1   Supporting information

3   **Chemical composition, optical properties, and oxidative potential of water- and**

4   **methanol-soluble organic compounds emitted from the combustion of biomass materials**

5   **and coal**

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S1. Biomass and coal samples

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

In some developing countries, such as China, coal is still an important fuel in rural areas and also makes a large contribution to the levels of atmospheric pollution. In this study, five coals were chosen for the investigation of their BrC fractions from CC. They consisted of four bituminous coals (B-1, B-2, B-3, and B-4, with volatile fractions of 34%, 32%, 25%, and 19%,

66 respectively) and one anthracitic coal (with a volatile fraction of 3.3%). These five coals

67 represented the major types of coal used for residential CC in China. After collection, the coals

68 were washed with water three times to remove dust and then air-dried. Then raw coal was

69 crushed, fully mixed, and made into coal briquettes.

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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

87 samples were also collected in the same combustion and sampling system. Sample collection

88 was 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 ℃ 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 ℃) 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.

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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 was removed by the cartridge, whereas the relatively hydrophobic HULIS

117   fraction was retained. Then the SPE column was rinsed with pure water to remove inorganics

118   and the retained organics were eluted with methanol. Finally, the HULIS solution was

119   evaporated to dryness under a gentle nitrogen stream.

120   The MSOC was obtained by a method developed by Cheng et al. (2016). Briefly, the

121   filter samples were immersed in 20 mL methanol (Macklin, >99.9%, Shanghai, China) for 2 h

122   and then filtered through a 0.22 μm PTFE syringe filter (Jinteng, Tianjin, China). Static

123   digestion without ultrasonic treatment can avoid the loss of particulate matter and facilitate

124   the determination of dissolved organic matter content. Finally, the dried residual filters and

125   untreated filters were analyzed to determine their carbon contents.

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

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

129   Sunset Laboratory Inc., Portland, OR, USA). The analysis was conducted according to the

130   National Institute of Occupational Safety and Health (NIOSH) 870 method (Chow et al.,

131   2001; Wu et al., 2016). The TOC content of WSOC and HULIS was determined by a

132   high-temperature catalytic oxidation instrument (VCPH analyzer, Shimadzu, Kyoto, Japan)

133   following the non-purgeable OC protocol. The detailed measurement method is provided in

134   the SI file. The content of the MSOC fraction was indirectly obtained by subtracting the TC

135   concentrations of the extracted filters from that of the untreated filters. The experiments were

136   all repeated three times and the concentrations reported here were corrected for their

137   respective blank concentrations.

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139   **S5. UV-visible properties**

140   The UV-visible absorption spectra of the BrC fractions (i.e., WSOC, HULIS, and MSOC)

141   were recorded between the wavelengths of 200 to 700 nm using a UV-2600 UV-vis

142   spectrophotometer (Shimadzu). The sample solution was placed in a 1-cm quartz cuvette and

143   analyzed at 1 nm intervals. Ultrapure water was used as a blank reference for the WSOC and

144   HULIS solutions, while pure methanol was used for the MSOC fraction. The field blank sample

145   solution was also used as the blank sample, and the interference from the instrument and

146   operating blank was determined.

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

148   the light absorption of BrC solutions (Cheng et al., 2016), which was calculated by the

149   following equation:

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

151   where A_λ is the absorbance derived from the spectrophotometer at a given wavelength λ (330–

152   400 nm) and K is a constant.

153   The mass absorption efficiency at 365 nm (MAE_{365}) is an important parameter used to

154   characterize the light absorbing ability of BrC. It was obtained using the following equation:

155    $$\text{MAE}_\lambda = \frac{A_\lambda}{c \cdot L} \times \ln(10) \qquad (3)$$

156   where A_λ is the absorbance at λ nm, c is the carbon concentration of BrC in solution (μgC

157   mL^{-1}), and L is the absorbing path length.

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164 **Table S1.** Region, excitation/emission wavelength maxima range and attribution of chromophores in BrC

165 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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170 **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±3.8	3.2±2.8	85±12
	RS	6.1±0.5	5.5±0.6	84±5.6
	CS	7.4±1.4	3.0±0.7	69±11
	PW	5.9±3.3	3.1±0.3	9.1±1.5
	CF	5.5±2.3	3.2±0.9	14±6.9
	WP	5.6±2.8	2.6±1.0	11±7.6
Coal combustion	B-1	1.6±0.2	1.1±0.1	7.7±0.8
	B-2	2.1±0.2	1.5±0.1	11±3.2
	B-3	0.5±0.1	0.5±0.1	3.2±1.7
	B-4	1.9±0.5	0.9±0.2	3.1±1.0
	AN	0.7±0.2	0.4±0.1	6.7±2.9

