Supplement of Atmos. Chem. Phys., 24, 6323–6337, 2024
https://doi.org/10.5194/acp-24-6323-2024-supplement

Supplement of

Comparison of water-soluble and water-insoluble organic compositions attributing to different light absorption efficiency between residential coal and biomass burning emissions

Lu Zhang et al.

Correspondence to: Guofeng Shen (gfshen12@pku.edu.cn)

S1. Data analysis.

ESI FT-ICR MS data processing

Custom software was used to determine possible formulas for ions with a signal-to-noise ratio higher than 5 in the m/z range of 150-800 using a mass tolerance of ± 1.0 ppm. The maximum number of atoms for the formula calculator was set to: 60 ^{12}C, 60 ^{1}H, 20 ^{16}O, 3 ^{14}N, 2 ^{32}S, 1 ^{13}C, 1 ^{18}O, and 2 ^{34}S. The identified formulas containing isotopomers (i.e. 13C, 18O, or 34S) were not included in the final discussion. The formulas identified were classified into four sorts including CHO, CHON, CHOS, and CHONS compounds. For the chemical formula $C_cH_hO_oN_nS_s$, where c, h, o, n, s represented the atom numbers of carbon, hydrogen, oxygen, nitrogen, and sulfur, respectively.

The double bonds equivalent (DBE) which indicates the unsaturated degree was calculated as:

$$DBE = (2c + 2 - h + n)/2$$

The modified aromaticity index (AI_{mod}) was calculated according to published studies [1,2]:

$$AI_{mod} = (1 + c - 0.5o - s - 0.5h)/(c - 0.5o - s - n)$$

The formulae with a negative AI_{mod} value were considered as value of zero, and treated as aliphatic compounds. The AI_{mod} value of larger than 0 to less than 0.5 was identified as olefinic compounds, aromatic compounds were identified as $0.5 \leq AI_{mod} < 0.67$ and $AI_{mod \geq 0.67}$ were condensed aromatic compounds.

To consider the intensity of each formula and its contribution to the overall property, the relative abundance weighted molecular weight, elemental ratios, DBE, and AI_{mod} were calculated based on the following equations

$$MW_w = \Sigma(In_i * MW_i)/\Sigma In_i$$

$$H/C_w = \Sigma(In_i * H/Ci)/\Sigma In_i$$

$$O/C_w = \Sigma(In_i * O/Ci)/\Sigma In_i$$

$$O/N_w = \Sigma(In_i * O/Ni)/\Sigma In_i$$

$$O/S_w = \Sigma(In_i * O/Si)/\Sigma In_i$$

$$DBE_w = \Sigma(In_i * DBEi)/\Sigma In_i$$

$$DBE/C_w = \Sigma(In_i * DBE/C_i)/\Sigma In_i$$

$$AI_{mod,w} = \Sigma(Ini * AI_{mod,i})/\Sigma In_i$$

Where Ini is the intensity for each individual molecular formula, i. and the MWi, H/Ci, O/Ci, O/Ni, O/Si, DBEi, DBE/Ci, and AIi, and OSi also indicate the MW, H/C, O/C, O/N, O/S, DBE, DBE/C, and AI_{mod} of the individual molecular formula, i.

S2. Tables.

Table S1 Solid fuel properties and stoves used in this work.

