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Technical note: Intercomparison study of the elemental carbon radiocarbon analysis methods using synthetic known samples

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Contents of this file

1. Analytical Methods

OC/EC and TOC analysis:

The OC and EC in the three combustion source samples were analyzed by the TOT method, performed with a laboratory OC/EC analyzer (Sunset Laboratory, USA) using the NIOSH2 thermal protocol.(Salma et al., 2004; Maenhaut et al., 2005) Details regarding the method can be found in the SI. The total organic carbon (TOC) concentration of the aerosols was also determined. For each sample, 4 punches (4.8 mm diameter) were placed in precombusted Ag capsules, and the inorganic carbon was removed by acidification, as described above. After drying, the TOC was quantified by using a high-temperature catalytic CHN elemental analyzer.

Carbon isotope analysis (Liu et al., 2013; Liu et al., 2017; Xu, et al., 2007):

The samples were analyzed for ^{13}C using a FLASH2000 Elemental Analyzer connected to a Thermo MAT-253 isotope ratio mass spectrometer. The results are reported using standard delta notation in permil units (‰): δ (‰) = $(R_{sample}–R_{reference})/R_{reference} \times 1000$, where δ (‰) stands for $\delta^{13}C$ (‰), and R_{sample} and $R_{reference}$ are the isotopic ratios of the sample and reference material, respectively. For carbon, the reference standard is Vienna Pee Dee Belemnite (VPDB). The analytical precision for the international and in-house reference materials was generally better than ±0.5‰ for $\delta^{13}C$. Replicate measurements of samples yielded similar standard deviations.

Preparation of graphite targets for accelerator mass spectrometry (AMS) analysis was performed using the graphitization line at Guangzhou Institute of Geochemistry of the Chinese Academy of Sciences (CAS) via the hydrogen and zinc reduction method (Xu et al., 2007). The $^{14}C/^{12}C$ ratios in the graphite samples were determined using a compact AMS instrument (NEC, National Electrostatics Corporation, USA) at the Guangzhou Institute of Geochemistry, CAS. AMS calibration was performed using standards (Oxalic Acid Standards I and II) and blanks. The $\delta^{13}C$ value was obtained during AMS measurements and applied to correct the ^{14}C measurements for isotopic fractionation. The fraction modern (f_m) was determined by comparing the measured $^{14}C/^{12}C$ ratio in a sample with that in a modern standard (NBS Oxalic Acid I in AD 1950). All of the reported f_m values were corrected for $\delta^{13}C$ fractionation and for ^{14}C decay over the time period between 1950 and the year of measurement.

^{13}C solid state NMR experiments:

All the ^{13}C solid state NMR experiments were performed using an AVANCE III 400-MHz NMR spectrometer (Bruker, Billerica, MA, USA). The resonance frequency of ^{13}C is 100.613/MHz, and glycine was used as a standard for chemical shift calibration. And NMR experiments were run with a Bruker 4 mm double-resonance probe head and a ZrO_2 rotor. Cross Polarization-Total Sideband Suppresion/Magic angle spinning (CP-TOSS/MAS) and Cross Polarization-Total Sideband

Suppresion with dipolar dephasing/Magic angle spinning (CP-TOSS-DD/MAS) spectra were run at a spinning speed of 5 kHz. The acquisition time is 5.12 μs, and the spectral width is 100 kHz. The 90° ^{13}C pulse length was 11 μs and the recycle delay time is 1s. And the number of scans is from 4k to 20k. (Zhang et al., 2019; Chen et al., 2020) The data was processed with Bruker.Topspin3.1 software.

Field emission scanning electron microscopy (FESEM):

FESEM was used to observe the particle characteristics of typical carbon aerosol samples. The field emission scanning electron microscope (Hitachi su8010, Hitachi, Japan) has higher resolution than the traditional scanning electron microscope, and its resolution can be as high as 2 nanometers under high voltage. It can be used to observe the micro surface morphology and composition distribution of various material particles, and has higher imaging quality. The scanning electron microscope was used to observe the morphology and particle size of amorphous organic matter in carbonaceous aerosol samples, as well as the relationship between amorphous organic matter and quartz membrane fiber under electron microscope. The low voltage mode (accelerating voltage of about 1-2 kV, beam current of 10 μ a, working distance of about 3-8 mm) was selected, or the deceleration mode under low voltage condition (working distance less than 3 The backscattering image was taken in a typical field of view with a magnification of 3000-100000 times.

2. Supplemental Tables:

Table S1. C%, OC/EC, EC/TC (TOT) %, $\delta^{13}C$ of the typical combustion samples.

Sample	C% (±3.0 %)	OC/EC	EC/TC(TOT)%	$\delta^{13}C$ ‰ (±0.5 ‰)
Corn straw combustion	24.64	18.47	5.14	-14.02
Pine wood combustion	22.99	17.10	5.52	-24.41
Vehicle exhaust	14.49	2.42	29.21	-27.10
Coal combustion	11.60	3.85	20.62	-24.32

Table S2. Composition ratio information (C% weight) of the six hybrid samples.

Sample	C% (Corn straw combustion)	C% (Vehicle exhaust)	C% (Coal combustion)	Sample	C% (Pine wood combustion)	C% (Vehicle exhaust)	C% (Coal combustion)
S1	56.29	14.99	28.72	S4	56.27	15.02	28.71
S2	65.92	19.81	14.27	S5	65.93	19.74	14.34
S3	70.77	19.71	9.52	S6	70.80	19.69	9.50

Table S3. The calculated and measured TC results of C% and $\delta^{13}C‰$, f_M for the six hybrid samples.