171 [a] error bars represent standard deviation based on quadruplicate test

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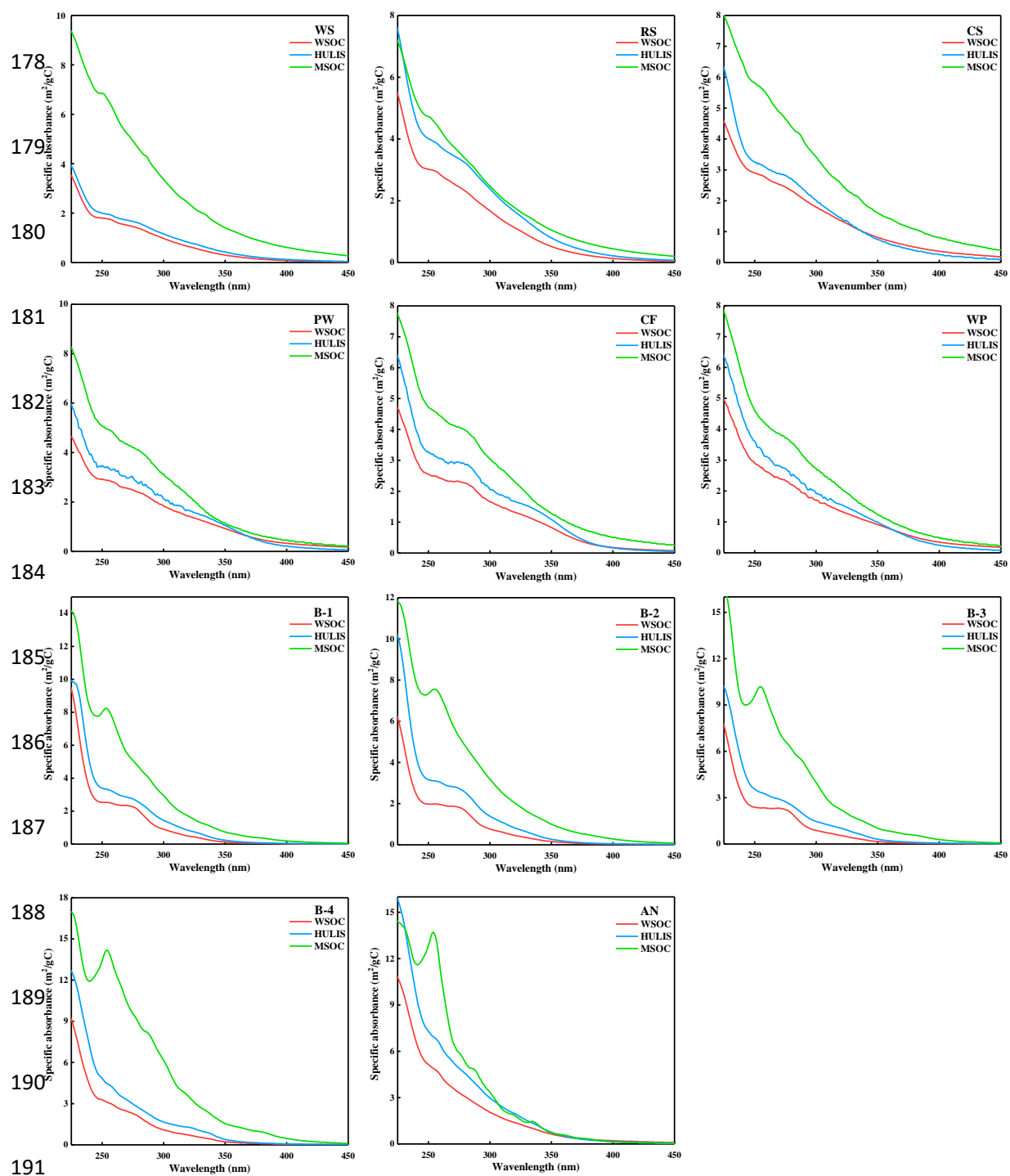
Figure S1. The normalized UV-vis spectra by organic carbon contents of WSOC, HULIS,