Fuel types	C, %	H, %	N, %	S, %	M_{ad}^{a}, %	V_{daf}^{b}, %	A_{ad}^{c}, %	LHV, MJ/kg	Rank[d]	Stove
Chunk coals										
Shanxi-1	82.7	2.89	0.915	0.527	2.46	4.49	5.97	30.6	AN	TS
Hebei-1	70.7	2.04	0.750	0.285	5.75	4.56	5.41	28.5	AN	TS
Shanxi-2	77.3	4.19	0.590	0.738	1.82	23.6	9.88	20.8	MVB	TS
Shanxi-3	71.7	4.49	0.680	0.315	7.73	27.8	1.24	26.8	MVB	TS
Shandong-1	71.2	4.68	0.610	0.303	6.91	29.4	1.68	27.0	MVB	TS
Shandong-2	56.6	4.25	0.545	1.36	12.4	29.8	11.4	36.1	MVB	TS
Inner Mongolia-1	57.2	3.38	0.475	0.303	4.58	30.8	48.1	28.3	MVB	TS
Hebei-2	72.7	4.66	0.650	0.317	4.91	32.4	2.29	26.2	HVB	TS
Inner Mongolia-2	32.9	3.65	0.645	0.872	15.9	34.1	12.1	17.6	HVB	TS
Shandong-3	70.2	5.17	0.985	0.617	6.52	36.3	2.33	26.5	HVB	TS
Briquetting coals (round)										
Hebei-3	62.8	3.00	0.870	0.317	3.64	8.76	38.7	24.4	SA	TS
Shanxi-4	57.9	2.73	0.725	0.392	2.88	11.3	30.3	22.0	SA	TS
Briquetting coals (honeycomb)										
Shanxi-5	26.8	1.62	0.275	0.727	1.26	5.68	35.2	14.1	AN	TS
Shanxi-6	49.9	2.40	0.705	0.426	1.54	9.83	34.6	24.4	SA	TS
Wood fuel										
birch wood	45.6	6.45	0.105	0.217	7.40	81.8	0.396	16.2		TS
pine wood	46.8	6.40	0.0600	0.228	7.03	77.4	1.23	17.2		TS&IS
poplar wood	46.4	6.32	0.120	0.191	7.15	76.7	1.18	16.5		TS
Crop straws										
bean straw	40.6	6.15	1.07	0.284	11.3	71.6	5.89	12.4		TS
corn straw	42.3	6.31	1.03	0.219	8.68	88.1	4.69	13.9		TS&IS
peanut straw	39.0	6.00	1.27	0.419	10.9	67.1	8.61	16.4		TS
rice straw	40.8	6.12	0.605	0.247	9.79	68.9	6.13	15.3		TS
wheat straw	36.2	5.84	0.680	0.255	8.17	65.7	11.0	14.0		TS
rape straw	41.9	6.27	0.305	0.376	10.1	75.7	3.87	15.1		TS&IS
sesame straw	39.1	5.50	1.21	0.582	11.7	66.9	8.25	13.8		TS
Corn cob	43.9	6.32	0.465	0.240	6.98	75.1	1.02	13.9		TS
Bamboo	44.9	6.24	0.420	0.380	6.64	75.1	2.09	17.3		TS
Pellet fuels										
corn straw	40.1	5.76	0.725	0.233	6.24	66.2	13.0	11.5		IS
pine wood	46.4	6.53	0.155	0.0915	5.12	76.5	3.12	16.4		IS
fruit tree logs	45.9	6.33	0.270	0.309	4.39	77.4	4.24	16.5		IS
rice husk	39.3	5.43	0.455	0.104	4.44	67.8	15.5	12.9		IS
Red wood	42.3	5.39	0.367	0.206	4.96	72.3	10.1	17.4		IS

Notes: [a]Moisture on an air-dry basis (%); [b]Volatile matter on a dry and ash-free basis (%); [c]Ash on an air-dry basis (%); [d]Rank by ASTM standard classification of coal [American Society for Testing and Material, 2004]. AN is for ordinary anthracite, SA is for semi-anthracite, MVB is for medium-volatile bituminous coal, and HVB is for high-volatile bituminous coal. In addition, the 14 coals were produced in Shanxi province (Shanxi 1-6), Shandong province (Shandong 1-3), Inner Mongolia province (Inner Mongolia 1-2), and Hebei province (Hebei 1-3). The fuel written in red color was chosen for further FT-ICR MS analysis.

Table S2. Number of formulas in each compound category and the average values of elemental ratios, molecular weight (MW), and double-bond equivalents (DBE) in WSOC and WIOC of different samples.

