM in aerosols

348 and DOM in aquatic and terrestrial environments; therefore, the fluorescence

349   classifications of DOM might not be applicable to atmospheric WSOM.

350   In general, the Ex and Em wavelengths of fluorescent components are mainly

351   associated with their chemical characteristics and structures (Table S1 and Fig. 1). In

352   the present study, C1 was similar to tryptophan-like fluorophores associated with

353   PRLIS in rainwater (Zhang et al., 2014; Zhou et al., 2017) and fog water (Bianco et

354   al., 2014; Bianco et al., 2016). However, this fluorophore might also be related to

355   small molecular aromatic compounds, such as aromatic acids (e.g.,

356   3,5-dihydroxybenzoic acid and 2-naphthalenecarboxylic acid) and PAHs (e.g.,

357   naphthalene, phenanthrene, and anthraquinone) (Fig. 1a) (Miyakawa et al., 2015; Wu

358   et al., 2019). In addition, this fluorophore could also contain traces of some phenolic

359   compounds, including catechol, hydroquinone, and 2-methoxyphenol. These organic

360   species might be generated by various types of combustion processes and

361   atmospheric oxidation reactions. It must be noted that investigations of the

362   fluorescent components in atmospheric WSOM should not only consider their

363   position in the fluorescence spectrum, but also their concentration and possibility of

364   trapping. Many previous studies have reported that the concentration of amino acids

365   in atmospheric aerosols is almost negligible, when compared with that of lower

366   molecular weight aromatic compounds such as aromatic acids and phenolic

367   compounds (Table S2) (Bianco et al., 2016; Song et al., 2017; Vione et al., 2019;

368   Mahamuni et al., 2020; and references therein). Therefore, fluorescent components

369   in this Ex/Em region could be attributed to small molecular aromatic species (e.g,

370   aromatic acids, phenolic compounds) rather than PRLIS. Moreover, this fluorophore

371 overlapped with that of WSOM from combustion process such as BB, CC, and VE

372 (Fig. 1b), suggesting significant contribution of the combustion process.

373 When compared with C1, C2 exhibited a strong fluorescence peak at longer

374 Ex/Em wavelength of 235(320)/390 nm, implying that this fluorescent component

375 presented a relatively larger molecular size and higher aromaticity than C1 (Pöhlker

376 et al., 2012). As shown in Fig. 1a, the fluorescence of C2 is similar to that of

377 aromatic compounds (e.g., 2-naphthalenecarboxylic acid, 2-hydroxybenzoic acid,

378 anthraquinone) and high-ring PAHs (e.g., pyrene, anthraquinone, anthracene,

379 chrysene) (Mahamuni et al., 2020), and overlaps with the fluorescence spectra of

380 FAs. In addition, this fluorophore has also been reported to be related to the

381 generation of SOAs from organic precursors emitted from biological/anthropogenic

382 emission and combustion processes (Wang et al., 2020). For example, the

383 aqueous-phase reactions of aldehydes with AS have been proposed as an important

384 source of atmospheric BrC, which present similar fluorescence spectral profiles

385 (Hawkins et al., 2016; Lee et al., 2013) (Fig. 1b). In addition, oxidative

386 oligomerization of phenols and their derivatives can also shift the Ex/Em wavelength

387 of these substances to longer wavelengths, falling into similar fluorescence regions

388 (Li et al., 2021; Tang et al., 2020a; Vione et al., 2019). As suggested by Chen et al.

389 (2016a), this fluorescent component may be a less-oxygenated fluorescent group

390 contributed by biomass combustion. Therefore, fluorophore C2 might be related to

391 the derivatives of biomass burning and/or biogenic molecules, with relatively lower

392 degree of oxidation (Chen et al., 2016a; Jiang et al., 2022).

