



Supplement of

Chemical composition, optical properties, and oxidative potential of water- and methanol-soluble organic compounds emitted from the combustion of biomass materials and coal

Tao Cao et al.

Correspondence to: Jianzhong Song (songjzh@gig.ac.cn)

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- 40 spectra due to MeOH and H₂O residues. The peaks were assigned to specific compounds
- 41 as follows: Levoglucosan (L), Phthalic acid (PA)

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44 **S1. Biomass and coal samples**

45 In this study, six biomass materials and five types of coal were collected and burned to
46 investigate the optical and chemical properties of brown carbon (BrC) fractions emitted from
47 biomass burning (BB) and coal combustion (CC) smoke. The six biomass materials consisted
48 of three types of crop straw (wheat straw [WS], rice straw [RS], and corn straw [CS]) and
49 three types of wood (pine wood [PW], Chinese fir [CF], and white poplar [WP]). The three
50 crop straws were chosen because they were the main types of crop straw burned in China.
51 These crop straws are usually used as fuels for heating in the winter or cooking in rural areas
52 throughout the year, and are also occasionally burned in agricultural fields after the harvest
53 season (Ke et al., 2019). The three wood materials are widespread in forests and are
54 commonly used as biomass fuels in some rural areas of China. The combustion of these crop
55 straws and woods has been reported to make a significant contribution to the atmospheric
56 aerosol in China (Fan et al., 2018; Shen et al., 2013). Therefore, these biomass materials were
57 selected as representative biomass fuels for the study of BB-derived BrC. In this study, WS,
58 RS, and CS were collected in the rural area of Bengbu, Anhui Province, China, while PW, CF,
59 and WP were collected from a forest area in Lu'an, Anhui Province, China. Before the
60 experiment, the crop straws and wood materials were washed with water and air dried for
61 seven days.

62 In some developing countries, such as China, coal is still an important fuel in rural areas
63 and also makes a large contribution to the levels of atmospheric pollution. In this study, five
64 coals were chosen for the investigation of their BrC fractions from CC. They consisted of
65 four bituminous coals (B-1, B-2, B-3, and B-4, with volatile fractions of 34%, 32%, 25%, and

66 19%, respectively) and one anthracitic coal (with a volatile fraction of 3.3%). These five
67 coals represented the major types of coal used for residential CC in China. After collection,
68 the coals were washed with water three times to remove dust and then air-dried. Then raw
69 coal was crushed, fully mixed, and made into coal briquettes.

70

71 **S2. Collection of smoke samples from BB and CC**

72 Samples of the smoke emitted from BB and CC were collected in a combustion and
73 sampling system that was introduced in our previous studies (Fan et al., 2018; Li et al., 2018).
74 The instrument was made of stainless steel and consisted of a combustion hood, clean air
75 dilution, and injection ports, smoke pipe, mixing fan, mixing chamber, PM_{2.5} sampler
76 (JCH-120F Intelligent medium flow PM sampler, Juchuang Environmental Protection Group
77 Co., Ltd, Qindao, China), and exhaust port. The smoke samples emitted from BB and CC
78 were then collected as follows:

79 (1) Biomass burning smoke samples. The biomass fuels were first prepared as small
80 pieces (length ~10 cm) and then placed on a combustion stove. After dropping 1 mL of
81 alcohol on the biomass fuels they were ignited with an electronic gas lighter. The smoke
82 particles were diluted and transported into the mixing chamber. Finally, smoke particles were
83 collected on quartz fiber filters (Ø 90 mm: Whatman, Maidstone, UK) in a PM_{2.5} sampler at a
84 flow rate of 80 L/min. Five complete experiments were conducted for each biomass fuel and
85 five smoke PM_{2.5} filter samples were obtained.

86 (2) Coal combustion smoke samples. The smoke particles emitted from the CC samples
87 were also collected in the same combustion and sampling system. Sample collection was

88 conducted according to the method introduced by Li et al. (2018). Briefly, two anthracite
89 briquettes were ignited in a burning coal honeycomb briquette stove and were then moved
90 into the other coal stove. After the burning stage of coal was reached and smoke emissions
91 were minimized, the coal stove was placed into the sampling system. Then, one honeycomb
92 sample was placed in the pre-burned coal stove. The resulting smoke was diluted and passed
93 into the mixing chamber. Finally, smoke samples were collected with the PM_{2.5} sampler at a
94 flow rate of 80 L/min. To obtain sufficient smoke sample for the comprehensive
95 characterization of the BrC fractions, each coal was burned at least for three cycles. All
96 quartz filters were baked for 6 h at 450 °C to remove any organics absorbed on the filters and
97 then wrapped with baked aluminum foil. After sampling, the filter samples were re-wrapped
98 with baked aluminum foil and stored in a refrigerator (−20 °C) prior to analysis.

99 Field blank quartz filters were collected before each group of combustion experiments
100 under conditions in which the fuels were not ignited. The field blank filters were used to
101 correct the mass of smoke PM_{2.5} and water-/methanol- soluble BrC, as well as the optical
102 signals and DTT consumption by BrC. To prevent contamination of the following sample, the
103 collection system was cleaned before each new combustion experiment.

104

105 **S3. Extraction and fractionation of BrC**

106 The BrC fractions (i.e., water-soluble organic compounds [WSOC], humic-like
107 substances [HULIS], and methanol-soluble organic compounds [MSOC]) were obtained with
108 solvent extraction and a solid-phase extraction (SPE) method, as indicated in our previous
109 studies (Fan et al., 2018; Fan et al., 2016; Li et al., 2018). The filter samples were

110 ultrasonically extracted three times with 20 mL ultrapure water for 30 min. The extracts were
111 filtered through a 0.22 μm polytetrafluoroethylene (PTFE) syringe filter to obtain the WSOC
112 fraction. The HULIS fraction in WSOC was isolated with an SPE method (Chen and Bond,
113 2010; Zhang et al., 2013; Cheng et al., 2016; Cheng et al., 2017). Briefly, the pH of the
114 WSOC solution was acidified to 2 with HCl, and the solution introduced into a
115 pre-conditioned SPE cartridge (Oasis HLB, 200 mg, Waters, Milford, MA, USA). The most
116 hydrophilic species and inorganic salt ions or metal ions was removed by the cartridge,
117 whereas the relatively hydrophobic HULIS fraction was retained. Then the SPE column was
118 rinsed with pure water to remove inorganics and the retained organics were eluted with
119 methanol. Finally, the HULIS solution was evaporated to dryness under a gentle nitrogen
120 stream. It is noted that HULIS is less polar components of the WSOC, which were also
121 usually refer to the relatively hydrophobic fraction of water-soluble organic carbon (Verma et
122 al., 2012, Zheng et al., 2013, Katsumi et al., 2018).