and MSOC fractions
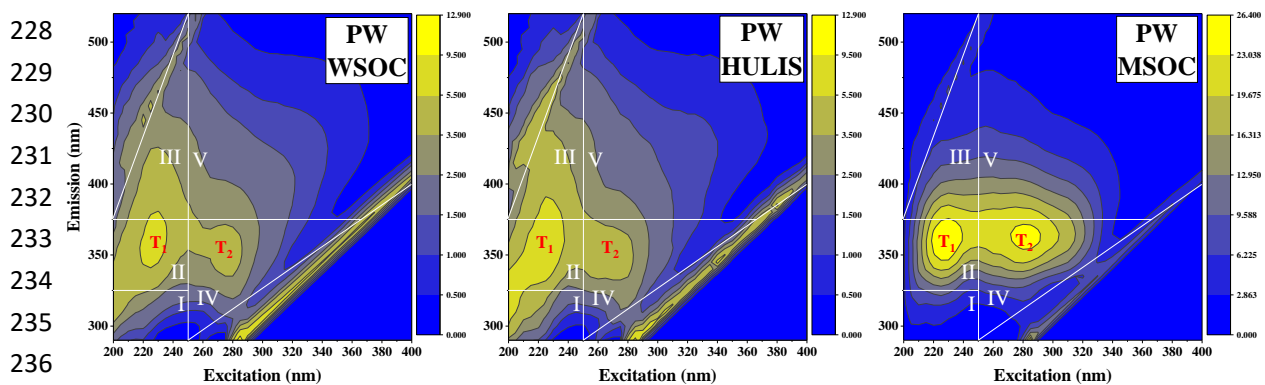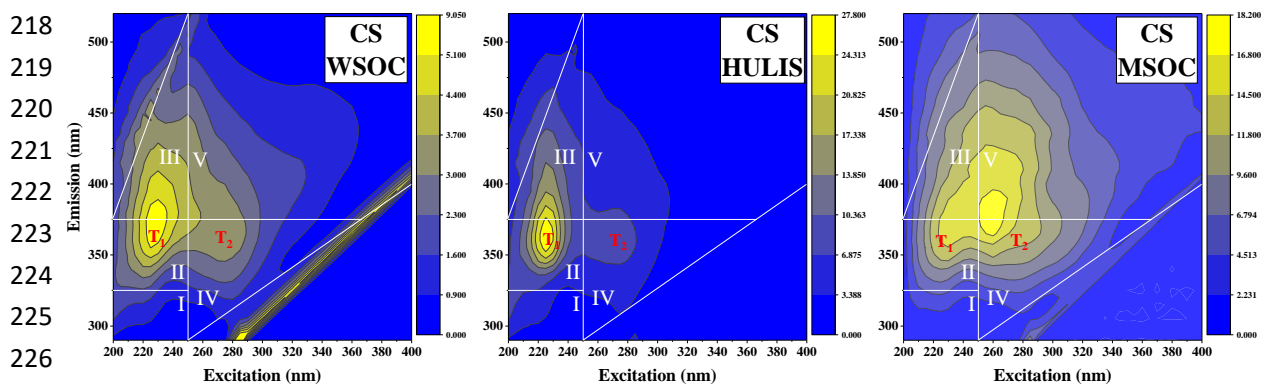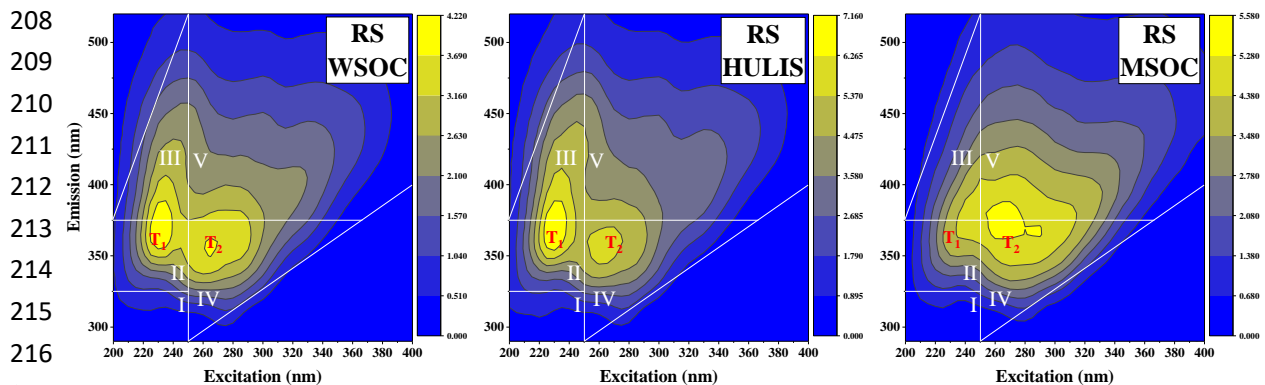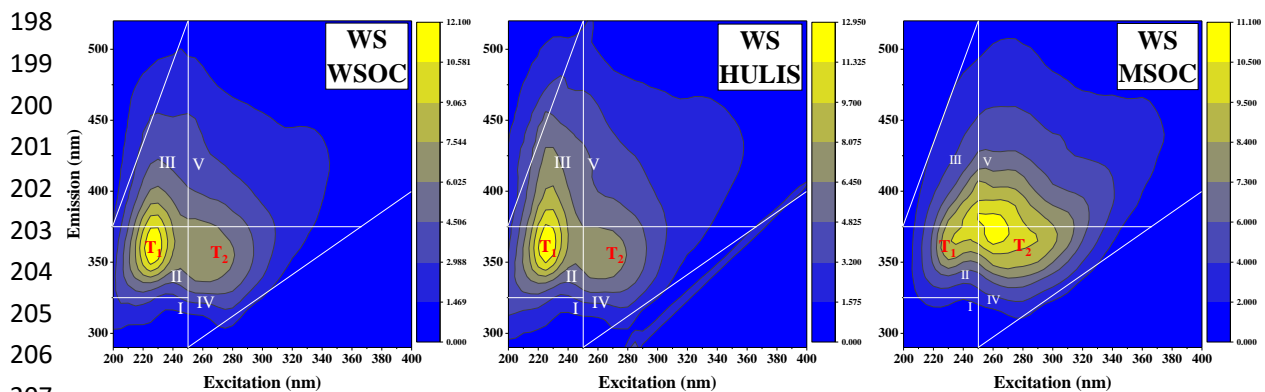