393   C3 presented a longer Em wavelength than C1 and C2, with two peaks at

394   around Ex/Em=250/455 nm and 355/455 nm (Fig. 3). This fluorescent component

395   overlaps with the fluorescence of high-ring PAHs and their derivatives, such as

396   fluoranthene,   benzo-b-fluoranthene,   benzo-a-pyrene,   indeno-123cd-pyrene,

397   1-naphthol, and N-heterocyclic compounds, including imidazole-2-formaldehyde

398   (Chen et al., 2020; Mahamuni et al., 2020). Furthermore, this fluorescent component

399   exhibited a similar Ex/Em wavelength to that of FAs and HAs (Fig. S5b), suggesting

400   the possible contribution of soil dust, and thus could be assigned as HULIS (Lin and

401   Guo, 2020). Similar fluorescent substances have also been identified in the study of

402   atmospheric aerosol fluorescent chromophores, such as the highly oxygenated

403   HULIS in Nagoya, Japan (Chen et al., 2016a), Lanzhou, China (Qin et al., 2018),

404   Xi'an, China (Chen et al., 2020), a haze event in Harbin (Ma et al., 2022), and

405   humic-like compounds with more aromatic and unsaturated bonds in Godavari,

406   Nepal (Wu et al., 2019) and Tianjin, China(Deng et al., 2022). Based on the

407   PARAFAC results with aerosol mass spectrometry data, C3 was considered to be a

408   fluorescent group with high oxygen content and high O/C ratio, close to that of aged

409   organic aerosols (Chen et al., 2016a; Jiang et al., 2022) (Fig. 1b). It must be noted

410   that low molecular weight organic compounds can further undergo oligomerization

411   to high molecular weight species with long Em wavelengths during the aging

412   process (Hawkins et al., 2016; Li et al., 2021; Tang et al., 2020b; Yu et al., 2016).

413   The resulting compounds may present a more complex structure than their precursor,

414   probably owing to the presence of condensed aromatic rings and other π-electron

415 systems with a high level of conjugation; thus, atmospheric aging is assumed to be a

416 potential contributor to C3 (Barsotti et al., 2016; De Laurentiis et al., 2013; Hawkins

417 et al., 2016).

418

419 **3.3.2. Spatial and seasonal variations in fluorescent components in WSOM**

420 The relative contributions of C1, C2, and C3 components to the total

421 fluorescence intensities ($F_{max}/\sum F_{max}$) were calculated (Fig. 4), and were found to be

422 similar for WSOM from CZ and GZ, exhibiting maximum C2 content and relatively

423 lower C1 and C3 contents. Furthermore, WSOM samples showed obvious spatial

424 and seasonal variations, similar to the results reported in other regions in China

425 (Zhang et al., 2022a, 2022b). First, CZ WSOM presented a relatively higher C3

426 content ($23\pm4\%$) than GZ WSOM ($17\pm3\%$), whereas GZ WSOM had a relatively

427 higher C2 content ($56\pm7\%$) than CZ WSOM ($49\pm4\%$) during the same sampling

428 period. Such differences in the composition of fluorescent components may be

429 ascribed to the variation in the primary emission sources and atmospheric aging

430 process at the two sites. The relatively higher C3 content in the CZ could be

431 attributed to the comparatively high contribution of soil dust in the suburban region,

432 which is consistent with the relatively higher Ca^{2+} contents in the CZ $PM_{2.5}$

433 ($1.8\pm1.2\%$) than in the GZ $PM_{2.5}$ ($1.5\pm0.8\%$) (Vasilatou et al., 2017; Wu et al., 2019).

434 In contrast, the relatively higher C2 content in GZ WSOM may be attributed to the

435 comparatively stronger atmospheric chemical reaction associated with bio-volatile

436 organic compounds (bio-VOCs) in the hot and humid region of GZ. This result was

437   consistent with the relatively higher humification index (HIX) and normalized

438   fluorescence volume (NFV) values (log(NFV)) of CZ WSOM (Fig. S6) (Chen et al.,

439   2020; Yang et al., 2022).