			WSOC								WIOC							
	Sample type	Elemental composition	Number of formulae	MW_W	H/C_W	O/C_W	O/N_W	DBE_W	DBE/C_W	$AI_{mod,W}$	Number of formulae	MW_W	H/C_W	O/C_W	O/N_W	DBE_W	DBE/C_W	$AI_{mod,W}$
Coal	HVB	Total	3119	380	1.1	0.33		10	0.52	0.43	2746	640	1.0	0.36		20	0.57	0.46
		CHO	971	328	0.91	0.30		11	0.61	0.53	853	375	0.86	0.24		14	0.62	0.57
		CHON	1222	377	1.1	0.35	5.3	10	0.54	0.46	854	649	0.73	0.26	6.8	26	0.69	0.65
		CHOS	550	428	1.3	0.32		10	0.42	0.29	473	670	1.2	0.45		14	0.43	0.27
		CHONS	376	518	1.6	0.36	5.0	7.5	0.30	0.17	566	707	1.1	0.44	9.7	19	0.52	0.38
	MVB	Total	2612	435	1.2	0.29		11	0.47	0.38	2968	552	0.89	0.24		20	0.61	0.55
		CHO	892	320	1.0	0.31		10	0.54	0.45	997	396	0.89	0.23		14	0.60	0.55
		CHON	756	456	1.1	0.29	5.3	13	0.51	0.43	972	539	0.88	0.26	5.2	20	0.63	0.58
		CHOS	459	425	1.4	0.38		8.8	0.37	0.24	442	548	1.4	0.37		11	0.35	0.24
		CHONS	505	540	1.3	0.22	4.3	12	0.39	0.31	557	640	0.80	0.21	3.9	25	0.66	0.60
Raw biomass	Rice straw	Total	6383	384	1.1	0.34		11	0.52	0.41	6946	476	1.2	0.27		12	0.44	0.35
		CHO	1580	338	1.1	0.39		10	0.53	0.40	2142	431	1.2	0.24		11	0.42	0.35
		CHON	2558	393	1.2	0.34	5.1	11	0.52	0.40	2477	472	1.2	0.29	6.0	12	0.46	0.38
		CHOS	1044	418	1.0	0.24		14	0.55	0.47	1138	533	1.2	0.29		14	0.41	0.33
		CHONS	1201	481	1.3	0.32	4.2	12	0.42	0.33	1189	590	1.3	0.33	5.2	14	0.43	0.32
	Pine wood	Total	4291	413	1.1	0.33		12	0.53	0.43	3525	549	1.0	0.29		17	0.53	0.44
		CHO	1978	374	1.0	0.32		12	0.56	0.47	1445	444	0.94	0.24		15	0.57	0.51
		CHON	763	437	1.2	0.37	6.2	12	0.47	0.36	690	563	0.95	0.26	5.4	20	0.59	0.53
		CHOS	922	486	1.1	0.28		15	0.49	0.42	884	613	1.2	0.36		14	0.42	0.27
		CHONS	628	570	1.3	0.40	5.7	11	0.41	0.25	506	642	1.1	0.35	5.6	18	0.50	0.38
	Pine wood-improved stove	Total	3991	412	1.1	0.33		11	0.49	0.39	3270	566	1.1	0.32		15	0.49	0.38
		CHO	1587	383	1.0	0.31		12	0.54	0.45	1240	455	1.0	0.26		15	0.54	0.47
		CHON	911	402	1.3	0.37	5.8	10	0.46	0.35	597	584	1.1	0.33	5.8	17	0.50	0.40
		CHOS	929	446	1.1	0.28		14	0.51	0.42	727	584	1.3	0.39		13	0.40	0.28
		CHONS	564	496	1.6	0.39	5.2	7.4	0.31	0.16	706	652	1.2	0.31	5.6	17	0.48	0.35
Biomass pellet	Crop straw pellet	Total	4371	403	1.2	0.39		10	0.49	0.36	2830	559	1.3	0.31		13	0.43	0.32
		CHO	1195	366	1.1	0.40		10	0.52	0.40	855	451	1.2	0.25		11	0.43	0.35
		CHON	1447	388	1.2	0.37	5.7	10	0.51	0.40	778	488	1.3	0.29	5.6	12	0.42	0.34
		CHOS	993	406	1.1	0.37		11	0.51	0.36	572	640	1.2	0.39		13	0.41	0.26
		CHONS	736	495	1.4	0.46	6.1	8.7	0.38	0.21	625	621	1.2	0.29	4.4	16	0.45	0.35
	Pine wood pellet	Total	3964	416	1.1	0.35		11	0.50	0.39	2778	552	1.2	0.29		15	0.45	0.35
		CHO	1399	387	1.0	0.34		12	0.53	0.43	969	453	1.2	0.23		12	0.45	0.39
		CHON	834	399	1.2	0.38	6.1	10	0.49	0.37	560	547	1.2	0.29	5.9	17	0.48	0.41
		CHOS	1111	426	1.0	0.32		13	0.53	0.41	651	520	1.5	0.35		9.3	0.31	0.21
		CHONS	620	509	1.4	0.42	5.7	9.4	0.38	0.24	598	639	1.2	0.30	5.1	17	0.48	0.36

Table S3: Stoichiometric ranges of VK classes.

Class	H/C	O/C
Lipids-like	1.5<H/C≤2.0	0≤O/C≤0.3
Aliphatic/peptides-like	1.5<H/C≤2.2	0.3<O/C≤0.67
Carboxylic-rich alicyclic molecules	0.67<H/C≤1.5	0.1≤O/C<0.67
Carbohydrates-like	1.5<H/C≤2.5	0.67<O/C<1.0
Unsaturated hydrocarbons	0.67<H/C≤1.5	O/C<0.1
Condensed aromatic structures	0.2<H/C≤0.67	O/C<0.67
Highly oxygenated compounds (HOC)	0.67<H/C≤1.5	0.67≤O/C≤1.0

Table S4. Relative percentage (%) of various types of compounds in total identified comp