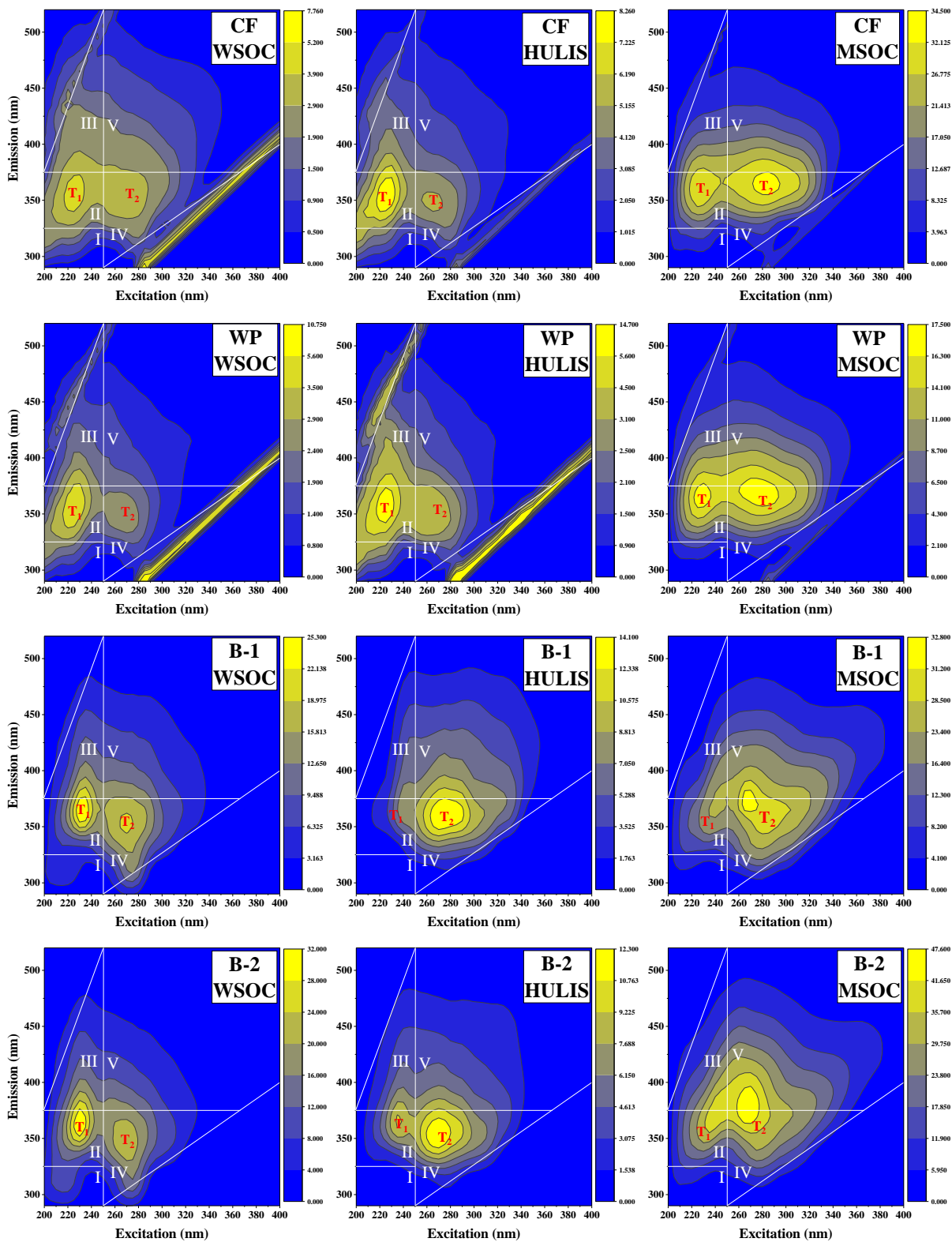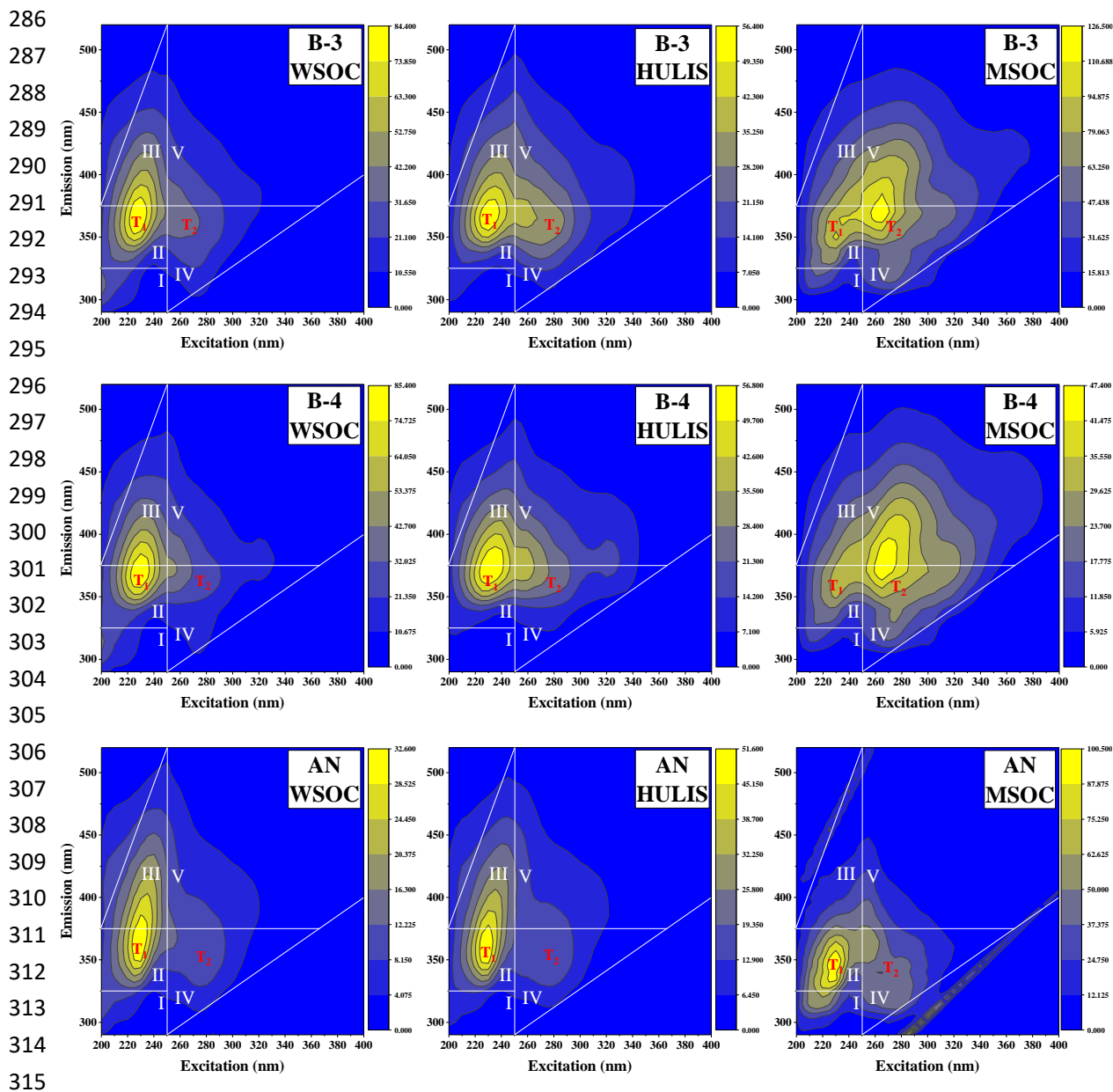
Figure S2. EEM fluorescence counter maps of corresponding WSOC, HULIS, MSOC of BB

