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1 **Chemical characteristics and brown carbon chromophores of**
2 **atmospheric organic aerosols over the Yangtze River channel: a**
3 **cruise campaign**

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22 **Key Points:**

23 (1) More than one thousand atmospheric particulate organics including seventy-six BrC
24 chromophores were determined over the Yangtze River channel.

25 (2) Brown carbon chromophores exhibit high degrees of unsaturation, suggesting being
26 aromatics, nitro-aromatics, or polycyclic aromatics.

27 (3) Biomass burning tracers contribute significantly to the total light absorption of
28 organic aerosols.

29 **Abstract.**

30 Organic aerosols (OAs) have important influences on the climatic implications and
31 health effects of atmospheric aerosols. Among the complex OA constituents, brown
32 carbon (BrC) accounts for a substantial mass fraction and is of special interest because
33 of its light-absorbing properties. In this study, the chemical composition of atmospheric
34 OAs over the middle-lower Yangtze River (MLYR) channel, as well as the BrC, was
35 investigated during a ship cruise campaign in winter 2015. In total, more than one
36 thousand molecular formulas were determined using a combination of ultra-high
37 performance liquid chromatography (UHPLC), a diode array detector (DAD), and
38 Orbitrap high-resolution mass spectrometry (HRMS). Large numbers and enhanced
39 signal abundances for known tracers as well as monocyclic and polycyclic aromatics
40 indicate that biomass burning and fossil combustion are important sources of OAs over
41 the MLYR channel. In addition, thirteen chromophores with strong light absorption,
42 mostly representing established biomass burning tracers, were unambiguously
43 determined by UHPLC/DAD/HRMS and contributed to 35-37% of the total light
44 absorption of OAs at 290 nm and 58-70% at 350 nm. Sixty-three previously identified
45 biomass burning chromophores were also positively identified in the mass
46 spectrometric analysis here but embedded in the humped signal during the
47 spectroscopic analysis. These BrC chromophores exhibit high degrees of unsaturation,
48 suggesting these compounds to be aromatic, nitro-aromatic, and polycyclic aromatic
49 type of species. Our results highlight the significant influence of biomass burning and
50 fossil combustion on atmospheric OAs over the MLYR channel in the winter, strongly

51 enhancing light-absorbing properties and decreasing air quality.

52 **1. Introduction**

53 Organic aerosols (OAs) contribute to around 20-50% of the submicron particulate
54 mass in continental mid-latitudes and can account for as much as 90% of the particulate
55 mass in tropical forested areas, exerting important influences on climatic processes and
56 human health (Andreae & Crutzen, 1997; Kanakidou et al., 2005). OAs can be released
57 through direct emissions from natural or anthropogenic sources and/or formed in the
58 atmosphere through chemical reactions of volatile organic compounds (VOCs) and the
59 subsequent gas-to-particle conversion of less volatile reaction products (Pöschl, 2005).
60 In addition to their diverse sources, the multiple chemical reactions of OA components
61 can significantly increase their complexity (Goldstein & Galbally, 2007). Eventually,
62 these OA components impact the physicochemical properties and the potential toxicity
63 of OAs (Ito et al., 2019; Lei et al., 2014; Tang et al., 2016).

64 Light-absorbing OA components, typically referred to as brown carbon (BrC),
65 exhibiting strong light absorption in the near-ultraviolet (UV) and visible wavelength
66 regions, thus, affecting climate forcing properties of aerosol particles (Bahadur et al.,
67 2012; Chung et al., 2012). The study of Feng et al. (2013) concluded that the radiative
68 forcing of climate by BrC can contribute up to $+0.25 \text{ W m}^{-2}$, higher than 25% of that
69 by black carbon (BC). Released from both fossil fuel and biomass burning, BC
70 represents soot-like particles with a broad light absorption from the UV up to the
71 infrared wavelength range and may be the second most important atmospheric

72 component for global warming in terms of direct forcing (Jacobson, 2001). It also
73 showed that BrC may be the dominant atmospheric light-absorbing material over the
74 regions of biomass burning and biofuel combustion such as South and East Asia, South
75 America, and subtropical Africa (Feng et al., 2013). In addition, global models
76 concluded that the absorption of solar radiation by BrC was 27%-70% of that by BC
77 (Lin et al., 2018). Moreover, the BrC absorption was shown to explain almost 30% of
78 the total aerosol absorption at 370 nm (Yang et al., 2009), and even at 550 nm to be as
79 high as 20% (Chung et al., 2012).

80 BrC constituents, compared to BC, are less characterized due to their complex
81 composition and properties (Andreae & Gelencsér, 2006). BrC is present in both
82 primary aerosols, emitted from combustion processes, and secondary organic aerosols
83 (SOAs). Several studies have identified a wide variety of light-absorbing chromophores,
84 including nitro-aromatics, polycyclic aromatic hydrocarbon derivatives, polyphenols,
85 and sulfur-containing compounds, by investigating the molecular composition of
86 freshly emitted biomass burning OAs (Budisulistiorini et al., 2017; Lin et al., 2016;
87 Fleming et al., 2018). The exact chemical composition and physicochemical properties
88 of light-absorption BrC chromophores are related to the fuel type that is burned
89 (Chakrabarty et al., 2010; Iinuma et al., 2007; Lin et al., 2016). Secondary BrC were
90 shown to be generated from multiphase chemistry, such as acid-catalyzed aldol
91 condensation, nitration of aromatic compounds, and the reactions of ammonium ions
92 and amino acids with carbonyls and dicarbonyls (Bones et al., 2010; De Haan et al.,
93 2009; Kampf et al., 2016; Kwamena & Abbatt, 2008; Shapiro et al., 2009). Furthermore,

94 numerous lab studies have shown that atmospheric processing such as solar irradiation,
95 oxidation, and changes in temperature and relative humidity can alter the composition
96 of BrC and significantly change their optical properties (Lambe et al., 2012; Lee et al.,
97 2013; Lee et al., 2014; Nguyen et al., 2012; Rincón et al., 2010; Zhao et al., 2015). For
98 example, Lee et al. (2014) show that SOAs formed from the photo-oxidation of
99 naphthalene under high NO_x and from the reaction of limonene with ozone (O₃) could
100 be potential sources of secondary BrC, but would “photobleach” meaning lose their
101 near-UV absorbance after solar radiation with effective half-lives of ~14 h and <0.5 h,
102 respectively. Therefore, based on the local emissions and atmospheric conditions at a
103 specific geographic location, the chemical composition and physicochemical properties
104 of atmospheric BrC components can be very different.

105 The Yangtze River is the longest river in China and passes by several highly
106 developed economic megacities with major petrochemical complexes and/or steel
107 industries (Li et al., 2018), leading to high emissions of anthropogenic pollutants
108 including particulate matters, VOCs, sulfur dioxide, and nitrogen oxides (Huang et al.,
109 2011). Meanwhile, the Yangtze River also plays an important role in shipping of goods
110 and leisure cruising. Therefore, atmospheric OAs produced/formed over the Yangtze
111 River channel are expected to be complex including abundant BrC components.

112 Here, we collected filter samples of atmospheric particles during a cruise campaign
113 carried out along the MLYR channel from November to December 2015 (i.e., Yangtze
114 River Campaign, YRC), and analyzed the samples to characterize their organic fraction.