123 The MSOC was obtained by a method developed by Cheng et al. (2016). Briefly, the
124 filter samples were immersed in 20 mL methanol (Macklin, >99.9%, Shanghai, China) for 2 h
125 and then filtered through a 0.22 μm PTFE syringe filter (Jinteng, Tianjin, China). Static
126 digestion without ultrasonic treatment can avoid the loss of particulate matter and facilitate
127 the determination of dissolved organic matter content. Finally, the dried residual filters and
128 untreated filters were analyzed to determine their carbon contents.

129

130 **S4. Organic carbon/elemental carbon (OC/EC) and total organic carbon (TOC) analysis**

131 The OC and EC in smoke filter samples were measured using an OC/EC analyzer (TOT,

132 Sunset Laboratory Inc., Portland, OR, USA). The analysis was conducted according to the
133 National Institute of Occupational Safety and Health (NIOSH) 870 method (Chow et al.,
134 2001; Wu et al., 2016). The TOC content of WSOC and HULIS was determined by a
135 high-temperature catalytic oxidation instrument (VCPH analyzer, Shimadzu, Kyoto, Japan)
136 following the non-purgeable OC protocol. After the removal of inorganic carbon, the sample
137 was oxidized at high temperature (680 °C) and the peak area of CO₂ was determined by a
138 non-dispersive infrared detector. The content of the MSOC fraction was indirectly obtained
139 by subtracting the TC concentrations of the extracted filters from that of the untreated filters.
140 The experiments were all repeated three times and the concentrations reported here were
141 corrected for their respective blank concentrations.

142 In this study, the “μgC” was used as weight unit that referring to the mass of carbon for
143 the OC, EC, WSOC, HULIS-C, and MSOC fractions.

144

145 **S5. UV-visible properties**

146 The UV-visible absorption spectra of the BrC fractions (i.e., WSOC, HULIS, and MSOC)
147 were recorded between the wavelengths of 200 to 700 nm using a UV-2600 UV-vis
148 spectrophotometer (Shimadzu, Japan). The sample solution was placed in a 1-cm quartz
149 cuvette and analyzed at 1 nm intervals. Ultrapure water was used as a blank reference for the
150 WSOC and HULIS solutions, while pure methanol was used for the MSOC fraction. The
151 field blank sample solution was also used as the blank sample, and the interference from the
152 instrument and operating blank was determined.

153 The absorption Ångström exponent (AAE) is a measure of the spectral dependence of

154 the light absorption of BrC solutions (Cheng et al., 2016), which was calculated by the
155 following equation:

$$156 \quad A_{\lambda} = K\lambda^{-AAE} \quad (2)$$

157 where A_{λ} is the absorbance derived from the spectrophotometer at a given wavelength λ (330–
158 400 nm) and K is a constant.

159 The mass absorption efficiency at 365 nm (MAE_{365}) is an important parameter used to
160 characterize the light absorbing ability of BrC. It was obtained using the following equation:

$$161 \quad MAE_{\lambda} = \frac{A_{\lambda}}{c \cdot L} \times \ln(10) \quad (3)$$

162 where A_{λ} is the absorbance at λ nm, c is the carbon concentration of BrC in solution (μgC
163 mL^{-1}), and L is the absorbing path length.

164

165 **S6. Principal component analysis (PCA)**

166 PCA is a widely used chemometric procedure that can transform the original variables to
167 the principal component by dimension reduction analysis. The principal component (two or
168 three) generally contain most of the original variable information (Popovicheva et al., 2020).
169 Thus, in this study, PCA was performed to find out the key factors that may affect the DTT
170 activities from a series of characteristic of BrC fraction (MAE_{365} , percentage content of four
171 fluorophores, and percentage content of R-H, H-C-C=, H-C-O, and Ar-H groups). The main
172 calculation is based on SPSS version 19 (IBM SPSS Statistics) (Shivani et al., 2019), and the
173 confidence interval is 95%.

174

175 **S7. Quality control**

176 The experimental blank and field blank were both analyzed in this study. The
177 experimental blank was treated in the same method as it for smoke samples, which was used
178 to assess the errors that may be introduced in the process of experimental operation and their
179 repeatability. In this study, the average blank values of sextuple collections of WSOC, HULIS
180 and MSOC were $0.28 \pm 0.07 \mu\text{gC}/\text{cm}^2$, $0.12 \pm 0.03 \mu\text{g C}/\text{cm}^2$ and $0.38 \pm 0.09 \mu\text{gC}/\text{cm}^2$,
181 respectively. The repeatability of analysis procedure was obtained based on one blank filter
182 sample, which were 3.1%, 2.2% and 4.5% for WSOC, HULIS and MSOC, respectively.

183 The field blank filter (ambient and ignition coal (for coal combustion only)) were
184 collected follow the procedure for sampling smoke $\text{PM}_{2.5}$ samples, but without ignited fuel
185 samples. The field blank filters were treated as the method for smoke samples. The average
186 values of WSOC, HULIS and MSOC were $1.8 \pm 0.2 \mu\text{gC}/\text{cm}^2$, $0.7 \pm 0.1 \mu\text{gC}/\text{cm}^2$ and 5.3 ± 0.9
187 $\mu\text{gC}/\text{cm}^2$, respectively. They were much less than the values of that in smoke particle.

188 In the present study, all the BrC results were blank-corrected by subtracting an average
189 field blank value for each sample. The data were present as a mean \pm standard deviation
190 based on triplicate analysis of filter sample for each combustion experiment.