			WSOC							WIOC						
	Sample type	Elemental composition	AI=0	0<AI<0.5	0.5≤AI<0.67	AI≥0.67	O/N≥3	O/S≥4	O/S≥7	AI=0	0<AI<0.5	0.5≤AI<0.67	AI≥0.67	O/N≥3	O/S≥4	O/S≥7
Coal	HVB	Total	18%	28%	38%	17%				21%	18%	31%	29%			
		CHO	2.8%	26%	51%	20%				1.4%	21%	51%	27%			
		CHON	16%	28%	37%	19%	86%			4.0%	8.1%	35%	53%	95%		
		CHOS	33%	34%	26%	7.0%		66%	32%	21%	62%	16%	1.2%		95%	69%
		CHONS	58%	28%	6.9%	7.7%	72%	69%	42%	40%	6.6%	30%	24%	88%	88%	72%
	MVB	Total	19%	47%	22%	11%				10%	20%	24%	46%			
		CHO	7.5%	39%	37%	16%				1.6%	27%	51%	20%			
		CHON	6.6%	61%	22%	10%	90%			7.2%	21%	23%	49%	86%		
		CHOS	40%	35%	20%	4.9%		70%	33%	37%	52%	8.3%	2.5%		78%	43%
		CHONS	35%	47%	7.3%	10%	76%	37%	21%	11%	8.9%	13%	67%	48%	48%	30%
Raw biomass	Rice straw	Total	13%	48%	23%	15%				19%	51%	20%	10%			
		CHO	10%	56%	25%	9.4%				16%	55%	24%	4.8%			
		CHON	4.3%	69%	16%	11%	71%			14%	57%	20%	10%	85%		
		CHOS	23%	9.2%	35%	33%		42%	25%	28%	41%	11%	19%		45%	33%
		CHONS	42%	17%	17%	24%	60%	56%	42%	30%	34%	17%	19%	63%	64%	40%
	Pine wood	Total	11%	45%	32%	12%				12%	36%	30%	22%			
		CHO	3.6%	49%	40%	7.5%				1.3%	37%	52%	10%			
		CHON	25%	42%	17%	16%	81%			8.1%	27%	27%	38%	86%		
		CHOS	23%	24%	22%	30%		52%	26%	21%	60%	10%	9.2%		72%	57%
		CHONS	34%	45%	6.4%	15%	81%	78%	57%	24%	25%	18%	33%	76%	75%	47%
	Pine wood-improved stove	Total	16%	44%	28%	13%				17%	43%	23%	17%			
		CHO	5.4%	48%	35%	11%				3.2%	46%	43%	7.6%			
		CHON	18%	51%	20%	11%	81%			14%	41%	13%	32%	91%		
		CHOS	19%	30%	29%	22%		56%	31%	29%	54%	8.1%	8.5%		77%	32%
		CHONS	54%	33%	6.4%	6.8%	79%	79%	43%	27%	33%	25%	16%	62%	71%	43%
Biomass Pellet	Crop straw pellet	Total	20%	46%	22%	12%				18%	58%	14%	10%			
		CHO	13%	48%	28%	11%				11%	63%	21%	5.2%			
		CHON	12%	52%	24%	12%	79%			23%	49%	15%	14%	87%		
		CHOS	18%	46%	22%	14%		71%	49%	15%	76%	7.1%	2.5%		87%	72%
		CHONS	53%	31%	5%	12%	85%	82%	54%	26%	33%	18%	23%	55%	63%	38%
	Pine wood pellet	Total	14%	49%	24%	13%				21%	42%	17%	20%			
		CHO	6.3%	54%	28%	11%				6.0%	64%	26%	3.9%			
		CHON	16%	53%	17%	14%	82%			21%	36%	13%	30%	89%		
		CHOS	12%	46%	27%	15%		67%	44%	43%	41%	9.2%	6.7%		76%	42%
		CHONS	46%	33%	8.1%	13%	80%	78%	48%	22%	32%	16%	29%	72%	76%	47%

S3. Figures

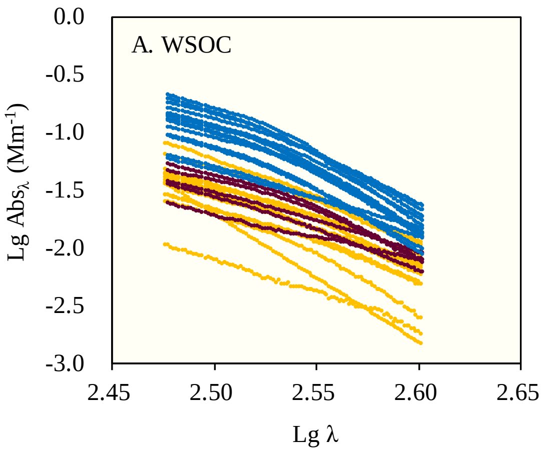

Fig. S1 Absorption Ångström exponent (AAE) calculation for average absorption spectrums in the wavelength of 300-400 nm in WSOC (A) and WIOC (B) extract from source samples.