115 In addition, light-absorbing BrC chromophores in the complex OAs were identified via
116 connection of mass spectrometric analysis and spectroscopic analysis. The relative
117 contribution of the strongest BrC chromophores to the total light absorption of OAs
118 was also evaluated. The results obtained help not only to better understand the sources
119 and physicochemical properties of atmospheric aerosols, but also to further characterize
120 the constituents of air pollution at a molecular level over the MLYR channel region.

121 **2. Material and methods**

122 **2.1 Collection of PM_{2.5} samples**

123 Atmospheric aerosol samples were collected onto 90 mm prebaked quartz-fiber
124 filters (Whatman Company, UK) using a middle-flow aerosol sampler (Qingdao
125 Hengyuan Tech Co., Ltd., HY-100) for six hours at a flow rate of 100 L min⁻¹, from
126 November 22nd to December 5th, 2015 along the Yangtze River channel between
127 Shanghai and Wuhan (Figure 1). Details about the YRC can be found in a previous
128 study (Li et al., 2018). In order to avoid the possible contaminations from self-emission
129 of the ship, the sampler was placed on the bow of the research vessel. In addition, only
130 filter samples during the time period with relative wind directions between -100° and
131 100° of the moving direction of the ship and with a relative wind speed of >1.0 m s⁻¹
132 were selected for further analysis. As a result, six samples with sample IDs of 1201M,
133 1201A, 1201N, 1202M, 1202N, and 1203A, respectively, were selected, where the
134 numbers represent the sampling date, M denotes “morning”, A denotes “afternoon”,
135 and N denotes “night”. Figure 1 and Table 1 show the route of the vessel during the

136 campaign and the start and end locations of these six samples. Field blank filters were
137 collected by placing prebaked quartz-fiber filters into a parallel sampler for one hour
138 without any air flow through the filter substrate. After collection, all filters were stored
139 at -20°C in a freezer until further analysis to avoid changes in aerosol composition.

140 **2.2 Aerosol sample analysis**

141 Detailed procedures for sample filter extraction can be found in previous studies
142 (Wang et al., 2017; Wang et al., 2016). Briefly, a quarter of each quartz filter was
143 extracted twice with 6 mL of acetonitrile (Optima® LC/MS, Fischer Scientific, USA)
144 and agitated for 20 min. Then the combined extracts were filtered through a 0.2 µm
145 polytetrafluoroethylene membrane (13 mm, Pall Corporation, USA), and concentrated
146 under a gentle stream of N₂. The extracts were then reconstituted in 1 mL of a 1:1
147 vol/vol mixture of water (Optima® LC/MS, Fischer Scientific, USA) and acetonitrile.
148 Lastly, 200 µL of the reconstituted extract was diluted by adding 100 µL of water before
149 further analysis due to the high concentrations of organics.

150 Then the diluted extracts were analyzed by an UHPLC/DAD/HRMS platform, which
151 is the combination of ultra-high performance liquid chromatography (UHPLC, Dionex
152 3000, Thermo Scientific, USA), a diode array detector (DAD, Dionex UltiMate3000,
153 Thermo Scientific, USA), and Orbitrap high resolution mass spectrometry (HRMS, Q
154 Exactive, Thermo Scientific, Bremen, Germany) using heated electrospray ionization
155 (HESI). Three replicate analyses were performed for each sample extract. The
156 separation was performed using a Waters Acquity HSS T3 column (1.8 µm, 100 × 2.1

157 mm), and the procedures of gradient elution were described in earlier studies (Wang et
158 al., 2017; Wang et al., 2016). In this study, the UV-Vis absorption was measured using
159 a DAD over the wavelength range of 280-480 nm with low baseline noise ($< \pm 10 \mu\text{AU}$
160 at 254 nm) and high linearity up to 2.0 AU. For the HRMS analysis, HESI voltages of
161 -2.6 and 3.2 kV were applied in negative and positive ionization mode (ESI- and ESI+)
162 measurements, respectively. The sheath gas flow rate was 42 arbitrary units (a.u.) and
163 the auxiliary gas flow rate was 25 a.u. The temperature of the Orbitrap capillary
164 temperature was set at 350 °C and the temperature of the HESI source at 250 °C. The
165 mass resolving power of the Q-Exactive mass spectrometer was 140 000 at m/z 200,
166 and a 2 mM sodium acetate solution was used to provide a series of negative and
167 positive adduct ions in the scanning range of m/z 50–750 Th to perform the daily
168 external mass calibration.

169 Pentafluorobenzylhydroxylamine (PFBHA) derivatization was used to identify
170 organic compounds with carbonyl functional group(s) (Borrás & Tortajada-Genaro,
171 2012). 200 μL of the reconstituted extract were mixed with 800 μL of *o*-(2, 3, 4, 5, 6-
172 pentafluorobenzyl) hydroxylamine hydrochloride (Sigma Aldrich, $\geq 99.0\%$) solutions
173 (1 mg/mL). The mixtures were then left in darkness at room temperature for 24 h, and
174 analyzed following the same procedure as earlier described in this session.

175 **2.3 Data processing**

176 Data were acquired using Xcalibur 2.2 (Thermo, USA). The subsequent non-target
177 screening approach was conducted using an MZmine 2.33 software package. Molecular

178 formulas were assigned to detected signals satisfying the following constraints: $C_{1-50}H_{0-100}O_{0-40}N_{0-5}S_{0-3}$ ($C_{1-50}H_{0-100}O_{0-40}N_{0-5}S_{0-3}F_{0-20}$ for PFBHA derivatives analysis) with a
179 mass tolerance of 2 ppm in ESI- and 3 ppm in ESI+; element count heuristics (i.e., H/C
180 ratio ($0.3 \leq H/C \leq 3$); NOPS/C ratios ($N/C \leq 4$, $O/C \leq 3$, $P/C \leq 2$, $S/C \leq 3$); multiple
181 element counts (if each of N, O, P, and S > 1 then $N < 10$, $O < 20$, $P < 4$, $S < 3$; if each
182 of N, O, and P > 3 then $N < 11$, $O < 22$, $P < 6$; if each of O, P, and S > 1 then $O < 14$,
183 $P < 3$, $S < 3$; if each of P, S, and N > 1 then $P < 3$, $S < 3$, $N < 4$; if each of N, O, and S >
184 6 then $N < 19$, $O < 14$, $S < 8$), ring and double bond equivalence (RDBE) restrictions
185 (in the range of 0-25), and isotope pattern matching. It should be noted that the
186 CAMERA algorithm was applied in order to avoid false detection from interferences of
187 multiply charged ions and adducts (Kuhl et al., 2012). Further details on the LC-MS
188 data processing are listed in Tables S1-S2.

190 In addition to RDBE, aromaticity equivalents (X_c) and Kendrick mass defect (KMD)
191 values were calculated, and more details about the calculation can be found in the
192 supplemental Text S1 and from our previous study (Wang et al., 2017). X_c has been
193 suggested to help identification and characterization of monocyclic and polycyclic
194 aromatic compounds, with $X_c \geq 2.50$ and $X_c \geq 2.71$ as unambiguous minimum criteria
195 for the presence of mono- and polycyclic aromatic compounds, respectively (Yassine
196 et al., 2014). KMD is useful to differentiate groups of similar compounds among a large
197 set of molecular formulas. In this study, CH_2 was chosen as a base unit, and thus,
198 molecules with identical KMDs differ only in the number of $-CH_2$ groups (Hughey et
199 al., 2001).