440   In addition, the resolved Ex and Em spectra for GZ WSOM were also similar in

441   different seasons, implying that the types of fluorophores contributing to WSOM

442   were predominantly the same throughout the year. However, the compositions of

443   fluorescent components varied in different seasons. In the dry season (October–

444   March), WSOM showed relatively higher contents of C3 fluorophores (17±4%),

445   whereas in the wet season (April–September), slightly higher contents of C2

446   fluorophores (69±4%) were detected (Fig. 4) (Chen et al., 2020; Wang et al., 2020).

447   These differences might be associated with the variations in the source composition

448   and aging effects of BrC in different seasons. The higher content of C3 in WSOM in

449   the dry season suggested the occurrence of more highly aromatic and highly

450   oxidized compounds. These results could be explained by the fact that more aged

451   organic aerosols and dust were transported from the northern region of China (Jiang

452   et al., 2021). In contrast, the slightly higher C2 content in the wet season may be

453   attributed to the relatively stronger secondary formation of bio-SOAs and

454   photodegradation effects in the high-temperature and relative humidity season.

455

456   **4. Conclusion and future prospects**

457   In this study, the fluorescence properties of BrC model compounds were

458   investigated to determine the chromophoric species that can be evaluated by the

459   EEM method. Accordingly, the aerosol WSOM samples at two sites (CZ and GZ)

460   were investigated by the EEM-PARAFAC method, and the chemical characteristics

461   and potential sources of fluorescent components were examined. The main

462   conclusions and future prospects are as follows:

463   (1) Fluorescent components have predominantly been evaluated based on the

464   knowledge of fluorophores in aquatic DOM, which often leads to misinterpretation.

465   In the present study, the chemical characteristics of fluorophores in different Ex/Em

466   regions were discussed based on the fluorescence properties of BrC model

467   compounds and their amounts in aerosols. In particular, the C1 fluorophore in

468   atmospheric WSOM, which has been frequently assigned to PRLIS because of the

469   similarity in fluorescence spectra, was demonstrated to mainly include aromatic

470   acids, phenolic compounds, and their derivatives, with negligible amounts of amino

471   acids.

472   (2) The fluorescence properties of target compounds are mainly influenced by

473   the aromatic system and characteristics of adjacent functional groups. Organic

474   compounds with high aromaticity and strong electron-donating groups (e.g.,

475   hydroxyl, methoxyl) generally exhibited strong fluorescence spectra at longer Em

476   wavelengths, whereas organic compounds substituted with electron-withdrawing

477   groups presented relatively weaker fluorescence intensities. In particular, aromatic

478   compounds containing nitro groups (i.e., nitrophenols) showed strong absorption and

479   were the major component of atmospheric BrC; however, they did not exhibit

480   significant fluorescene. Thus, the fluorescence method could only measure a subset

481   of chromophores in aerosol BrC and should be used with caution for the

482   investigation of aerosol BrC.

483   (3) The EEM spectra for aerosol WSOM were very similar; however, the

484   relative contents of certain fluorescent components significantly varied with the

485   sampling site and season. For example, more fluorescent components associated

486   with soil and secondary oxidation of small molecular compounds from combustion

487   emission were identified in CZ WSOM, whereas more fluorescent components

488   derived from atmospheric chemical reaction of bio-VOCs were observed in GZ

489   WSOM. In addition, GZ WSOM exhibited more highly aromatic and highly

490   oxidized compounds in the dry season.

491   Although many studies have applied the EEM-PARAFAC method to investigate

492   atmospheric WSOM and have obtained useful data, there are still challenges and

493   gaps that must be addressed. First, caution should be taken for credible

494   interpretations of the fluorescent components in atmospheric WSOM because of the

495   differences in chemical characteristics of organic matter derived from different

496   sources. In addition, the same fluorophores may exhibit different Ex/Em ranges and

497   intensities in different environmental conditions (e.g., pH, coexisting metal ions and

498   inorganic salts). Therefore, more theoretical and experimental studies are necessary

499   to understand the relationship between the fluorescent groups and positions of

500   fluorescence peaks, as well as the influences of sources and chemical formation

501   process of the fluorescent groups on fluorescence peaks.