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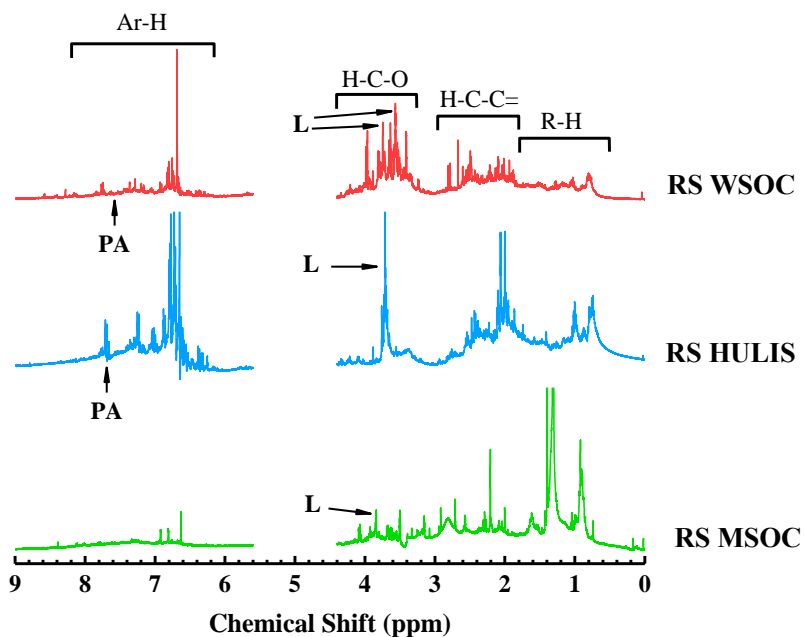
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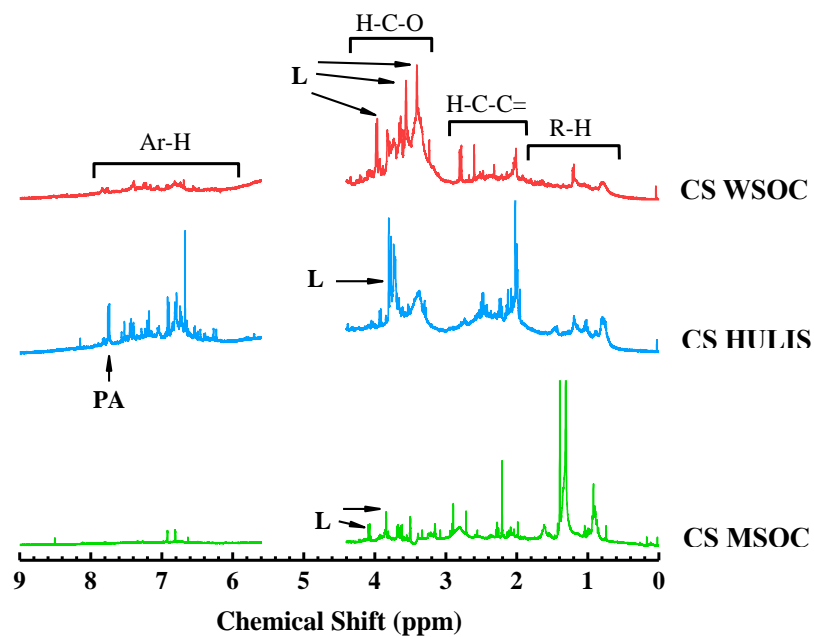
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