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193 **Table S1.** Region, excitation/emission wavelength maxima range and attribution of chromophores in BrC
 194 emitted from BB and CC

Region	λ_{ex} max(nm)	λ_{em} max(nm)	Fluorescent compounds	References
I	220-250	290-320	protein-like amino acid	(Cui et al., 2016; Coble, 1996)
II	220-250	320-380	protein-like UV region	(Mostofa et al., 2011; Mounier et al., 2010)
III	220-250	380-460	fulvic-like	(Chen et al., 2003; Santos et al., 2012)
IV	250-380	280-380	tryptophan-like/microbial byproduct	(Santos et al., 2012; Cui et al., 2016)
V	250-380	380-460	humic-like organic	(Chen et al., 2003; Qin et al., 2018)

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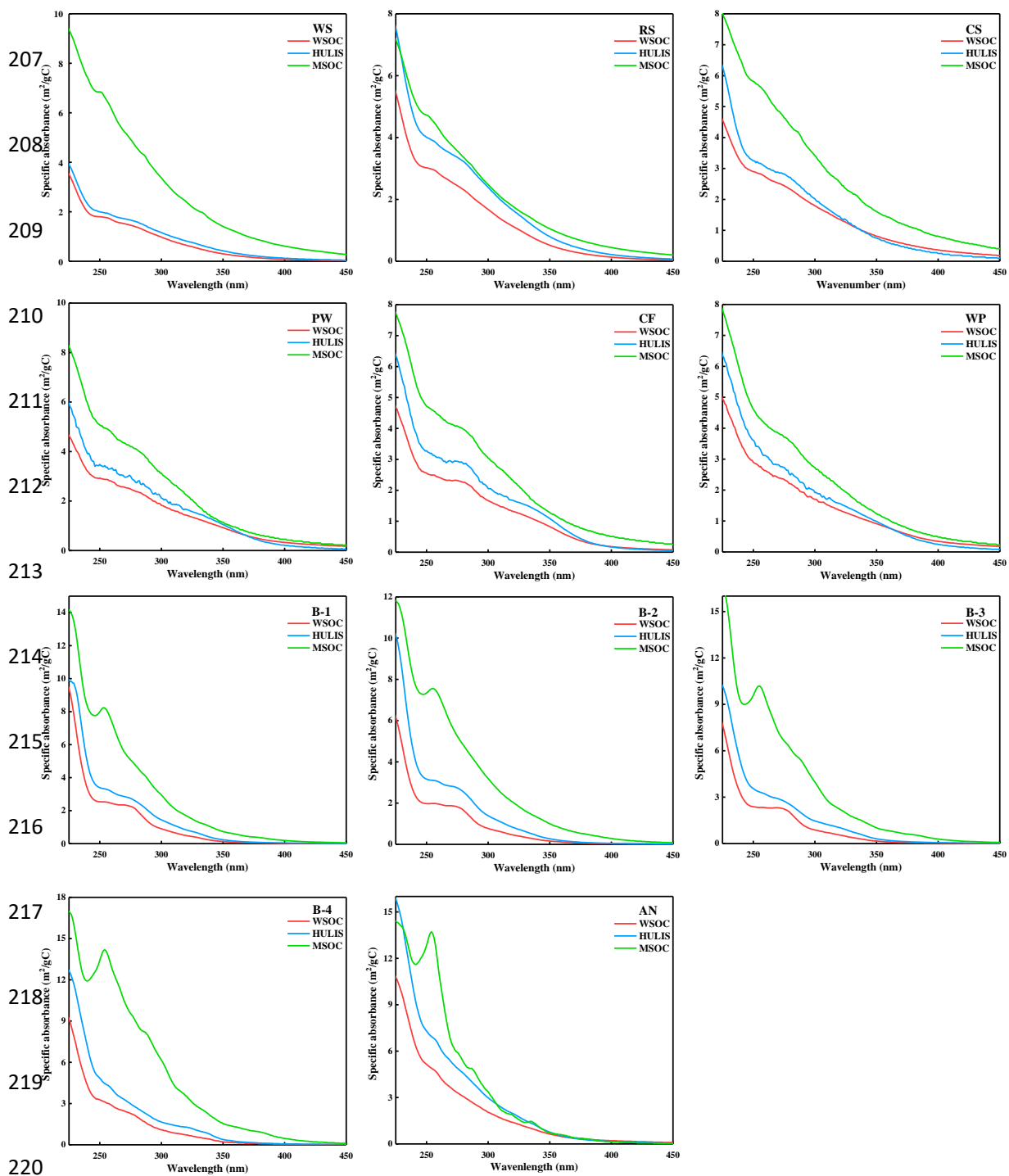
Table S2. Results of DTT assay conducted on the WSOC, HULIS and MSOC of smoke samples

	Samples	Calculated by PM mass(pmol/min/ μg)		
		WSOC	HULIS	MSOC
Biomass burning	WS	4.5 \pm 3.8	3.2 \pm 2.8	85 \pm 12
	RS	6.1 \pm 0.5	5.5 \pm 0.6	84 \pm 5.6
	CS	7.4 \pm 1.4	3.0 \pm 0.7	69 \pm 11
	PW	5.9 \pm 3.3	3.1 \pm 0.3	9.1 \pm 1.5
	CF	5.5 \pm 2.3	3.2 \pm 0.9	14 \pm 6.9
	WP	5.6 \pm 2.8	2.6 \pm 1.0	11 \pm 7.6
Coal combustion	B-1	1.6 \pm 0.2	1.1 \pm 0.1	7.7 \pm 0.8
	B-2	2.1 \pm 0.2	1.5 \pm 0.1	11 \pm 3.2
	B-3	0.5 \pm 0.1	0.5 \pm 0.1	3.2 \pm 1.7
	B-4	1.9 \pm 0.5	0.9 \pm 0.2	3.1 \pm 1.0
	AN	0.7 \pm 0.2	0.4 \pm 0.1	6.7 \pm 2.9

202 ^a error bars represent standard deviation based on quadruplicate test

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221 **Figure S1.** The normalized UV-vis spectra by organic carbon contents of WSOC, HULIS,