502

Data availability

The research data can be accessed in the Harvard Dataverse (https://doi.org/10.7910/DVN/ULCIU9, Song, 2022)

Author contributions. J. Song designed the research. T. Cao and C. Xu, analyzed the model compounds and WSOM samples by UV-Vis and EEM. T. Cao and X. Fan resolved the EEM by PARAFAC tool. M. Li carried out the $PM_{2.5}$ sampling experiments. T. Cao and J. Song wrote the paper. J. Li, W. Jia, and P. Peng commented and revised the paper.

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

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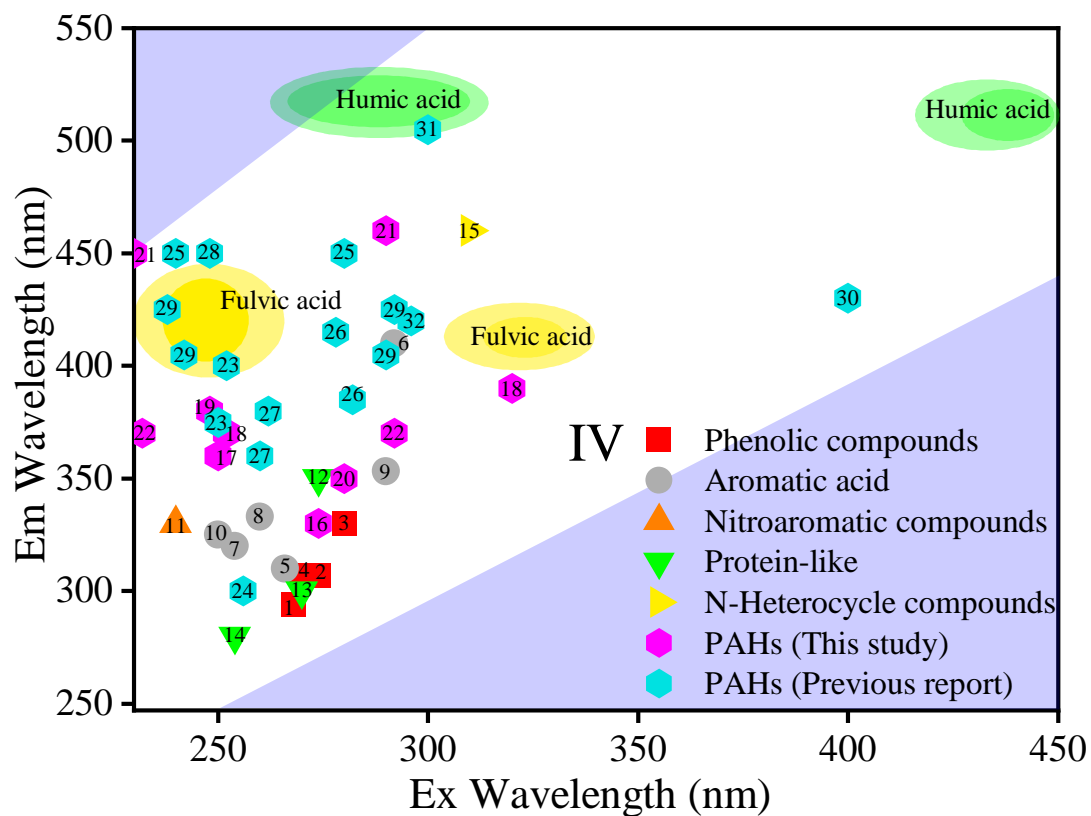
(a)