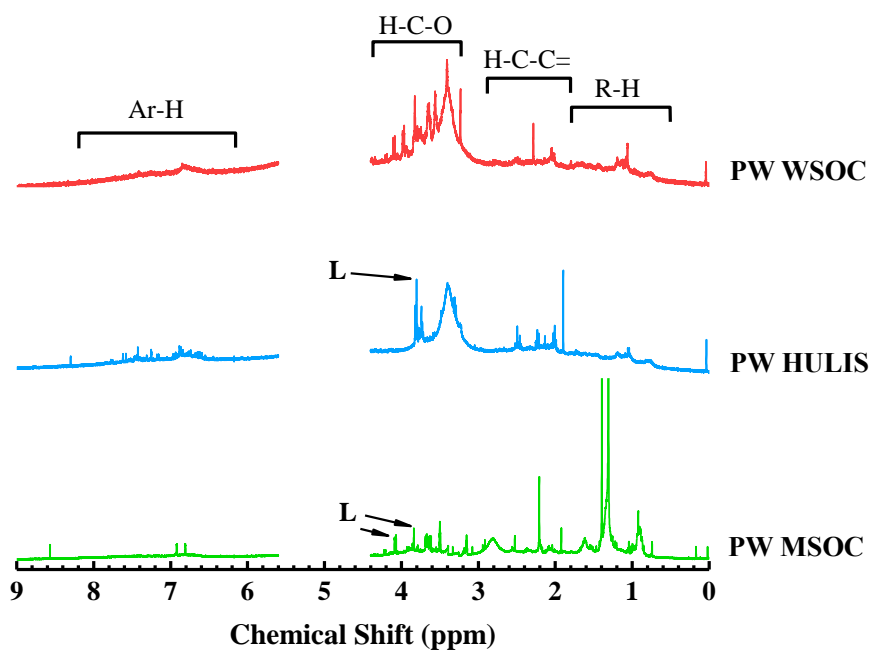
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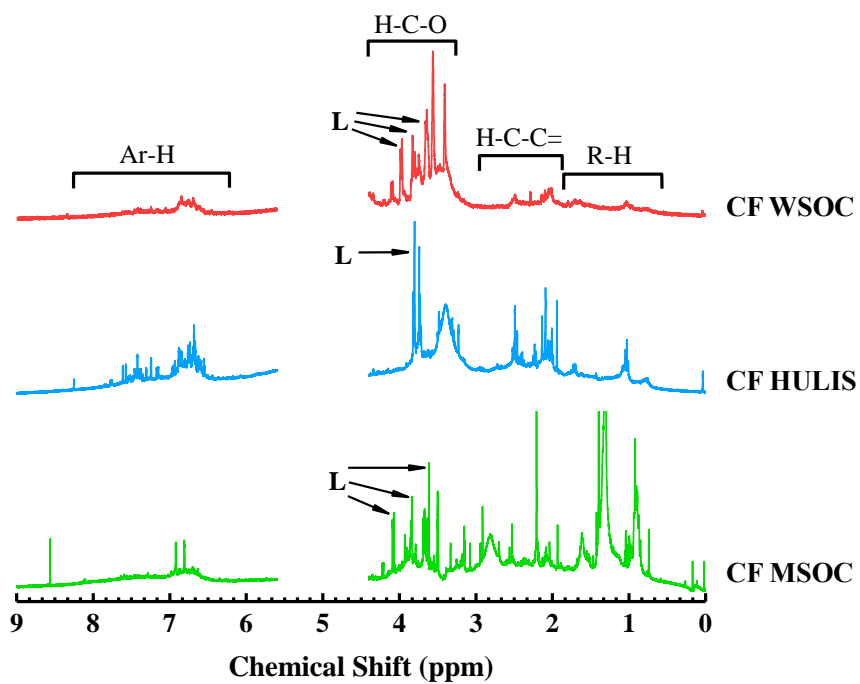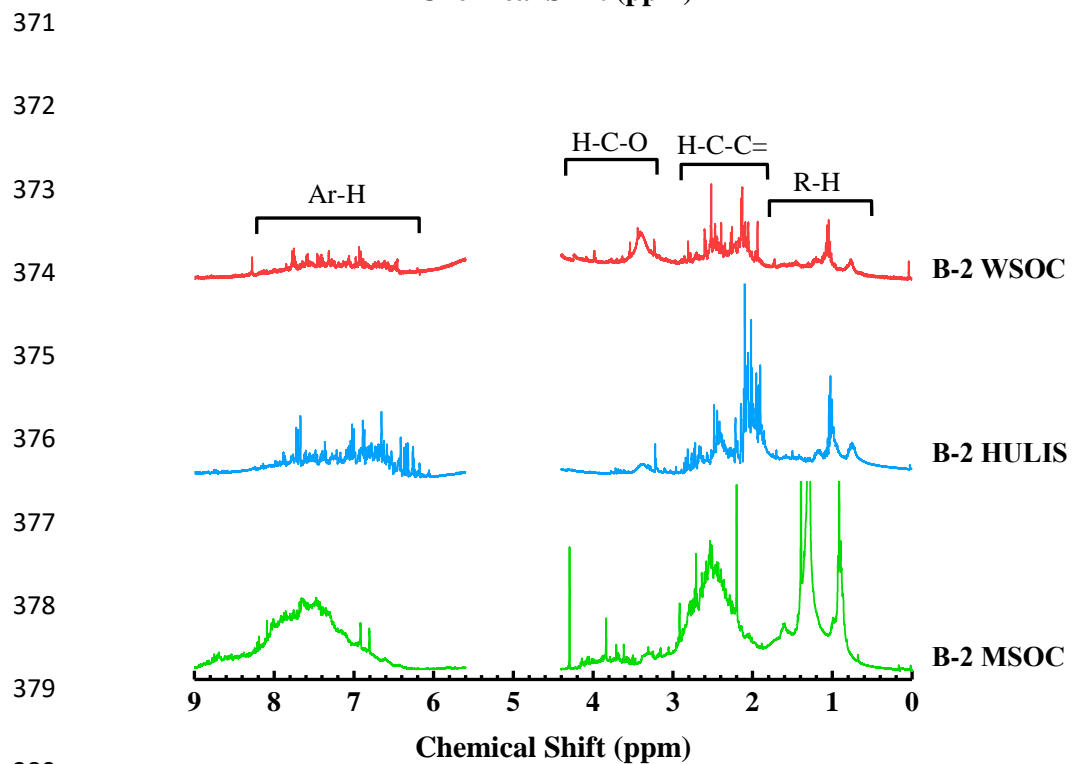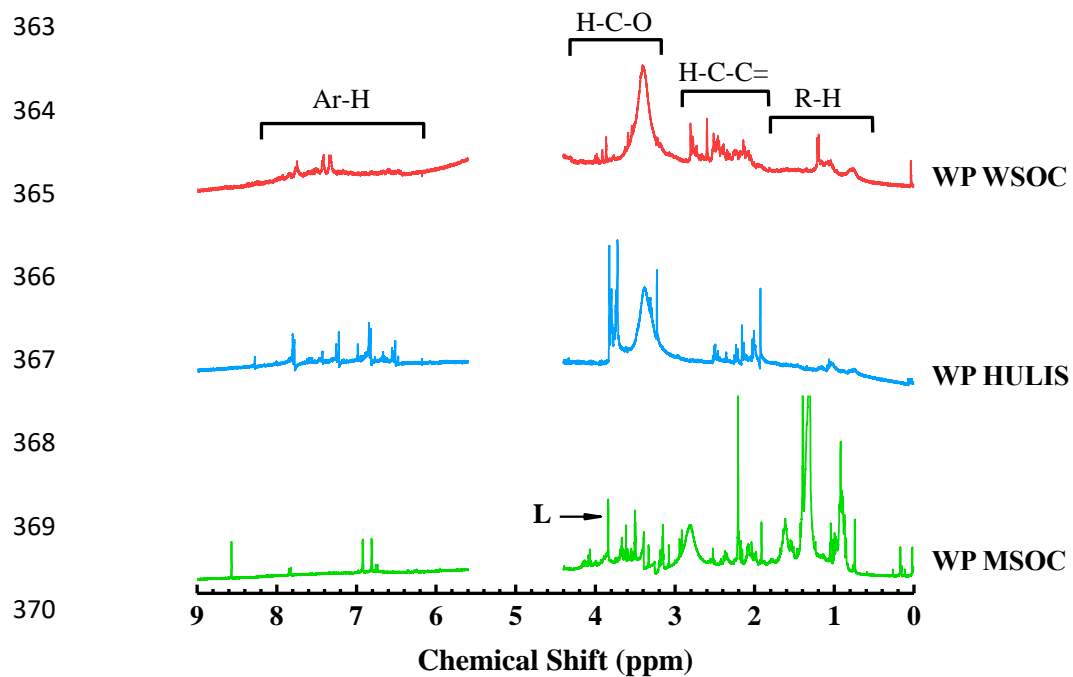