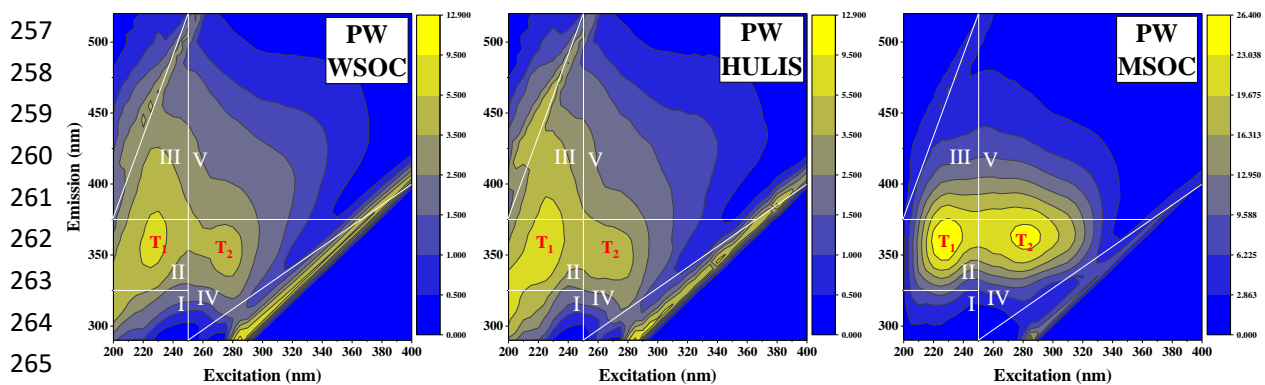
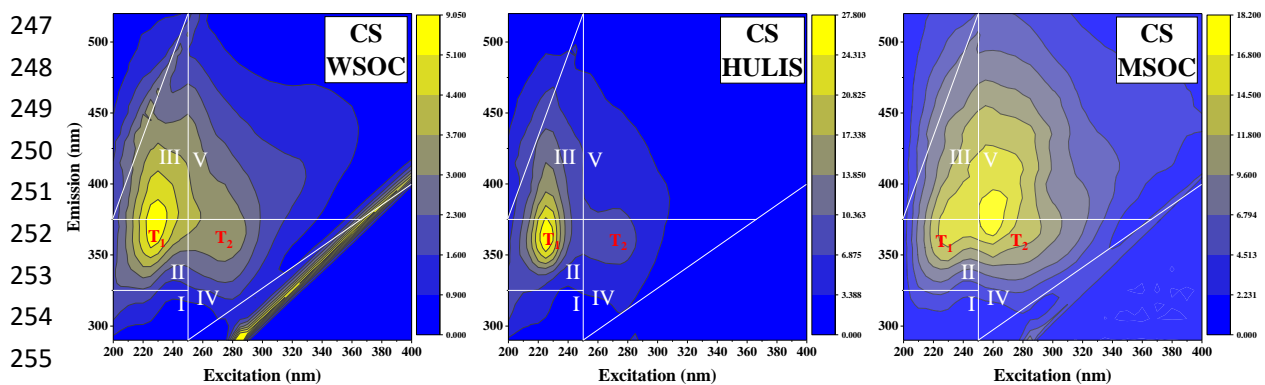
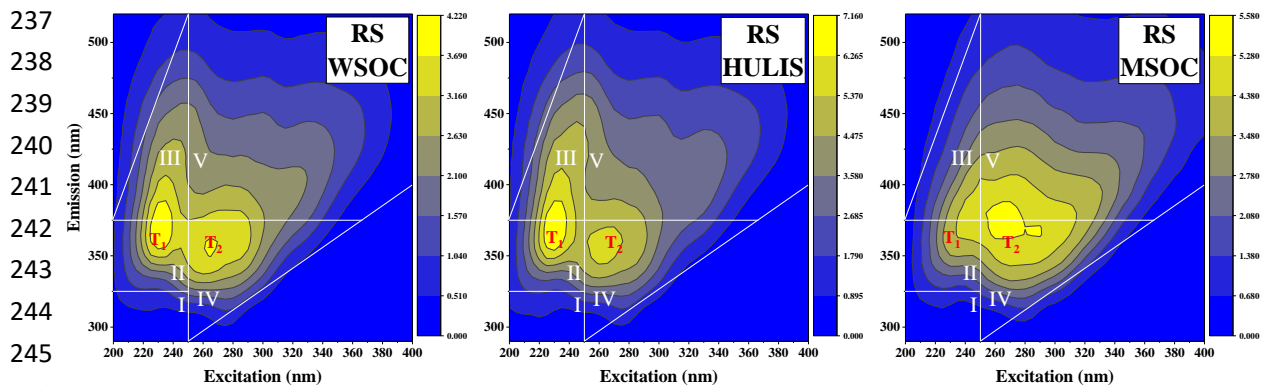
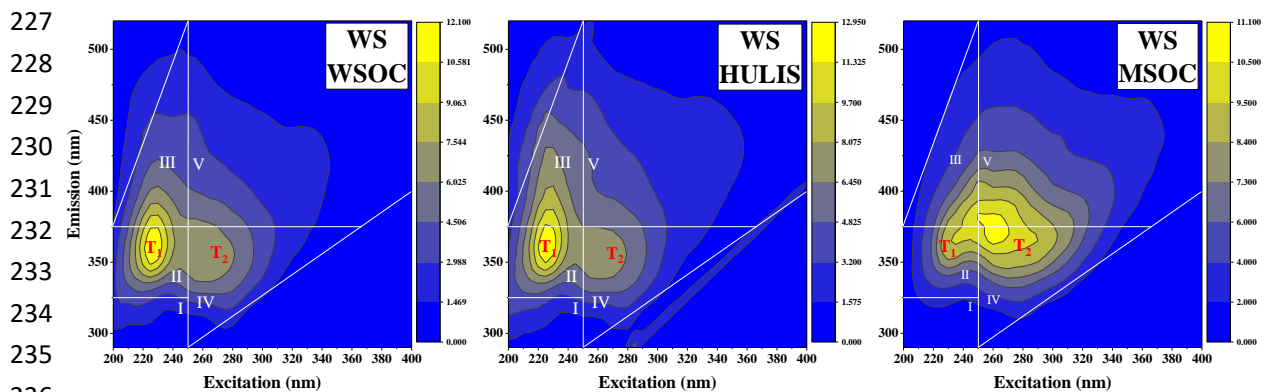
222 and MSOC fractions