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4: 2-Methoxyphenol	5: Benzoic acid	6: 2-Hydroxybenzoic acid
7: 4-Hydroxybenzoic acid	8: 4-Hydroxy-3, 5-dimethoxybenzoic acid	9: 3, 5-Dihydroxybenzoic acid
10: Vanillic acid	11: 4-Nitrocatechol	12: DL-Tryptophan
13: DL-Tryosine	14: Phenylalanine	15: midazole-2-formaldehyde
16: Naphthalene	17: Phenanthrene	18: Pyrene
19: Anthraquinone	20: 9-Fluorenone	21: 1-Naphthol
22:2-Napphthalenecarboxy lic acid	23: Anthracene	24: Fluorene
25: Fluoranthene	26: Benzo-a-Anthracene	27: Chrysene
28: Benzo-b-Fluoranthene	29: Benzo-k-Fluoranthene	30: Perylene
31: Indeno-123cd-Pyrene	32: Benzo-ghi-Perylene	

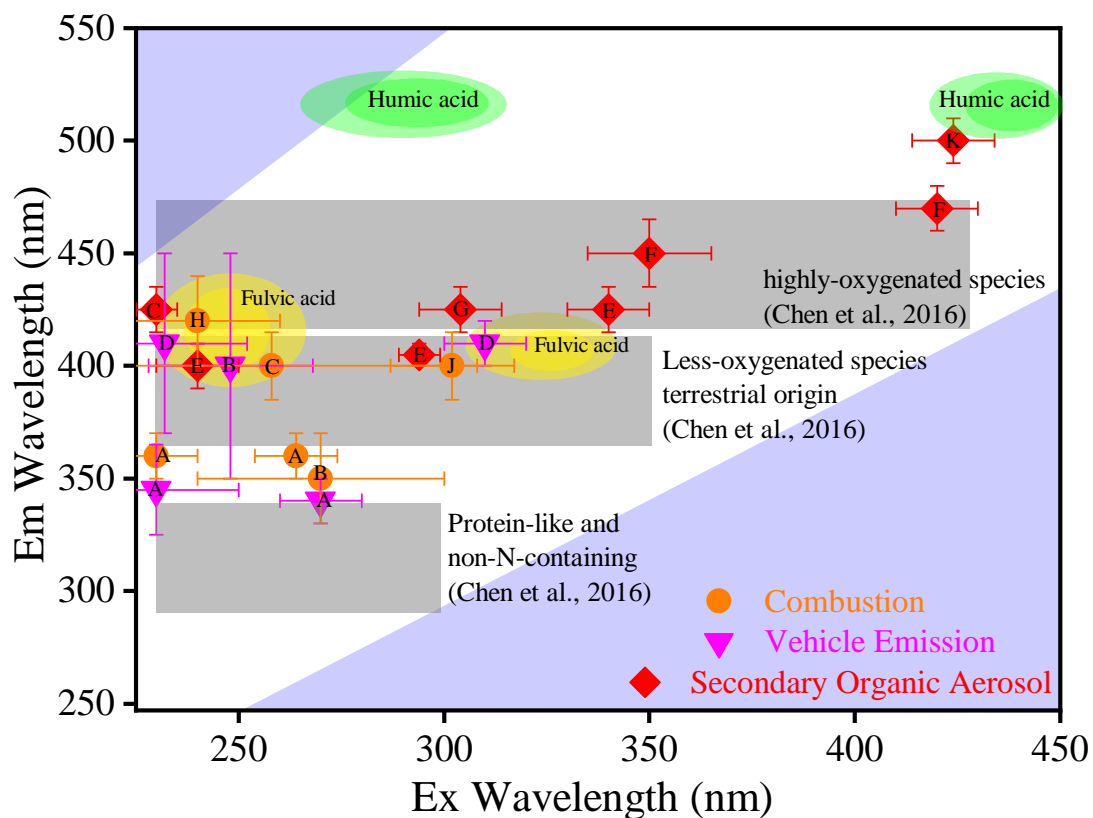
(b)

A: This study	B: Yang et al., 2022
C: Chen et al., 2020	D: Tang et al., 2020b
E: Hawkins et al., 2016	F: Bones et al., 2010
G: Lee et al., 2013	H: Mahamuni et al., 2020
J: Yan and Kim 2017	K: Powelson et al., 2014

 Figure 1. Comparison of chemical characteristics of molecules assigned to each

 fluorescence component of BrC model compounds (a) and source WSOM (b).