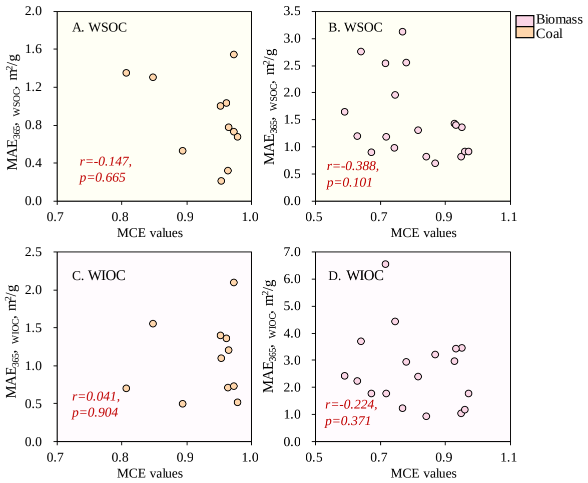

Fig.S2 Correlation between the MCE values with $MAE_{365,\ WSOC}$ values from coal combustion smokes (A), and biomass smokes(B); as well as with $MAE_{365,\ WIOC}$ from coal combustion smokes (C), and biomass smokes (D)

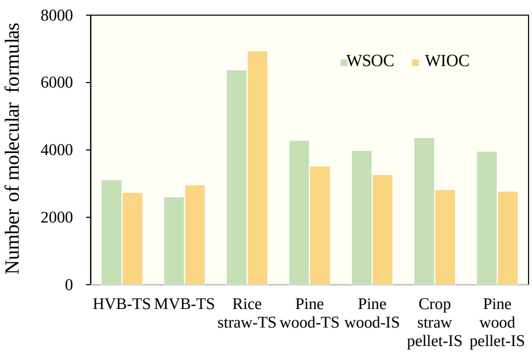

Fig.S3 Number of molecular formulas in each source sample, the different colors present WSOC and WIOC extract, respectively.

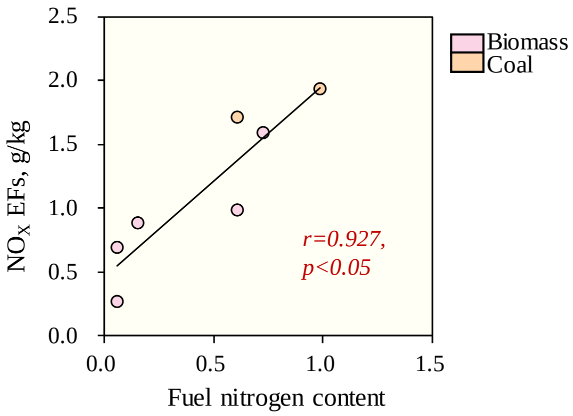

Fig. S4 Correlation between fuel nitrogen contents and emission factors of NO_X (NO_X EFs).

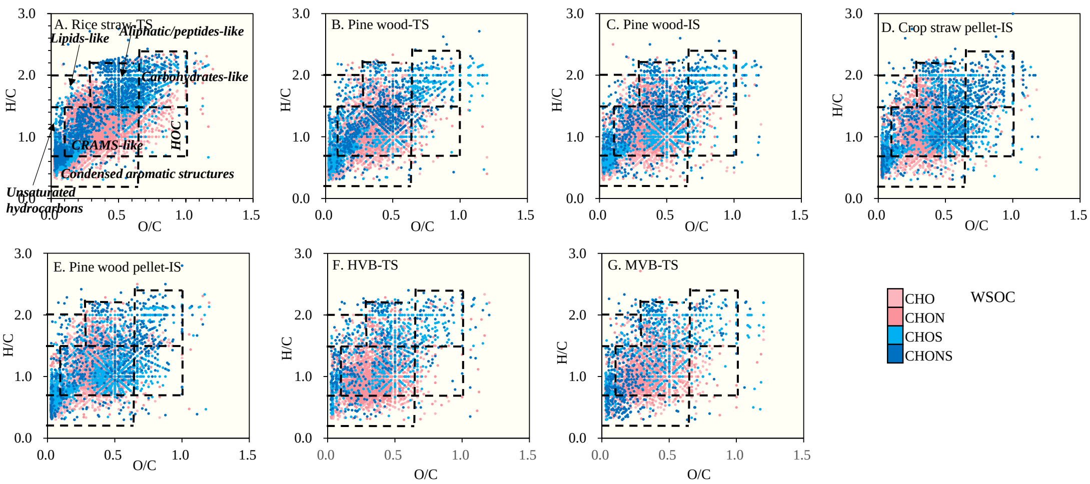

Fig. S5 Van Krevelen diagrams of WSOC of the seven aerosol samples. Different color indicates different identified group of CHO, CHON, CHOS, and CHONS