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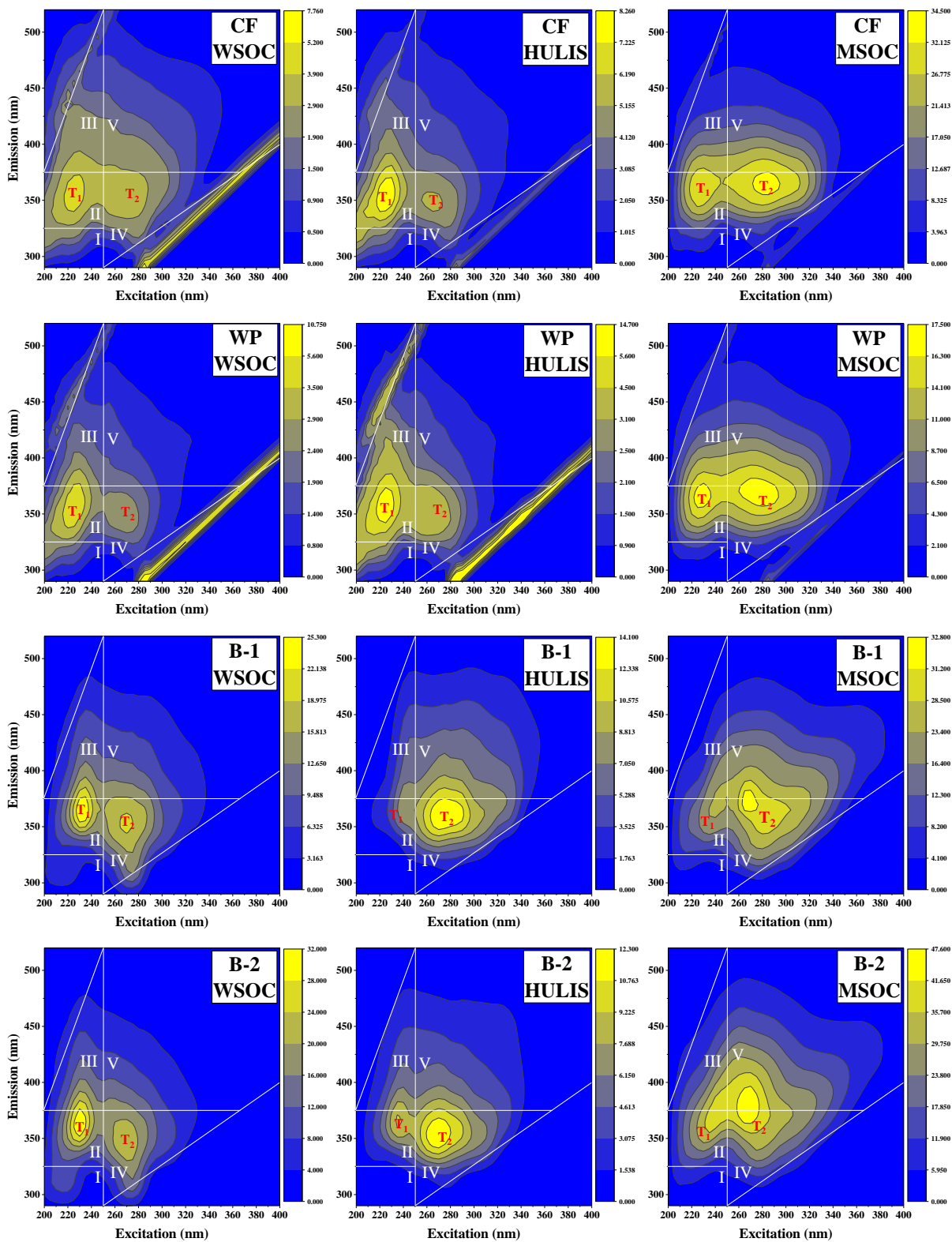
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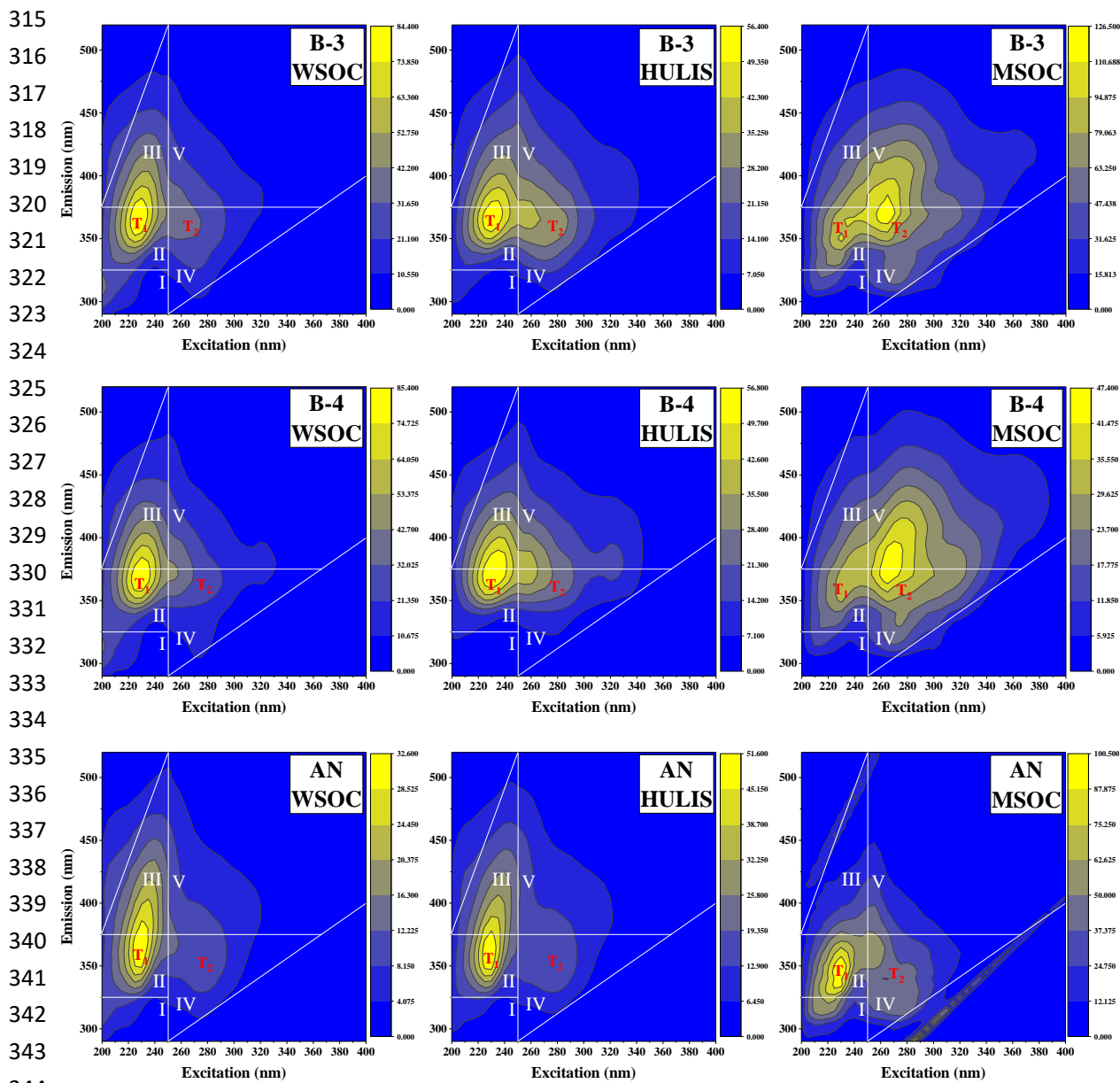
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345 **Figure S2.** EEM fluorescence counter maps of corresponding WSOC, HULIS, MSOC of BB
 346 and CC smoke samples, presented as specific intensity (a.u. L(mg C⁻¹))