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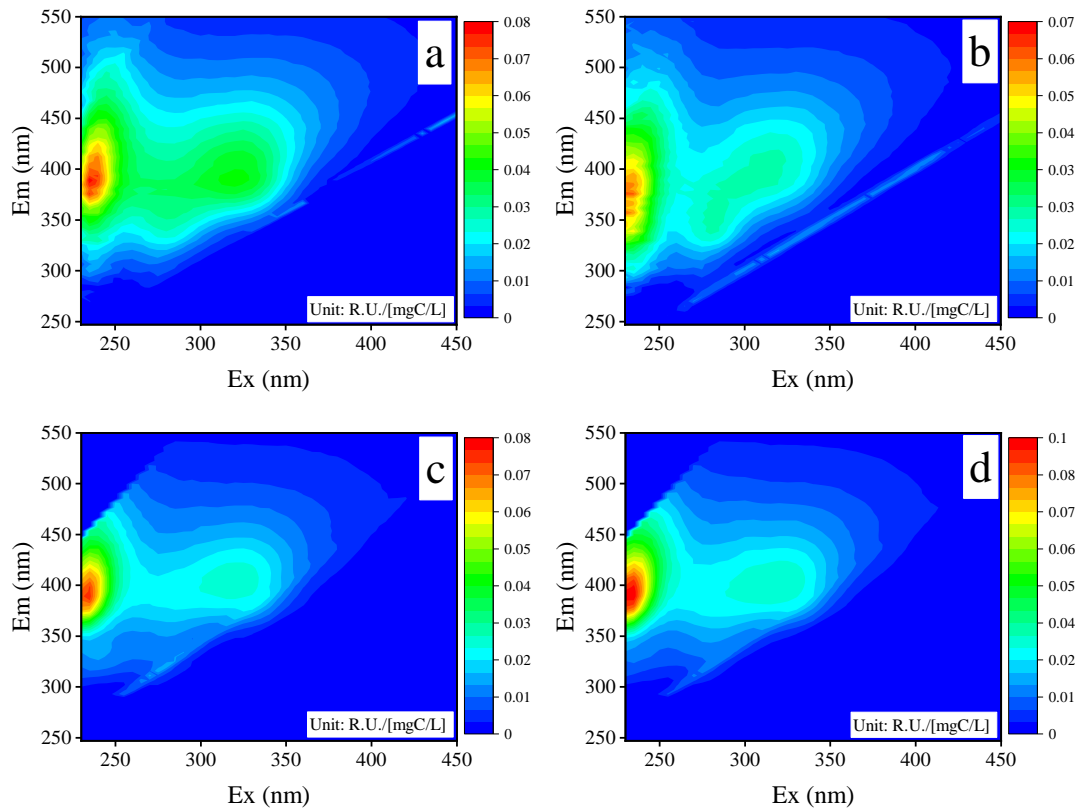
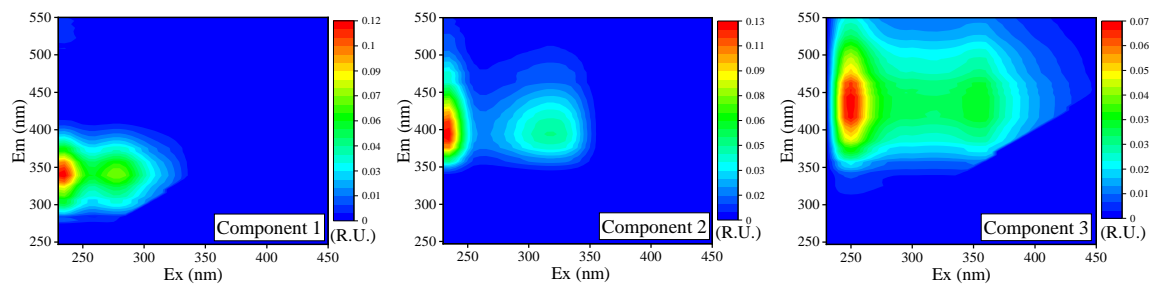