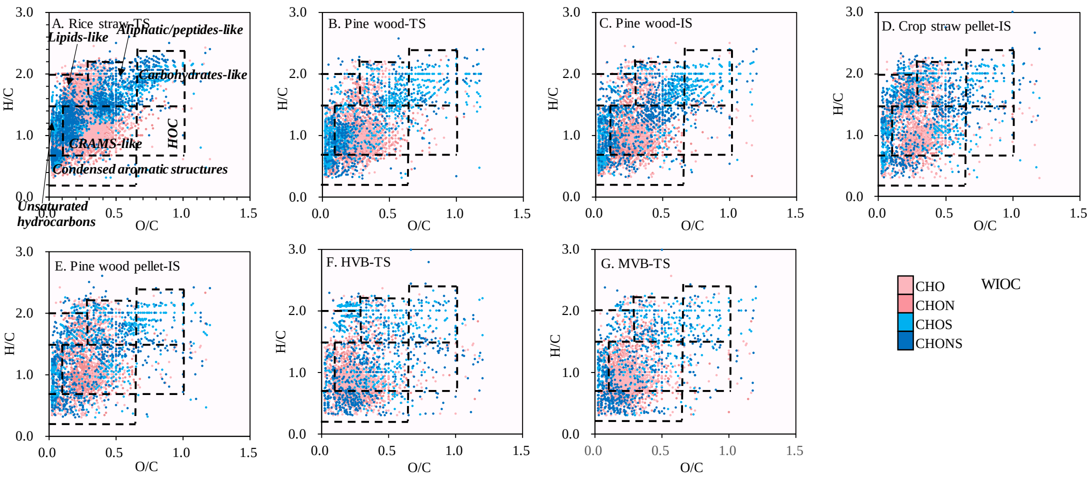

Fig. S6 Van Krevelen diagrams of WIOC of the seven aerosol samples. Different color indicates different identified group of CHO, CHON, CHOS, and CHONS

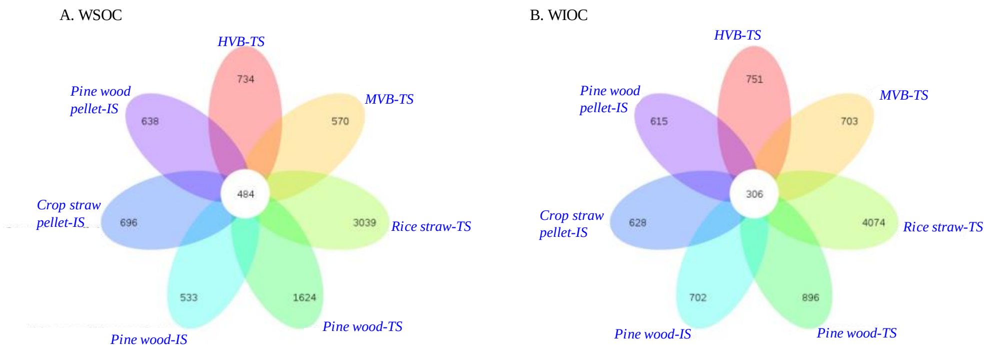

Fig. S7 Venn diagrams for the relative distributions of all molecular formulas in WSOC from the seven source samples. The areas of overlap are the common elements in all samples. The areas with no overlap are unique to that individual sample.