200 The assigned formulas were subdivided into seven groups: compounds containing
201 only carbon, hydrogen, and oxygen atoms in the ESI- and ESI+ (hereafter referred to
202 as CHO- and CHO+, respectively); nitrogen-containing organics (hereafter referred to
203 as CHON- and CHON+, respectively); sulfur-containing organics and compounds
204 containing both nitrogen and sulfur in ESI- (hereafter referred to as CHOS- and
205 CHONS-, respectively); and finally, organics without oxygen in ESI+ (hereafter
206 referred to as CHN+). Similarly to our previous study (Wang et al., 2017), CHOS+ and
207 CHONS+ compounds were also observed but accounted merely for a few percentages,
208 so they were not further considered here.

209 It should also be noted that although LC separation might help reducing ion
210 suppression effects, only a semi-quantification of organic compounds can be proposed.
211 Using ESI, significant uncertainties originate also from different ionization efficiencies
212 of particulate organic components which typically exhibit a wide range of different
213 structures and functional groups (Lin et al., 2012). Due to the large variety of
214 compounds and the technical impossibility of providing calibration factors for
215 individual species, we assumed that the determined compounds have a similar signal
216 response and the total peak areas of organics can be compared among different samples.

217 **3. Results and discussion**

218 **3.1 Organic aerosols over the MLYR channel**

219 In this study, 695-1187 and 450-695 molecular formulas were determined in ESI-
220 and ESI+, respectively (Table 1). Due to the inherent differences in the ionization

221 mechanisms between ESI⁻ and ESI⁺, a minor fraction of the detected compounds
222 appears in both modes as shown by the formula lists (see Dataset 1). Data from ESI⁻
223 and ESI⁺ can provide complementary information to characterize the molecular
224 composition of complex OAs (Lin et al., 2018). However, non-polar compounds, which
225 may be part of BrC, are difficult to be ionized by ESI (Kuang et al., 2018). Therefore,
226 contributions from non-polar compounds might be underestimated in this study. The
227 number and percentage of molecular formulas for each subgroup tentatively identified
228 in each sample were listed in Table 1. The greatest number of formulas was detected in
229 the 1202M sample, giving 600 more compounds than the 1203A sample, which showed
230 the lowest number of detected compounds. This large difference in the number of
231 compounds clearly demonstrates not only the complexity but also the variety of organic
232 species in the aerosol samples. In addition, the number of CHON species including
233 CHON⁻ and CHON⁺ accounted for significantly higher percentages in the 1202M and
234 1202N samples compared to any other sample, indicating the different sources for these
235 compound classes.

236 The pie charts in Figures 2 and S1 show the relative abundances (i.e., based on peak
237 areas) of all subgroups in each sample. It was reported that the relative contributions of
238 CHO⁻, CHON⁻, CHON⁺, CHOS⁻, and CHN⁺ species to wintertime OAs in urban
239 Shanghai were close (Wang et al., 2017). However, within the present study, the relative
240 abundances of CHON⁺ and CHNO⁻ species are much greater, whereas CHOS⁻ species
241 represent a less fraction (Figures 2 and S1). This difference in abundances indicates that
242 nitrogen-containing compounds, such as organonitrates, likely dominated the

243 physicochemical properties of aerosol particles over the MLYR channel region,
244 whereas sulfur-containing compounds, such as organosulfates, played only a minor role
245 compared to urban Shanghai areas.

246 In addition to molecular formulas, the abundances, element ratios, RDBE, the
247 number of carbonyl group, and the values of KMD and Xc for detected species were
248 listed in the Dataset 1. In the present study, large amounts of organics with low
249 saturation degrees were observed in all samples. In both ESI- and ESI+, 62-72% of the
250 determined formulas are characterized by high RDBE values ($RDBE \geq 4$) and 39-52%
251 of the formulas show Xc values ≥ 2.50 , indicating that most of these compounds are
252 aromatics (Wang et al., 2017; Yassine et al., 2014). A further analysis shows that around
253 15-23% of the formulas in ESI+ and 23-28% of the formulas in ESI- were probably
254 polycyclic aromatics ($Xc \geq 2.71$), representing more than half of the number of aromatic
255 molecules. These results suggest that anthropogenic emissions made important
256 contributions to the atmospheric OAs over the MLYR channel.

257 Li et al. (2018) classified the air pollution during the cruise campaign into eight
258 distinct episodes based on sampling locations, backward trajectories, and
259 photochemical processes. We note that the sampling duration for the 1201M, 1201A,
260 and 1201N samples corresponds to episode #5 in an overview paper of the cruise
261 campaign (Li et al., 2018), whereas that for the 1202M and 1202N samples overlaps
262 episode #6, and the 1203A sample coincides with episode #7, respectively. Based on
263 the concentrations of carbon monoxide, and trace elements and levoglucosan in

264 particulate matters, episode #5 and episodes #6-7 are cases strongly influenced by coal
265 combustion and biomass burning, respectively (Li et al., 2018). The larger numbers and
266 higher abundances of sulfur-containing compounds in the 1201M and 1201A samples
267 (Figure 2 and Table 1) are probably caused by coal combustion, which is in agreement
268 with Li et al. (2018). In addition to the most intense species detected in ESI- and ESI+
269 (see Figures 2 and S1, and Tables 2 and S3), other organics detected with high
270 abundances in the samples, including C_7H_7NO , C_8H_7NO , and C_9H_7NO were assigned
271 to the benzamide, 4-hydroxy-benzene acetonitrile, and 3-(4-hydroxyphenyl)
272 propionitrile, respectively, which are well known tracers derived from biomass burning
273 (Laskin et al., 2009; Lin et al., 2016; Ma & Hays, 2008). In addition to the cities and
274 factories, there are farmland and rural areas along the Yangtze River. Compound J'
275 (Figure 2, referred to $C_{10}H_{17}NO_7S$), with the highest abundance in the 1201M sample,
276 is tentatively assigned to be derived from monoterpene oxidation in the presence of
277 NO_x and SO_2 (Brüggemann et al., 2015; Seinfeld et al., 2008; Wang et al., 2018). It
278 should be noted that these tracers may also be formed from chemical processing and
279 cannot be distinguished in the present study, but precursor molecules with aromatic
280 structures likely originated from the same sources. Overall, biomass burning and fossil
281 fuel combustion could be important organic aerosol sources over the MLYR channel
282 (Li et al., 2018).

283 **3.2 Molecular characterization of BrC chromophores**

284 BrC chromophores were distinguished by matching the absorption chromatograms

285 with the DAD detector to the extracted ion chromatograms. The mass spectrum before
286 and at a major absorption were compared to help identifying the potential
287 chromophores, as shown in Figure S2. We note that only chromophores with high ion
288 abundances and strong light absorptions can be unambiguously determined by this
289 approach. Indeed, the highly complex composition of the aerosol samples can lead to
290 overlapping peaks in both extracted ion chromatograms and UV-Vis absorption spectra.
291 Note that only the 1201M, 1201A and 1202N samples, which were analyzed with a
292 good DAD performance, were chosen to determine the BrC chromophore.

293 UHPLC-DAD absorption chromatograms between 290-480 nm wavelengths were
294 blank-corrected, normalized by the volume of the sample, and subsequently plotted in
295 Figures 3 and S3-S4. Intense absorption at near UV wavelengths (290-350 nm) is
296 evident. Much higher light absorption was observed in the 1202N sample than in the
297 1201M and 1201A samples, likely due to the greater concentrations of BrC
298 chromophores in the 1202N sample (Figures 2 and S1). For example, the relative
299 abundances of $C_6H_5NO_3$ in the 1201M and 1201A samples only account for around 17%
300 and 15% of that in the 1202N sample, respectively. The presence of complex mixtures
301 of chemicals including isomeric chromophores could have contributed to the humped
302 light absorption in these chromatograms (Budisulistiorini et al., 2017).