Figure 2. The 3D-EEM spectra of WSOM in atmospheric PM$_{2.5}$ samples (a:

Chuzhou (CZ); b: Guangzhou (GZ); c: GZ wet season; d: GZ dry season)

868

869 **Figure 3.** The EEM components derived from the PARAFAC model of WSOC in

870 atmospheric PM$_{2.5}$ samples collected at Chuzhou (CZ) and Guangzhou (GZ) sites.

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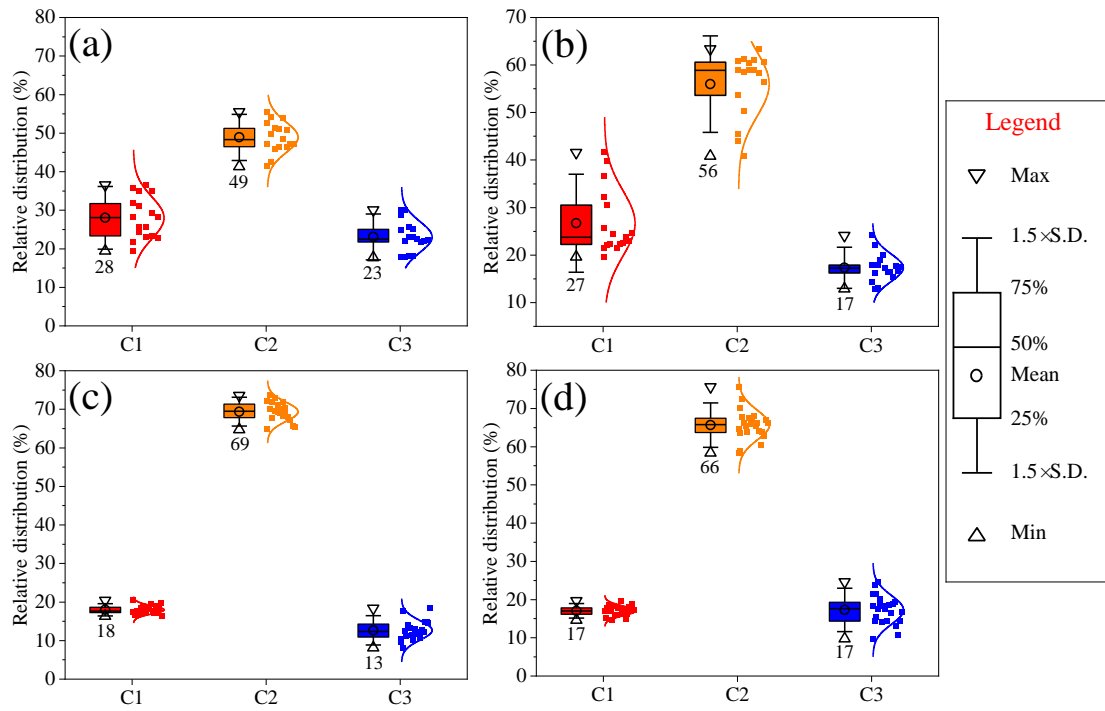
Figure 4. Relative contribution of individual fluorophores of atmospheric WSOM. (a: Chuzhou (CZ); b: Guangzhou (GZ); c: wet season of GZ; d: dry season of GZ)