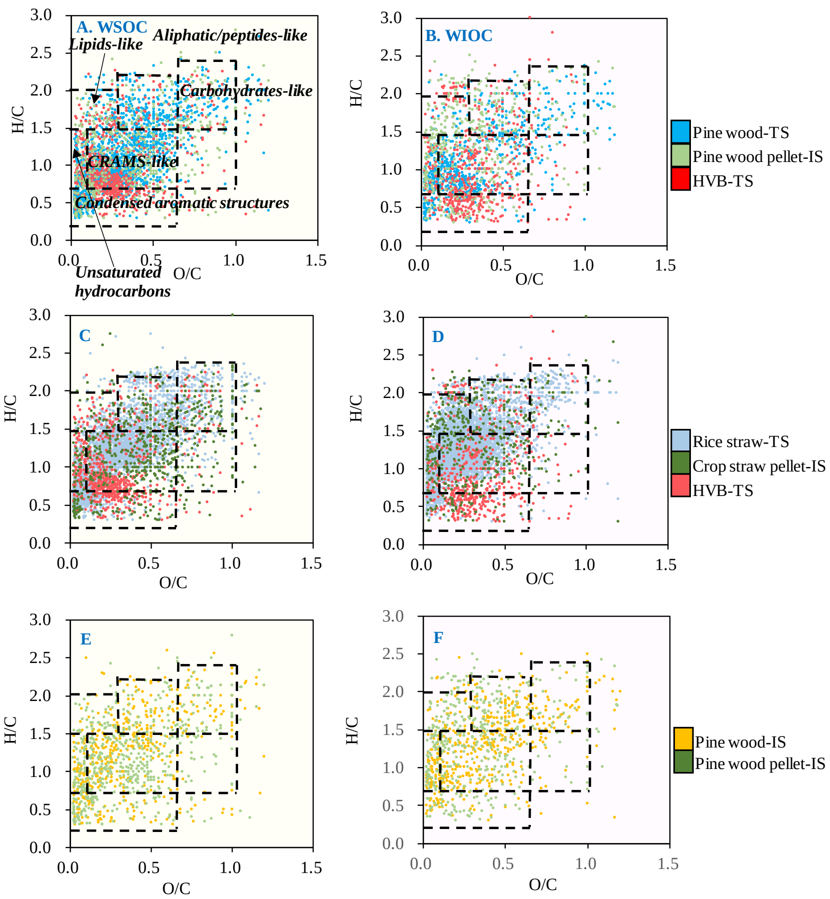

Fig. S8 Van Krevelen diagrams of WSOC (a) and WIOC (b) from the source samples. Different color indicates unique formulas detected in each sample of solid fuel combustion.

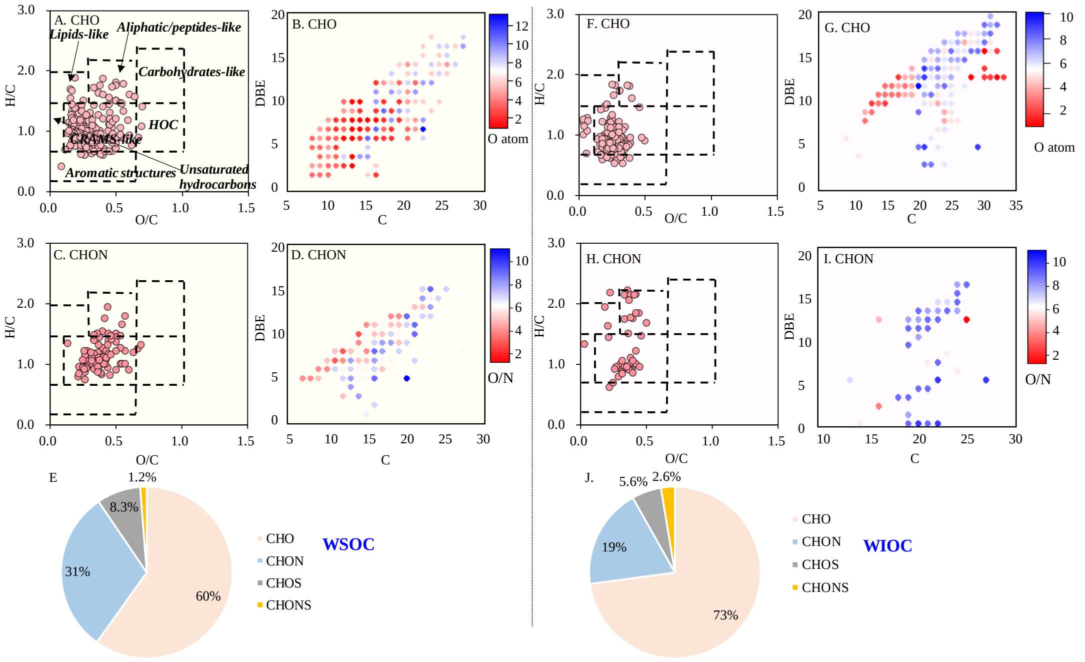

Fig. S9 Van Krevelen diagrams of common formulas in all samples of CHO group (A: WSOC, F: WIOC) and CHON group (C: WSOC, H:WIOC), and DBE vs C number for common formulas of CHO group (B: WSOC, G:WIOC) and CHON group (D: WSOC, I:WIOC), as well as the pie charts showing the relative intensities of different formula groups in the commonly detected formulas (E: WSOC, J: WIOC)