303 Following the UHPLC/DAD/HRMS protocol in Figure S2, we identified thirteen
304 BrC chromophores and their formulas were labelled next to the corresponding
305 absorption peaks in Figures 3 and S3-S4. All of them are characterized with high

306 unsaturation degrees ($\text{RDBE} \geq 4$), indicating the presence of poly-conjugated double
307 bonds. For example, $\text{C}_6\text{H}_5\text{NO}_3$, presumably nitrophenol, is the most abundant species
308 in the six samples and derived from biomass burning (Mohr et al., 2013). Nitrogen-
309 containing chromophores including $\text{C}_6\text{H}_5\text{NO}_4$, $\text{C}_7\text{H}_5\text{NO}_5$, $\text{C}_7\text{H}_7\text{NO}_3$, $\text{C}_7\text{H}_7\text{NO}_4$,
310 $\text{C}_8\text{H}_7\text{NO}_3$, and $\text{C}_7\text{H}_6\text{N}_2\text{O}_5$ also exhibit high degrees of unsaturation and were assigned
311 to nitro-aromatics that are also known to be emitted from biomass burning (Desyaterik
312 et al., 2013; Lin et al., 2016). In addition to the presence of monoaromatics, products
313 formed from the photooxidation of polycyclic aromatic hydrocarbons (PAHs) were
314 observed (Riva et al., 2015). As an example, $\text{C}_7\text{H}_6\text{O}_2$ assigned to benzoic acid was
315 identified in large amount in the different samples. It is worth pointing out that such
316 carbonyl-containing compounds are well-suited candidates to act as photosensitizer,
317 potentially inducing chemical reactions at the surface and in the bulk of aerosol particles
318 (George et al., 2015; McNeill & Canonica, 2016). In total, more than seventy carbonyl-
319 containing formulas were determined based on the PFBHA derivatization, with 6-24%
320 of carbonyl-containing formulas in ESI- and 35-45% in ESI+ belonging to aromatic
321 compounds (i.e., $X_c \geq 2.50$, see Dataset 1). In addition, polycyclic aromatics including
322 $\text{C}_{17}\text{H}_{10}\text{O}$ ($\text{RDBE} = 13$, $X_c = 2.83$), $\text{C}_{19}\text{H}_{10}\text{O}$ ($\text{RDBE} = 15$, $X_c = 2.86$) and $\text{C}_{13}\text{H}_8\text{O}_2$
323 ($\text{RDBE} = 15$, $X_c = 2.75$) were contributors to light absorption (Figures 3 and S3-S4),
324 and the latter of which ($\text{C}_{13}\text{H}_8\text{O}_2$) is an important tracer for biomass burning (Lin et al.,
325 2016). Finally, due to the large presence of $\text{C}_{14}\text{H}_{11}\text{NO}$ ($\text{RDBE} = 10$ and a $X_c = 2.78$;
326 Figure S1) that is assigned to benzyloxybenzotrile species, microorganism is another
327 potential source of BrC compounds (Garcia-Alcega et al., 2017) within the Yangtze

328 River channel.

329 In addition to unambiguously determining the thirteen chromophores by the
330 UHPLC/DAD/HRMS analysis, we compared the mass list of organic species in our
331 samples and those in previously observed during biomass burning experiments
332 (Budisulistiorini et al., 2017; Lin et al., 2016). As a result, sixty-three BrC
333 chromophores including 31 formulas were observed only in ESI-, 14 formulas only in
334 ESI+, and 18 formulas in both modes. The retention time of all these species
335 corresponded to the light absorption region of the chromatogram but did not match an
336 outstanding absorption peak. Their molecular weights are greater than 120 Da, but less
337 than 350 Da (Figure S5) and have high RDBE values (ranging from 4 to 12), indicating
338 that such species are likely aromatics. In addition, Figure S6 shows the distribution of
339 the number of nitrogen (0-2) and oxygen (1-7) atoms of these seventy-six BrC
340 chromophores. During biomass burning and fuel combustion, OH-initiated oxidation
341 may lead to the formation of oxygenated organic compounds, producing light absorbing
342 species (Saleh et al., 2014). Three reduced nitrogen-containing aromatic chromophores
343 with $O/N < 3$, such as $C_{14}H_{11}NO$, were identified in ESI+, whereas more than twenty
344 nitro-aromatic chromophores with $O/N \geq 3$ were preferably detected in ESI- (Zhang et
345 al., 2013). These nitrogen-containing aromatics were probably produced by
346 heterogeneous reactions of aromatics with NO_2 and nitrate radicals (NO_3) (Kwamena
347 & Abbatt, 2008) and/or oligomerization of dicarbonyls reacting with ammonium during
348 combustion (Budisulistiorini et al., 2017; Kampf et al., 2016).

349 Figures 4 and S7-S11 show the CH₂-Kendrick and Van Krevelen (VK) diagrams for
350 the 1201M, 1201A, and 1202N samples with the seventy-six identified BrC
351 chromophores being color-coded. Homologous compounds line up a horizontal line in
352 the CH₂-Kendrick diagrams but a tilted one in the VK diagrams, suggesting that the
353 homologues could have variable degrees of saturation and oxidation but possible
354 similar structure and physicochemical properties. This leads to tentative assignments of
355 over 120 species to BrC chromophores. These species were not outstanding either in
356 the mass spectra or in the absorption chromatography, but could have contributed to the
357 humped light absorption signal.

358 Many studies show that nitrogen-containing heterocyclic imine and imidazole
359 compounds that are derived from reactions of carbonyls and dicarbonyls with
360 ammonium, ammonia or amino acids, can absorb at wavelengths of 300-500 nm (De
361 Haan et al., 2009; Kampf et al., 2016; Nguyen et al., 2013; Nozière et al., 2009; Sareen
362 et al., 2009). For example, C₆H₈ON₂ could be formed from the reaction of
363 methylglyoxal with ammonium, being an important BrC chromophore (Lin et al., 2015).
364 However, its relative abundances only account for less than 0.6% of the most abundant
365 ion (i.e., C₁₆H₃₃NO in 1201A sample) in 1201M, 1201A and 1202N samples. In this
366 study, 173-334 CHON⁺ species and 87-136 CHN⁺ species were determined according
367 to their exact mass. These CHON⁺ compounds are characterized with low degrees of
368 oxidation with average values of O/N lower than 1.53, indicating the presence of
369 reduced nitrogen in the formula. In addition, 57-59% of CHON⁺ and 70-78% of CHN⁺
370 have high unsaturation degrees with RDBE \geq 4, whereas 24-27% of CHON⁺ and 29-

371 36% of CHN⁺ belong to monoaromatics ($2.71 > X_c \geq 2.50$) and 6-13% of CHON⁺ and
372 34-44% of CHN⁺ belong to polycyclic aromatics ($X_c \geq 2.71$), respectively, suggesting
373 that many of these reduced nitrogen-containing compounds probably contain
374 conjugated systems and possess light absorption abilities.

375 **3.3 Light absorption contribution of determined strong chromophores**

376 Figure 5 shows the light absorption contribution from the 13 strong BrC
377 chromophores unambiguously determined by UHPLC/DAD/HRMS to the total light
378 absorption of OAs at 290-480 nm. The light absorption for each chromophore was
379 summed up based on the corresponding ion chromatogram.