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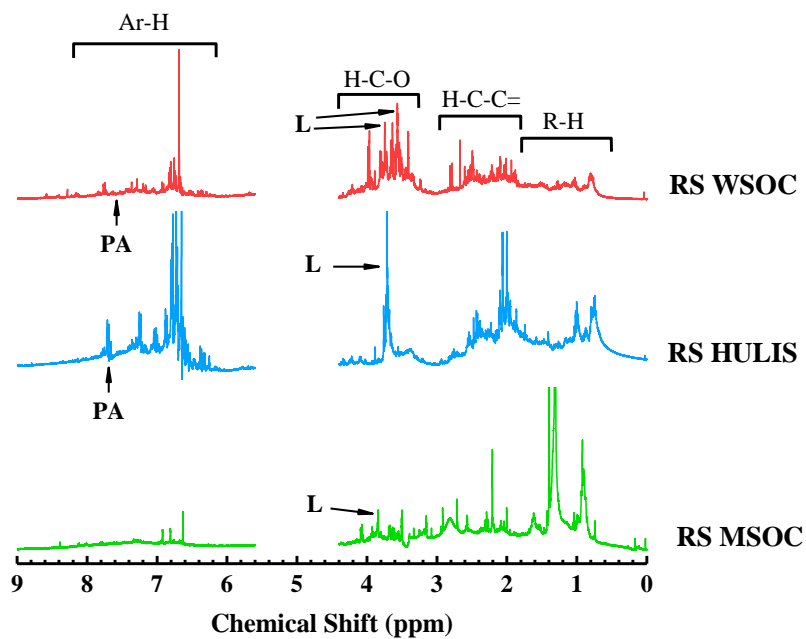
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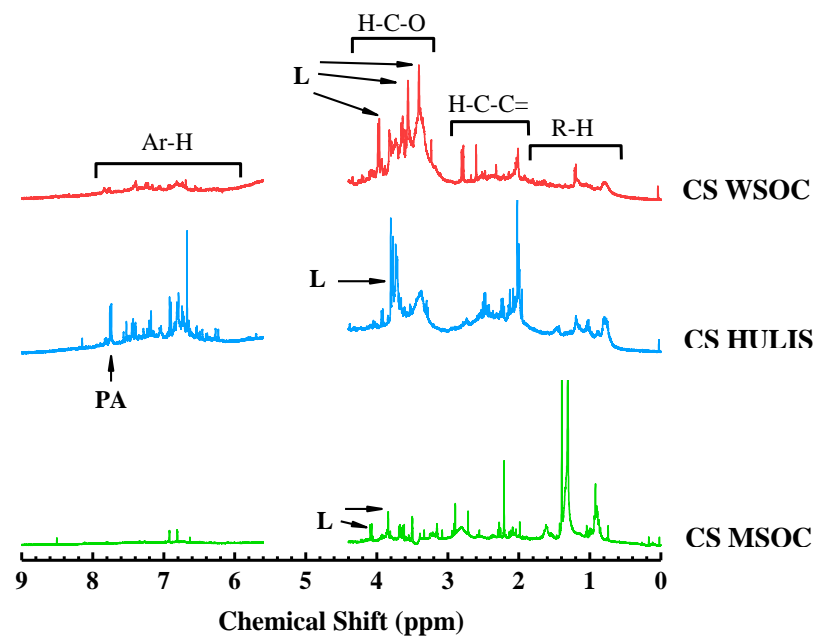
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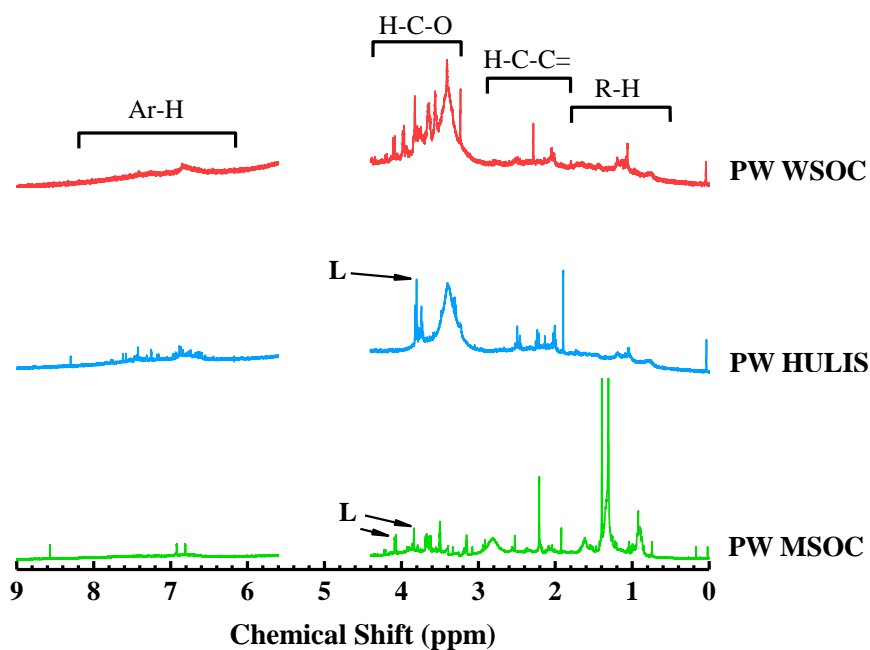