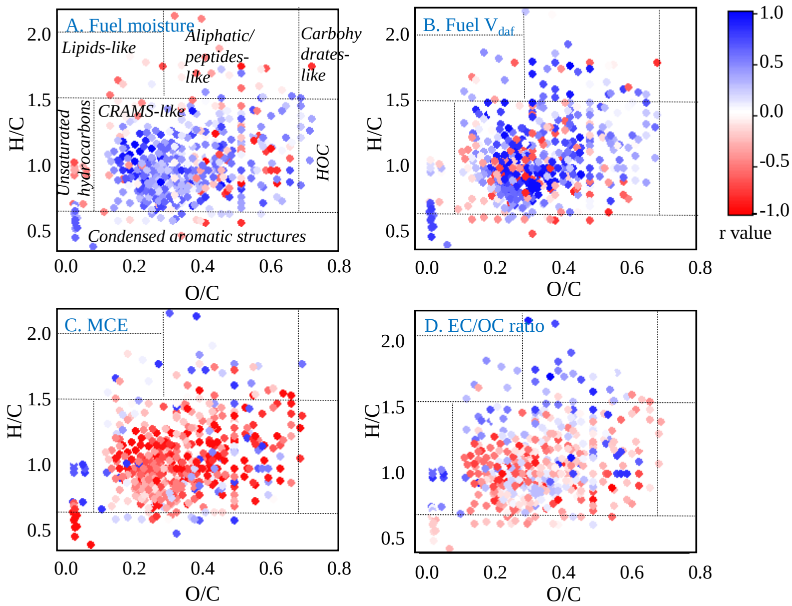

Fig. S10 Van Krevelen plots of WSOC and associations between individual molecules and (A) Fuel moisture, (B) Fuel V_{daf}, (C) MCE, and (D) EC/OC ratios. Significant Spearman correlations ($p < 0.05$) of individual molecules are presented. Color bar indicates direction and strength of the correlation (red, negative; cyan, negative). Circles indicate individual molecules. Black lines show class identification. The stoichiometric ranges set as boundaries of the classifications are reported in Table S3.

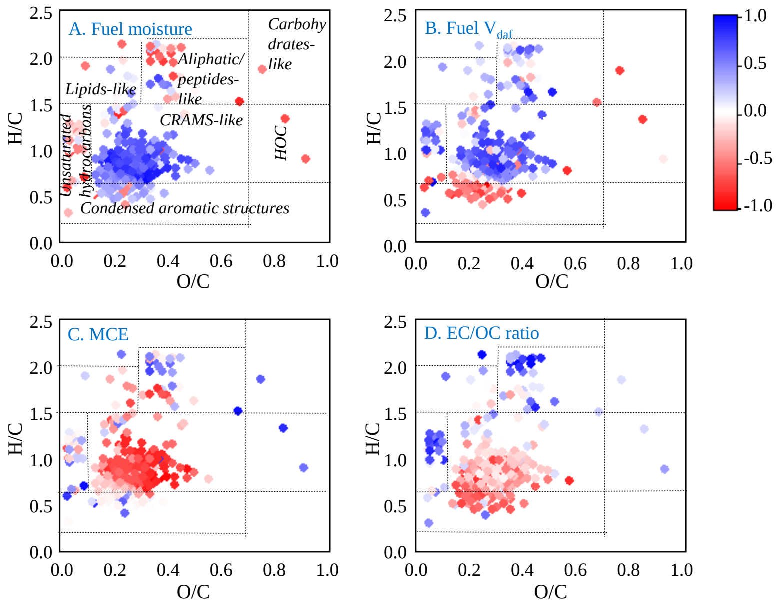

Fig. S11 Van Krevelen plots of WIOC and associations between individual molecules and (A) Fuel moisture, (B) Fuel Vdaf, (C) MCE, and (D) EC/OC ratios. Significant Spearman correlations ($p < 0.05$) of individual molecules are presented. Color bar indicates direction and strength of the correlation (red, negative; cyan, negative). Circles indicate individual molecules. Black lines show class identification. The stoichiometric ranges set as boundaries of the classifications are reported in Table S3.

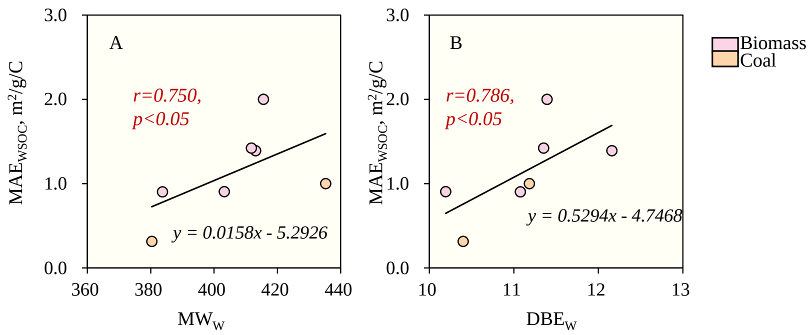

Fig. S12 Correlations of MAE_{365} with the MW values (A) and DBE (B) of the potential BrC molecules from the source aerosol samples, respectively.

S4. Reference

(1) Song, J. Z.; Li, M. J.; Zou, C. L.; Cao, T.; Fan, X. J.; Jiang, B.; Yu, Z. Q.; Jia, W. L.; Peng, P. A. Molecular Characterization of Nitrogen-Containing Compounds in Humic-like Substances Emitted from Biomass Burning and Coal Combustion. *Environ. Sci. Technol.* **2022**, *56* (1), 119-130. DOI: 10.1021/acs.est.1c04451.

(2) Bianco, A.; Deguillaume, L.; Vaitilingom, M.; Nicol, E.; Baray, J.-L.; Chaumerliac, N.; Bridoux, M. Molecular Characterization of Cloud Water Samples Collected at the Puy de Dome (France) by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Environ. Sci. Technol.* **2018**, *52* (18), 10275-10285, Article. DOI: 10.1021/acs.est.8b01964.