380 Overall, the total light absorption of OAs is the highest for the 1202N sample and the
381 lowest for the 1201A samples. The maximum absorption was observed at 290 nm, and
382 the total absorption decreased as the wavelength increased, showing a similar trend to
383 that in the study of Lin et al. (2016). However, in this study, the light absorptions are
384 almost zero at wavelength of 400 nm, and thus, lower than those of the study of Lin et
385 al. (2016). This weakened absorption probably indicates larger concentrations of
386 chromophores in biomass burning aerosols collected in their study compared to the
387 ambient aerosol samples collected over the MLYR channel. At 290 nm, around 35-37%
388 of the light absorption of OAs can be attributed to the 13 strong BrC chromophores,
389 whose contribution increased to around 58-70% at 350 nm. In particular, the determined
390 nitro-aromatics (i.e., $C_6H_5NO_3$, $C_6H_5NO_4$, $C_7H_7NO_3$, $C_7H_7NO_4$, $C_7H_5NO_5$, $C_8H_7NO_3$,
391 $C_8H_9NO_3$, and $C_7H_6N_2O_5$) alone contribute to about 25-27% at 290 nm and 55-65% at

392 350 nm of the total light absorption of OAs. Moreover, it should be noted that the light
393 absorption of the chromophores from biomass burning (i.e., C₆H₅NO₃, C₆H₅NO₄,
394 C₇H₅NO₅, C₇H₇NO₃, C₇H₇NO₄, C₈H₇NO₃, C₇H₆N₂O₅, and C₁₃H₈O₂) account for 27-
395 28% at 290 nm and 55-68% at 350 nm, further indicating that biomass burning is
396 potentially the most important sources for light-absorbing species in aerosol particles
397 in the MLYR region.

398 **4. Conclusions**

399 Nearly one-third of the Chinese population live along the Yangtze River; the air
400 pollution over the MLYR channel region can impact the aquatic ecosystem, the health
401 of local residents, and regional climate. Therefore, it becomes crucial to characterize
402 the constituents and sources of air pollutants over the MLYR channel region. To the
403 best of our knowledge, YRC is the first comprehensive cruise observation of air quality
404 along the MLYR channel. The chemical composition of the organic fraction of
405 atmospheric particles over this region was investigated, for the first time, using
406 UHPLC/DAD/HRMS with a special focus on BrC chromophores in the present study,
407 which will significantly improve our understanding of BrC compositions, sources and
408 optical properties in this region. So far, only a few studies have investigated
409 atmospheric BrC at such a detailed molecular level. In total, 695-1187 and 450-695
410 molecular formulas were determined in ESI⁻ and ESI⁺, respectively. In addition, 62-
411 72% of the organic compounds exhibit high degrees of unsaturation (RDBE ≥ 4).
412 Furthermore, 39-52% and 15-23% of these organics have an X_c ≥ 2.50 and X_c ≥ 2.71,

413 indicating that they are aromatics and polycyclic aromatics, respectively. Moreover,
414 high signal abundances and large numbers of known tracers indicate that biomass
415 burning and fossil fuel combustion are important sources for OAs in the MLYR region.

416 In total, thirteen strong chromophores were determined by UHPLC/DAD/HRMS
417 analysis. Most of these compounds are probably derived from biomass burning. Apart
418 from that, more than sixty chromophores identified in previous biomass burning
419 experiments were also detected in this study, further confirming the abundance of
420 biomass burning emissions in the MLYR. All of these chromophores were characterized
421 by a low degree of saturation, and Xc values indicating aromatic, nitro-aromatic, and
422 polycyclic aromatic structures. Based on KMD and VK analyses, around one hundred
423 homologues to the identified chromophores were detected, probably having similar
424 structures and light-absorption properties. A large amount of reduced nitrogen-
425 containing compounds and potential photosensitizers (i.e., carbonyl-containing
426 compounds) were found, probably contributing further to the light absorptions of
427 aerosols in the MLYR.

428 We found that the determined thirteen strong chromophores contribute to around 35-
429 37% at 290 nm and 58-70% at 350 nm of the overall light absorption of OAs,
430 respectively. The light absorption contributions of chromophores from biomass burning
431 were estimated to 27-28% at 290 nm and 55-68% at 350 nm, highlighting the
432 importance of such anthropogenic emissions for light-absorption properties of aerosol
433 particles over the MLYR channel region.

434

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703 Table 1. Summary of the sampling location, sampling time, and the number of assigned formulas in both ESI- and ESI+ mass spectra.

Sample ID	Time	Start point	End point	Number of Formulas (Fraction %)								
				CHO-	CHON-	CHOS-	CHONS-	All in ESI-	CHO+	CHON+	CHN+	All in ESI+
1201M	1 Dec, 2015, 7:30 am -12:00 am	(30.10°N, 115.32°E)	(29.82°N, 115.73°E)	261 (26.2%)	238 (23.9%)	253 (25.4%)	243 (24.4%)	995 (100%)	209 (41.7%)	202 (40.3%)	90 (18.0%)	501 (100%)
1201A	1 Dec, 2015, 12:00 am -6:00 pm	(29.82°N, 115.73°E)	(29.90°N, 116.48°E)	251 (26.2%)	259 (27.0%)	241 (25.1%)	208 (21.7%)	959 (100%)	190 (42.2%)	173 (38.4%)	87 (19.3%)	450 (100%)
1201N	1 Dec, 2015, 6:00 pm -12:00 pm	(29.90°N, 116.48°E)	(30.37°N, 116.89°E)	295 (26.5%)	323 (29.0%)	253 (22.7%)	242 (21.7%)	1113 (100%)	232 (38.0%)	246 (40.3%)	133 (21.8%)	611 (100%)
1202M	2 Dec, 2015, 6:00 am -12:00 am	(30.63°N, 117.24°E)	(31.10°N, 117.76°E)	291 (24.5%)	367 (30.9%)	258 (21.7%)	271 (22.8%)	1187 (100%)	235 (36.6%)	269 (41.8%)	139 (21.6%)	643 (100%)
1202N	2 Dec, 2015, 6:00 pm -12:00 pm	(31.42°N, 118.35°E)	(32.05°N, 118.69°E)	289 (26.1%)	353 (31.9%)	222 (20.0%)	244 (22.0%)	1108 (100%)	225 (32.4%)	334 (48.1%)	136 (19.6%)	695 (100%)
1203A	3 Dec, 2015, 12:00 am -6:00 pm	(32.22°N, 119.21°E)	(32.21°N, 119.55°E)	201 (28.9%)	209 (30.1%)	155 (22.3%)	130 (18.7%)	695 (100%)	209 (40.5%)	191 (37.0%)	116 (22.5%)	516 (100%)

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713 Table 2. Potential identities and sources for the most abundant species in the ESI- mass spectra.