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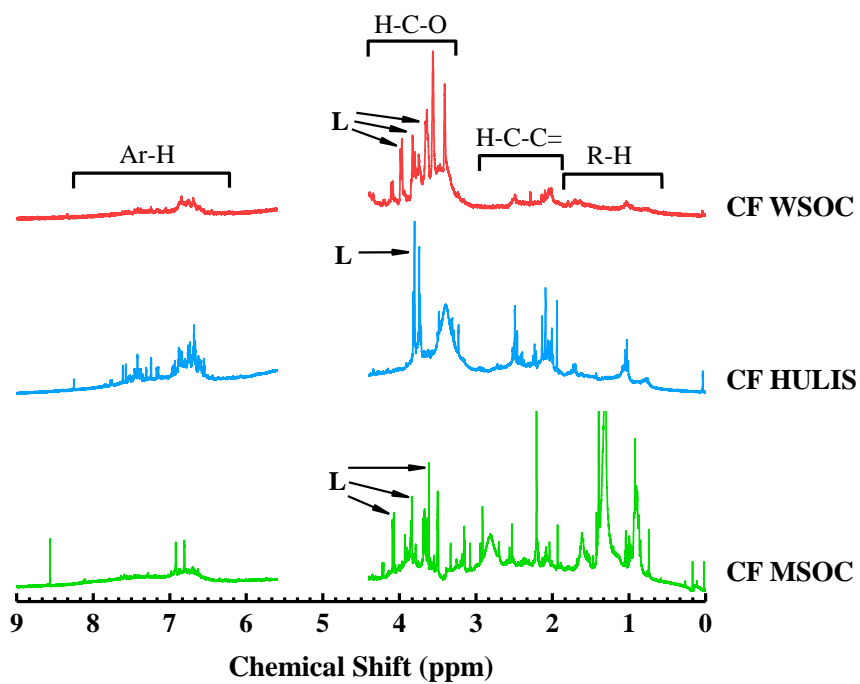
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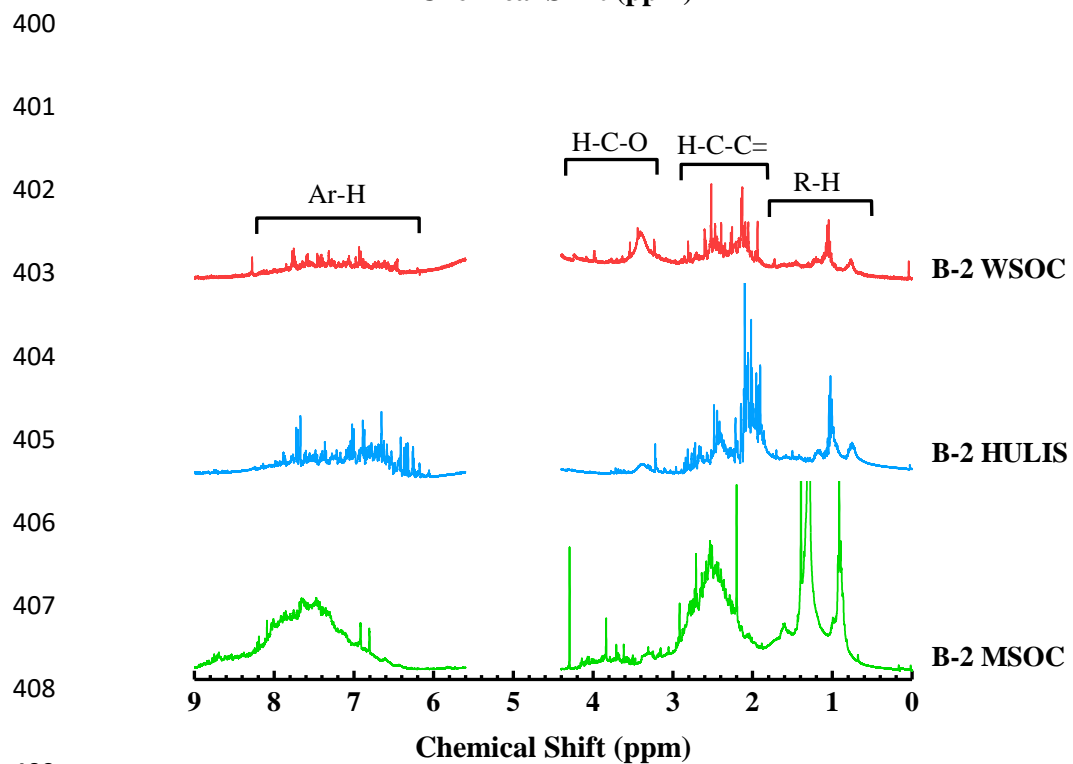
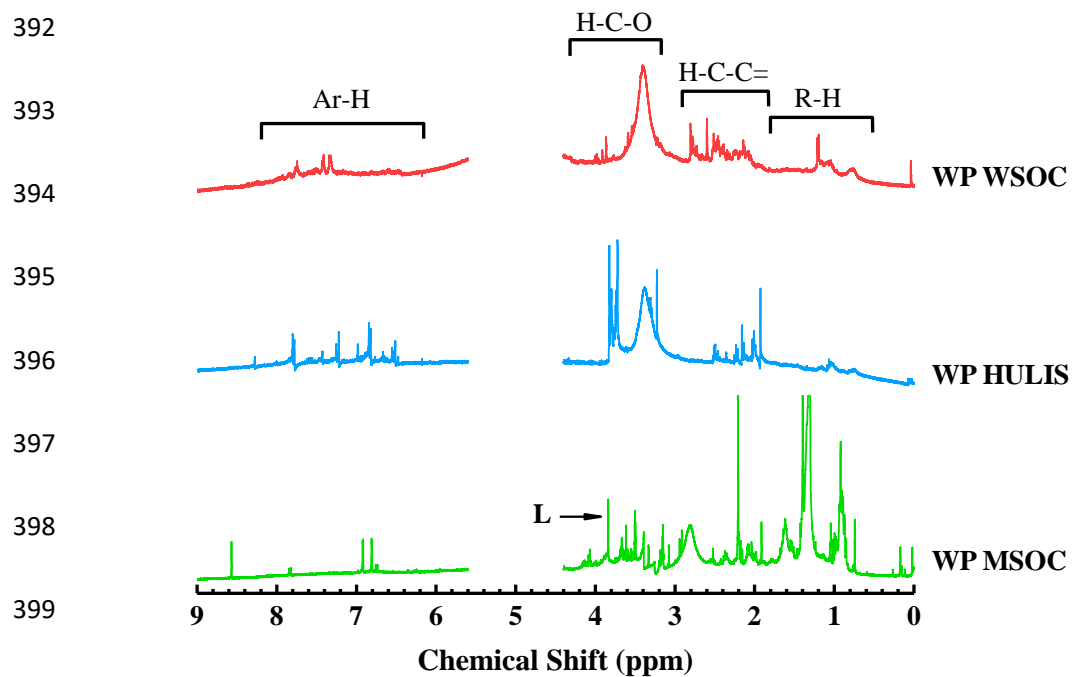