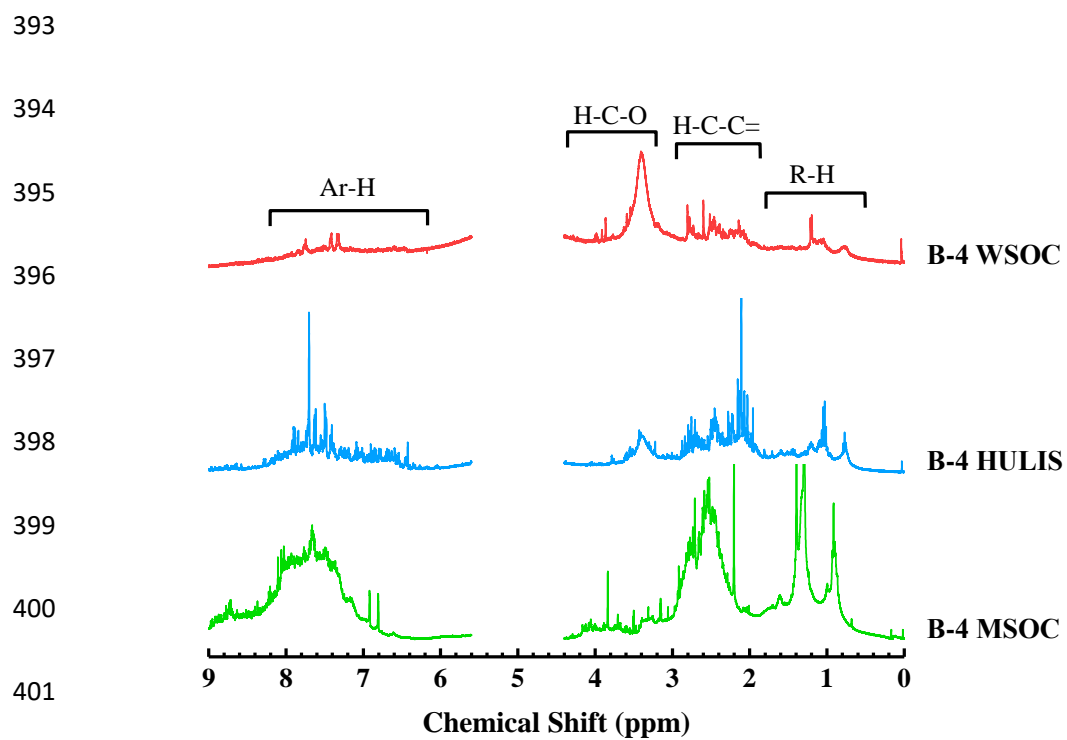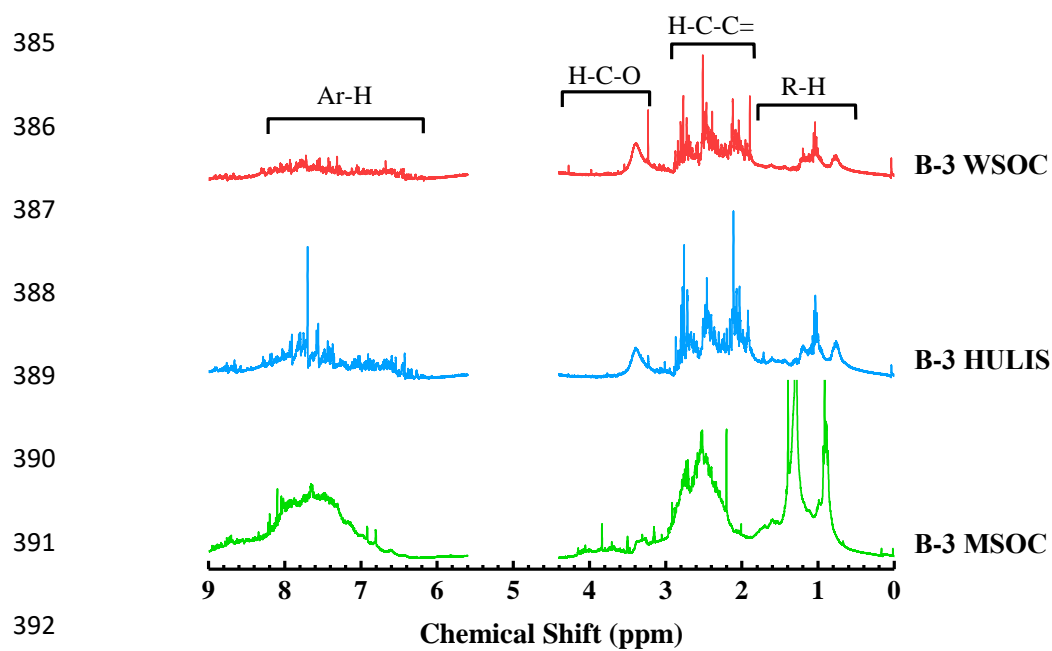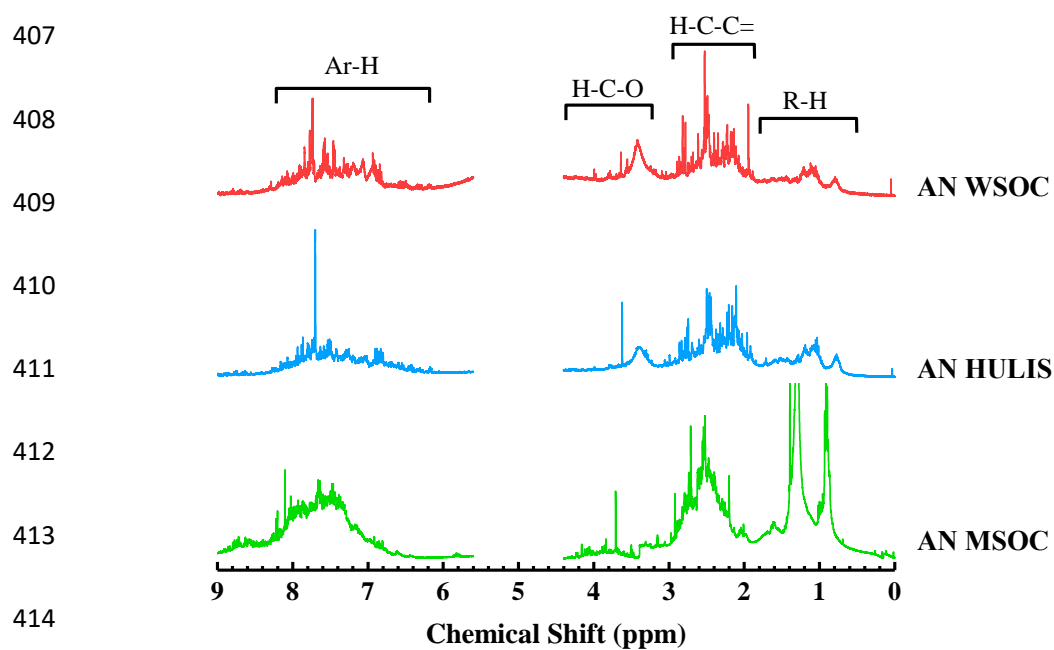
416   **Figure S3.** ^{1}H-NMR stacking diagram of corresponding WSOC, HULIS, MSOC of BB and

417   CC smoke samples. The segment from 4.40 to 5.60 ppm was removed for NMR spectra due

418   to MeOH and H_2O residues. The peaks were assigned to specific compounds as follows:

419   Levoglucosan (L), Phthlic acid (PA).

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