ID	Retention Time (min)	Neutral Mass (Da)	Formula	RDBE ^a	Xc ^b	Potential Identity	Potential Source/ Precursor	Reference
A'	6.09; 6.67; 7.21	122.0366	C ₇ H ₆ O ₂	5	2.50	Benzoic acid	Naphthalene	(Riva et al., 2015)
B'	8.56	139.0268	C ₆ H ₅ NO ₃	5	2.50	Nitrophenol	Biomass burning	(Mohr et al., 2013)
C'	9.15; 9.42	153.0424	C ₇ H ₇ NO ₃	5	2.50	Methyl nitrophenol	Biomass burning	(Mohr et al., 2013)
D'	7.73; 8.57	155.0217	C ₆ H ₅ NO ₄	5	2.33	Nitrocatechols	Biomass burning and vehicle emissions	(Mohr et al., 2013)
E'	6.02; 7.60; 9.15; 9.53	165.0553	C ₈ H ₇ NO ₃	6	2.60	Nitroacetophenone	Biomass burning	(Lin et al., 2016)
F'	6.10; 6.67; 6.76	166.0264	C ₈ H ₆ O ₄	6	2.50	Phthalic acid	Naphthalene	(Riva et al., 2015)
G'	7.39; 8.32; 8.58; 8.70; 8.82; 9.47	169.0473	C ₇ H ₇ NO ₄	5	2.33	Methyl nitrocatechols	Biomass burning and diesel exhaust	(Yoshiteru Iinuma et al., 2010)
H'	7.84; 8.10; 9.01; 9.34; 9.55; 10.15	183.0699	C ₈ H ₉ NO ₄	5	2.33	Dimethoxynitrobenzene	Biomass burning	(Desyaterik et al., 2013)
I'	9.80; 9.96; 10.42	198.0492	C ₇ H ₆ N ₂ O ₅	6	2.50	Methyl dinitrophenol	Toluene; biomass burning	(Jang & Kamens, 2001; Desyaterik et al., 2013)
J'	8.33; 8.61; 8.79; 8.91	295.0721	C ₁₀ H ₁₇ NO ₇ S	3	0	A nitrooxy organosulfate	α-pinene; β-pinene; α-terpinene; Terpinolene	(Gómez-González et al., 2012)

714 ^aRing and double bond number. ^bAromaticity equivalents.

Figure Captions

715

716 **Figure 1.** The start and end points for the filter sampling along the Yangtze River
717 channel.

718

719 **Figure 2.** Mass spectra of detected CHO-, CHOS-, CHON-, and CHONS- compounds,
720 reconstructed from extracted ion chromatograms (UHPLC-Orbitrap MS analysis, ESI-).
721 Note that the abundance of C₆H₅NO₃ in the 1202N sample (the most abundant one in
722 all samples) was set arbitrarily to 100%. The sizes of pie charts are proportional to the
723 total abundance of all subgroups in each sample.

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725 **Figure 3.** UHPLC-DAD absorption chromatograms for the 1202N aerosol sample.
726 Panel (a) shows the blank-subtracted absorption chromatograms at two selected
727 wavelengths (i.e., 300 and 350 nm). Panel (b) shows the blank-subtracted absorption
728 chromatograms at 290-480 nm. The absorption peaks are labeled with the most likely
729 formula of the light-absorbing chromophore. Molecular formulas in red, blue, and black
730 colors represent detection in ESI-, ESI+, and both modes, respectively.

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732 **Figure 4.** (a-b) CH₂-Kendrick diagrams and (c-d) Van Krevelen diagrams for CHO-
733 and CHON- species in the 1202N aerosol sample, respectively. Purple and orange
734 points denote the light-absorbing CHO- and CHON- compounds, respectively. The size
735 of the points corresponds to the abundance of the corresponding ion signal.

736

737 **Figure 5.** Relative contribution of the thirteen BrC chromophores to the total light
738 absorption of OAs for the (a) 1201M, (b) 1201A, and (c) 1202N samples. Note that the
739 light-absorption at 290 nm in the 1202N sample (the highest light absorption signal in
740 all samples) was set arbitrarily to 100%.