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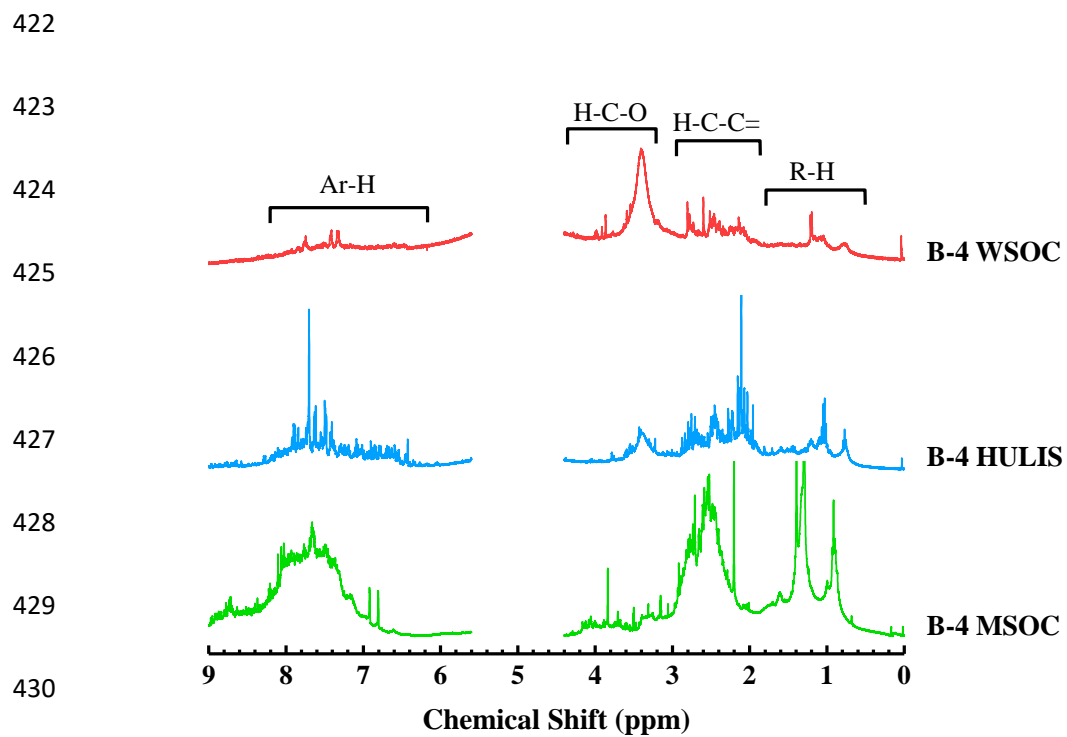
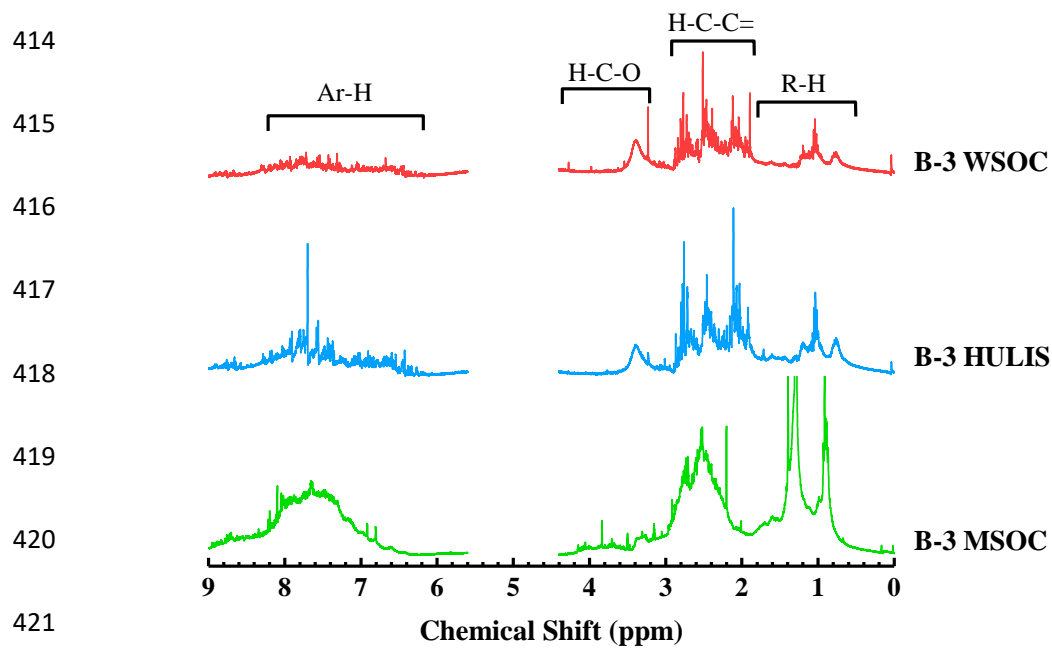
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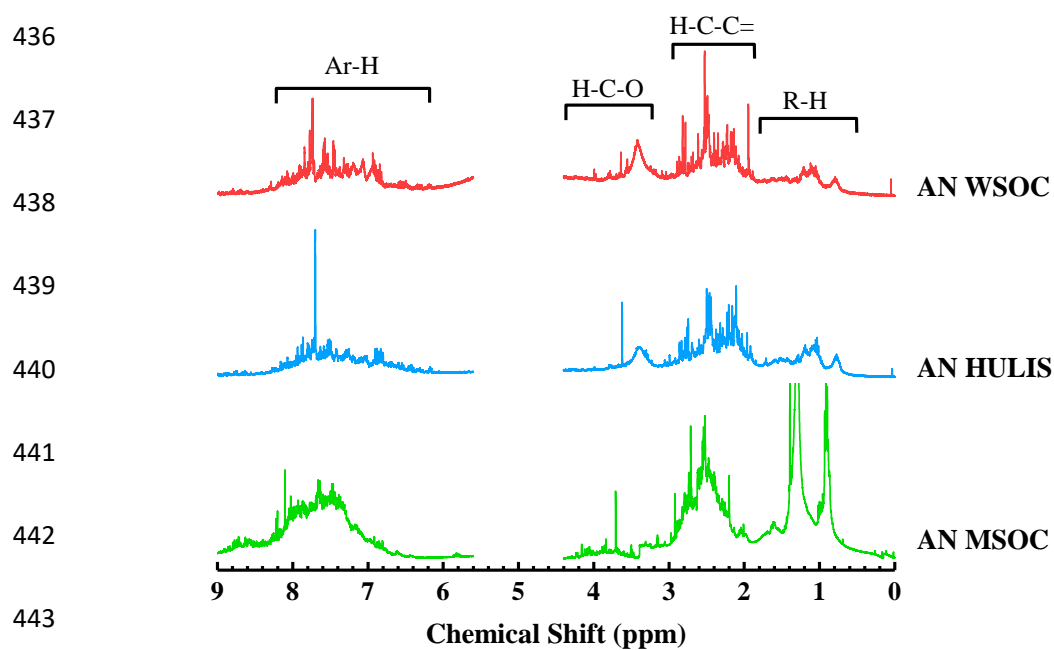
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445 **Figure S3.** $^1\text{H-NMR}$ stacking diagram of corresponding WSOC, HULIS, MSOC of BB and
 446 CC smoke samples. The segment from 4.40 to 5.60 ppm was removed for NMR spectra due
 447 to MeOH and H_2O residues. The peaks were assigned to specific compounds as follows:
 448 Levoglucosan (L), Phthalic acid (PA).

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