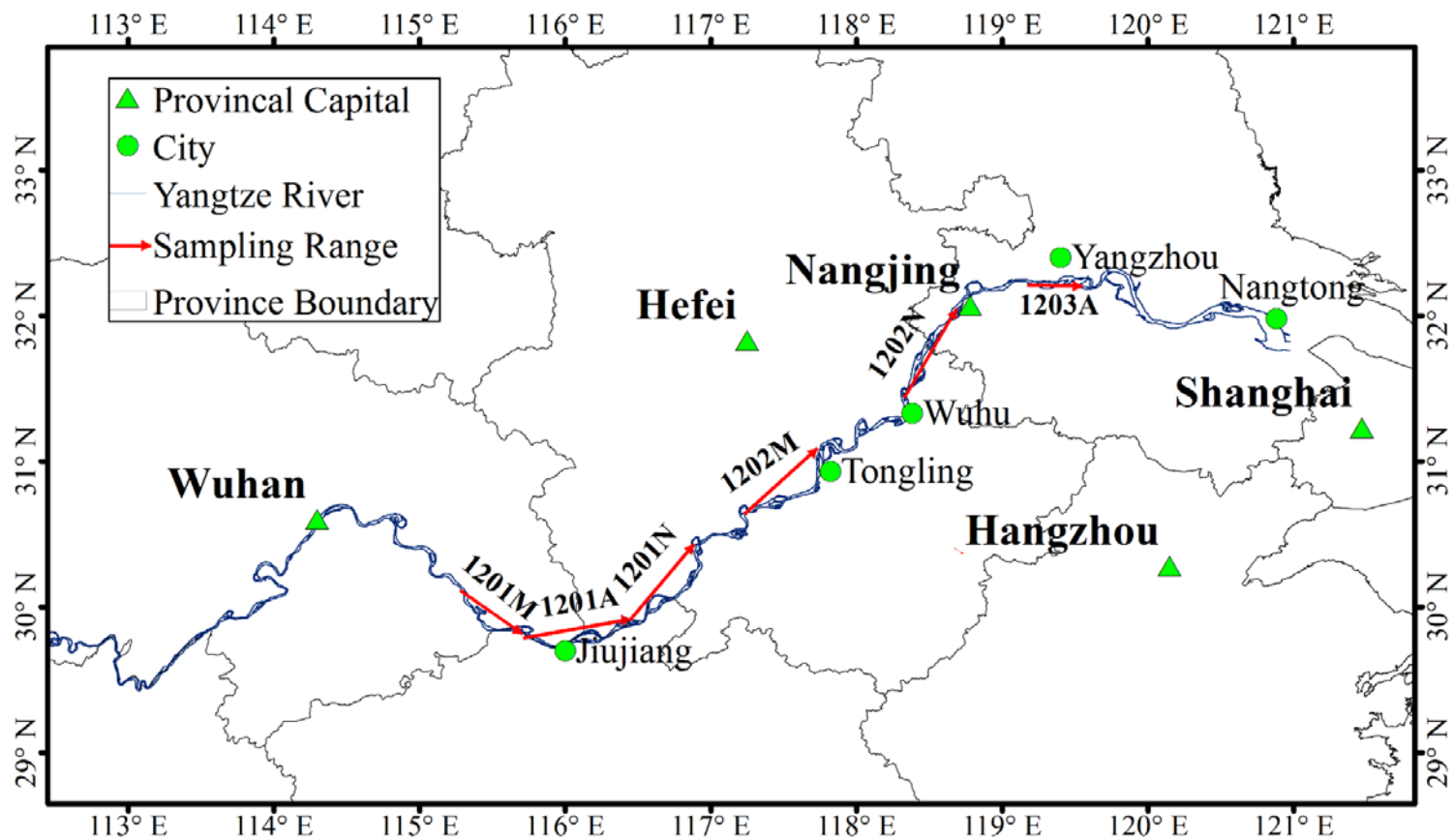


Figure 1

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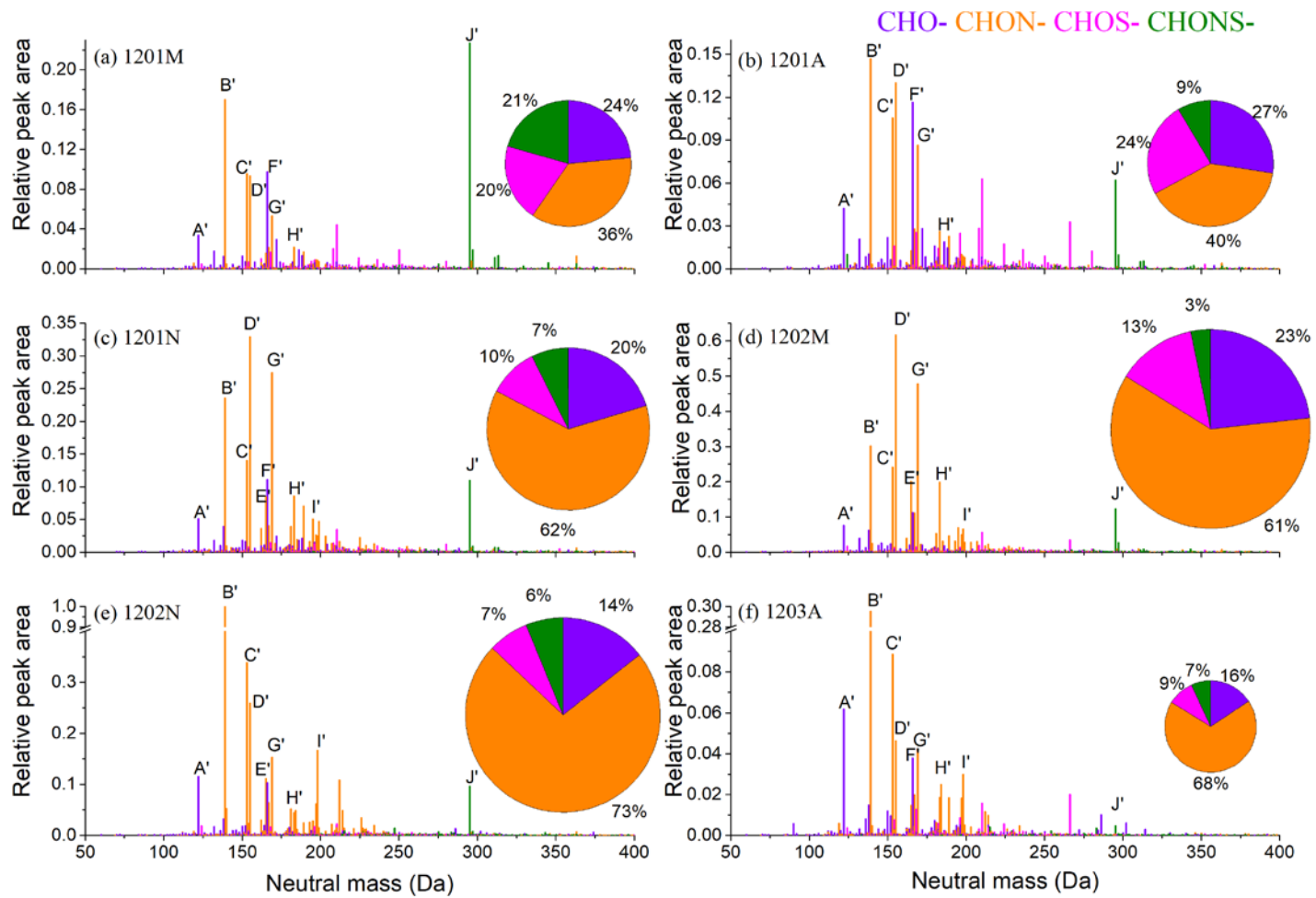


Figure 2

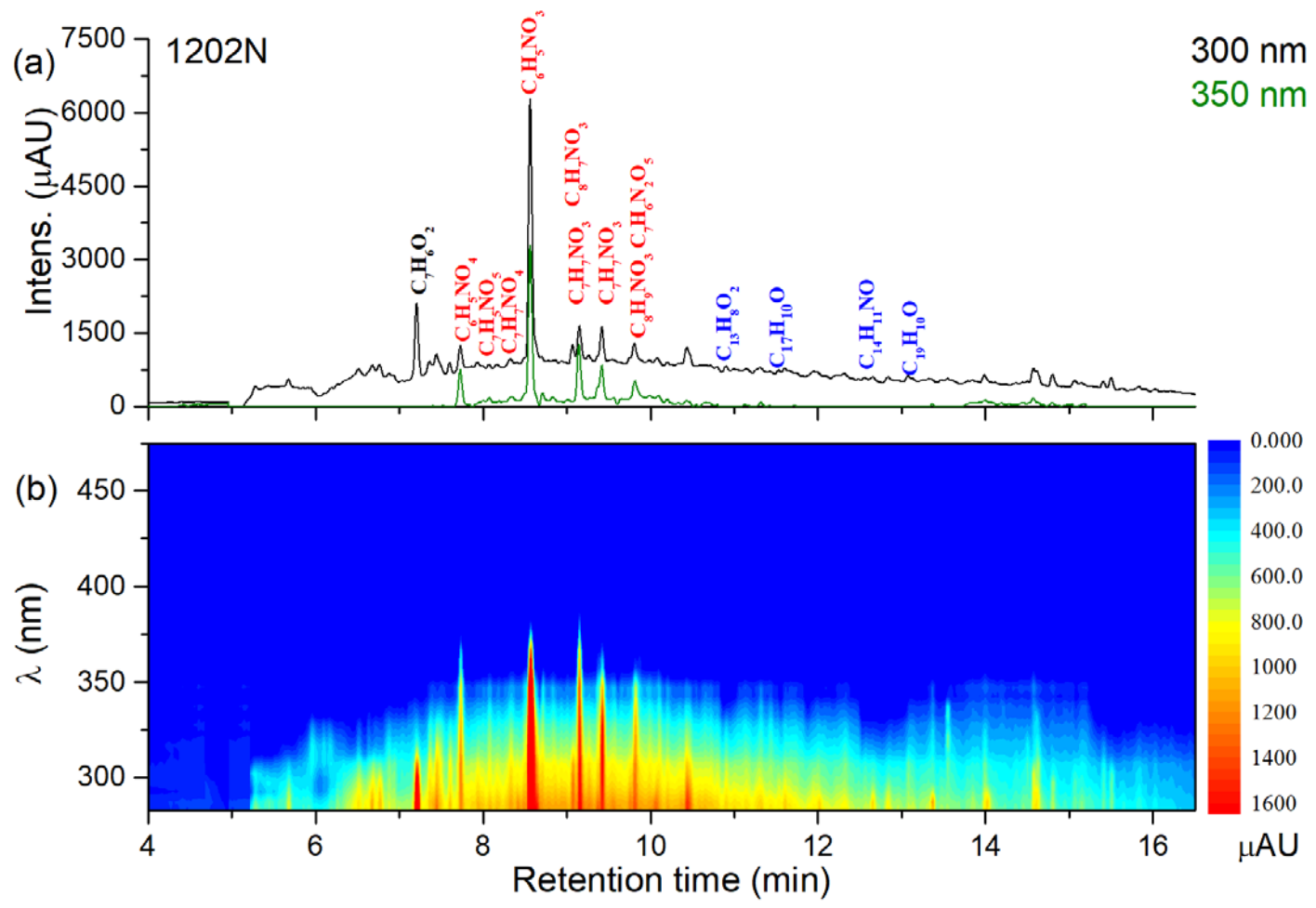


Figure 3

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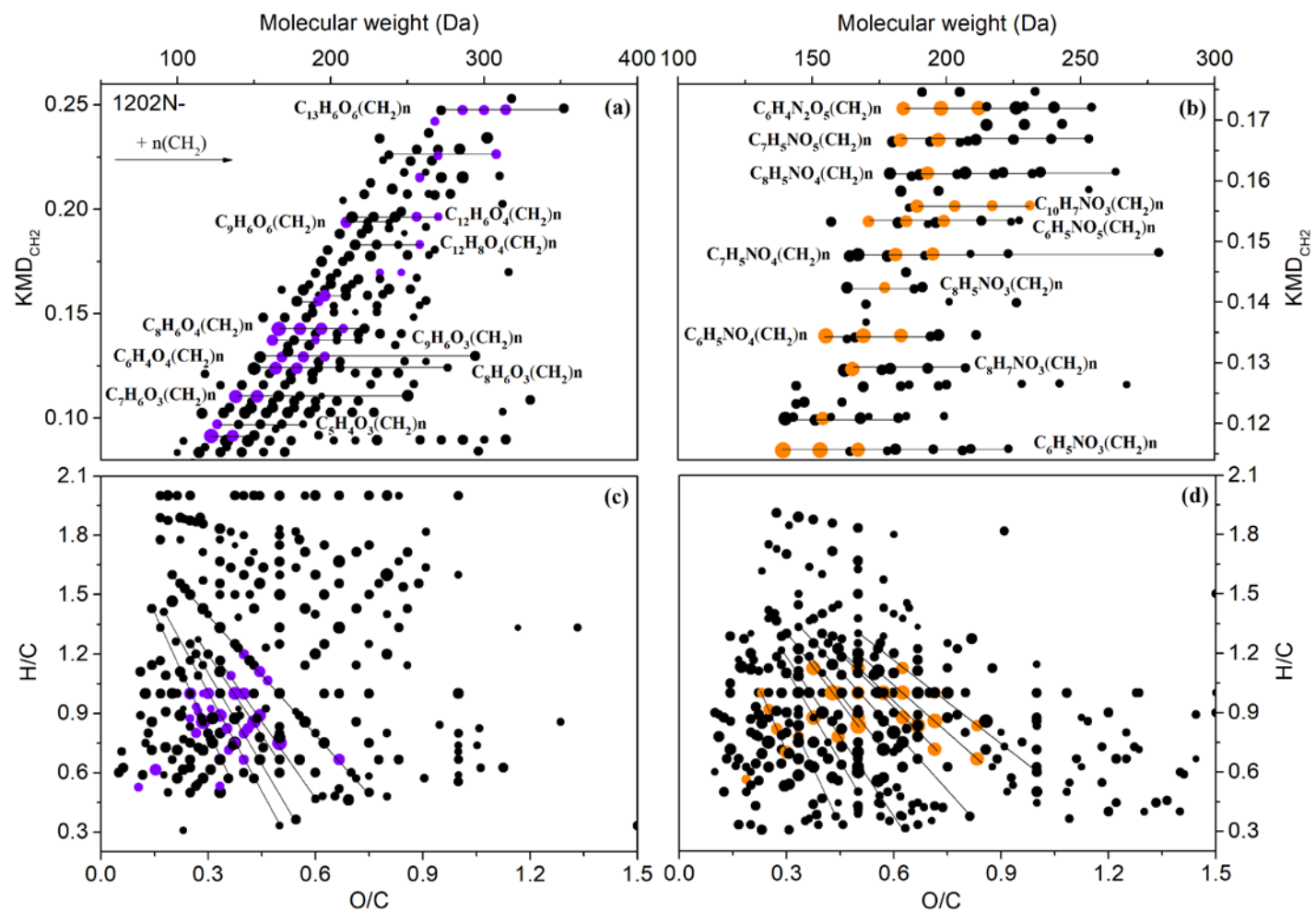


Figure 4

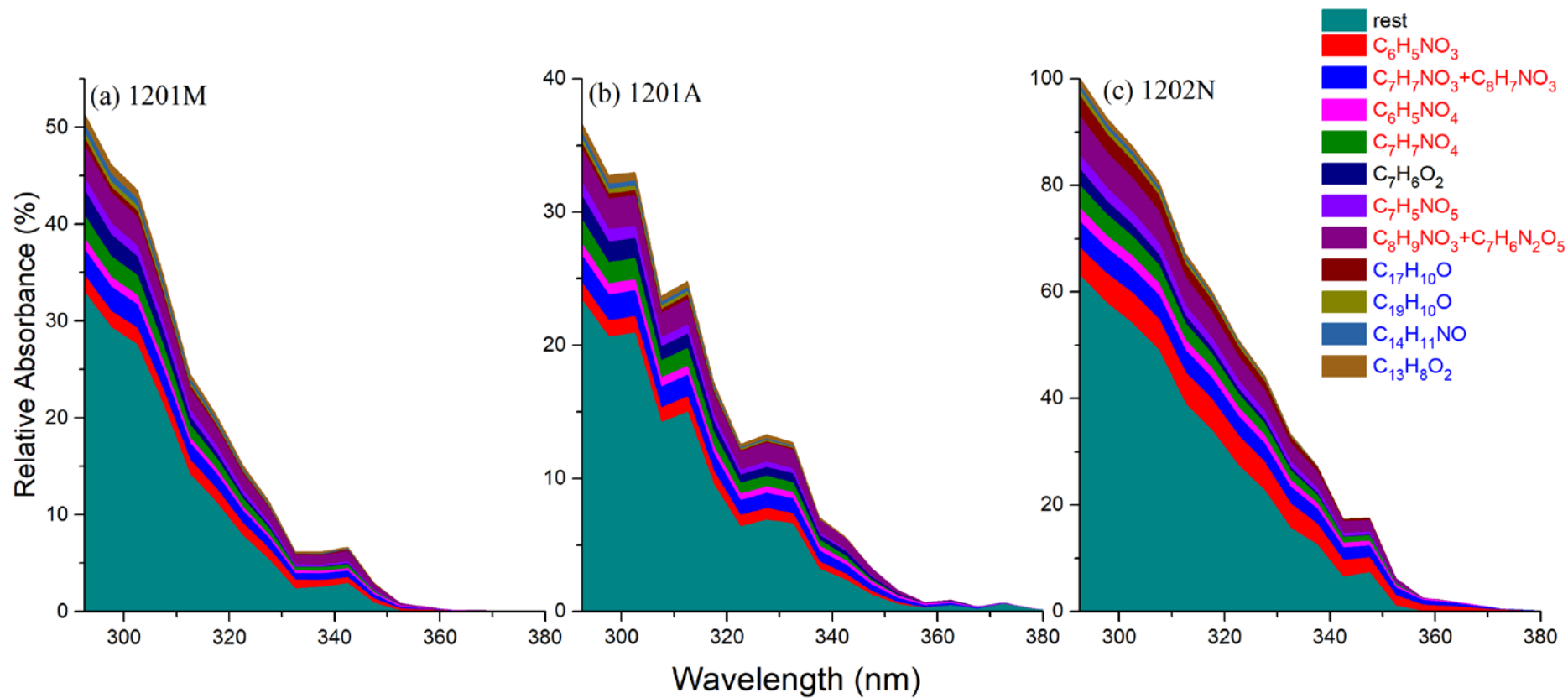


Figure 5

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