Sample	C% (TC) (calculated)	C% (TC) (measured) (±3.0 %)	$\delta^{13}C‰$(TC) (calculated)	$\delta^{13}C$ ‰(TC) (measured) (±0.5 ‰)	f_M(TC) (calculated)	f_M(TC) (measured)
S1	17.26	17.70	-18.94	-18.71	0.5629	0.5930±0.0021
S2	18.97	19.10	-18.08	-17.74	0.6592	0.6831±0.0021
S3	19.79	19.39	-17.58	-17.40	0.7077	0.7220±0.0021
S4	17.76	18.18	-24.56	-24.66	0.5869	0.6117±0.0030
S5	19.17	19.31	-24.65	-24.67	0.6818	0.7157±0.0039
S6	19.82	20.08	-24.63	-24.63	0.7290	0.7705±0.0038

Table S4. The EC/TC results of samples, including four combustion source samples and six synthetic known samples, isolated by four purification methods.

Sample	EC/TC(TOT) %	EC/TC(Hypy) %	EC/TC(CTO-375) %	EC/TC($EC_{He/O2-475}$) %	EC/TC(EC_{LARA}) %
Corn straw combustion	5.14	2.49	0.38	8.54	1.92
Pine wood combustion	5.52	11.40	0.47	35.30	37.57
Vehicle exhaust	29.21	22.94	5.74	12.37	15.38
Coal combustion	20.62	20.76	1.34	13.64	9.84
S1	13.19	17.32	0.87	4.29	8.10
S2	12.11	14.16	0.52	3.86	8.44
S3	11.35	10.60	0.48	4.31	6.88
S4	14.09	16.68	0.09	29.00	23.59
S5	13.75	13.65	0.22	29.55	25.64
S6	12.56	11.52	0.18	28.32	27.87

Table S5. Solid-state ^{13}C NMR structural parameters for Corn straw combustion, Pine wood combustion, Vehicle exhaust and Coal combustion.

Sample	fa	fa^C	fa'	fa^H	fa^N	fa^P	fa^S	fa^B	fal	fal^H	fal^*	fal^O	C	FAA	FMA	Cn'	faC+ 0.5*(faP+ falO)* 100
Corn straw combustion	0.48	0.03	0.46	0.21	0.25	0.05	0.08	0.32	0.52	0.22	0.14	0.22	64	0.28	0.27	6.5	13.53
Pine wood combustion	0.51	0.01	0.50	0.22	0.28	0.04	0.1	0.35	0.49	0.18	0.16	0.2	68	0.28	0.33	4.9	12.01
Vehicle exhaust	0.41	0.03	0.38	0.09	0.29	0.03	0.07	0.28	0.59	0.3	0.15	0.18	86	0.26	0.25	8.43	10.53
Coal combustion	0.73	0.06	0.67	0.29	0.38	0.08	0.14	0.45	0.27	0.11	0.09	0.08	56	0.33	0.33	1.93	8.06

Structural parameter	Chemical shift range (ppm)	Carbon type	Parameter	Definition	Description
fa	90-240	Aromatic-carboxyl-carbonyl-amide	C		Average carbons per aromatic cluster[49]
fa^C	165-240	Carboxyl-carbonyl-amide	FAA	$(fa^P + fa^S)/fa'$	Fraction of aromatic carbons with attachments
fa'	90-165	Aromatic	FMA	fal^*/fal	Fraction of methyl in aliphatic
fa^H	90-165	Protonated aromatic (w/o DD)	Cn'	fal/fa^S	Average aliphatic carbon chain length
fa^N	90-165	Non-protonated aromatic (w/ DD)		$fa^C + 0.5(fa^P + fal^O)*100$	A lower limit estimate for organic oxygen
fa^P	150-165	Phenoxy-phenolic			
fa^S	135-150	Alkyl-substituted aromatic			
fa^B	90-135	Bridgehead aromatic			
fal	0-90	Aliphatic			
fal^H	22-50	Methylene/methine			
fal^*	0-22 & 50-60	Methyl/methoxy			
fal^O	50-90	Alcohol/ether			

Table S6. The deviation between the results of different separation methods and the theoretical values, according to the ratio of herbaceous to woody combustion.

	Biomass*		Hypy	CTO-375	$EC_{He/O2-475}$	EC_{LARA}
	Herbaceous	Woody				
Africa	0.79	0.21	-37.38±1.36	93.88±20.79	57.85 ±6.84	14.80 ±6.84
Asia	0.55	0.45	-21.15±3.28	85.12±16.08	73.51 ±4.33	44.76 ±5.22
Australia/Oceania	0.91	0.09	-45.49±3.35	98.27±23.21	50.02 ±8.12	-0.19 ±7.74
Central America/Caribbean	0.10	0.90	9.27±11. 26	68.68 ±8.61	102.88 ±1.97	100.94±3.90
Europe	0.27	0.73	-2.22±8.23	74.89±11.06	91.79 ±1.93	79.72 ±4.00
North America	0.10	0.90	9.27±11.26	68.68 ±8.61	102.88 ±1.97	100.94±3.90
South America	0.39	0.61	-10.34±6.10	79.27±13.11	83.96 ±2.80	64.74 ±4.40
Global average	0.58	0.42	-23.18±2.76	86.21±16.66	71.56 ±4.64	41.01 ±5.41

* The ratio of herbaceous and woody was calculated according to the reference (Bond et al., 2004; Zhang et al., 2004; Streets et al., 2003; Stevens et al., 2017)

3. Supplemental Figures:

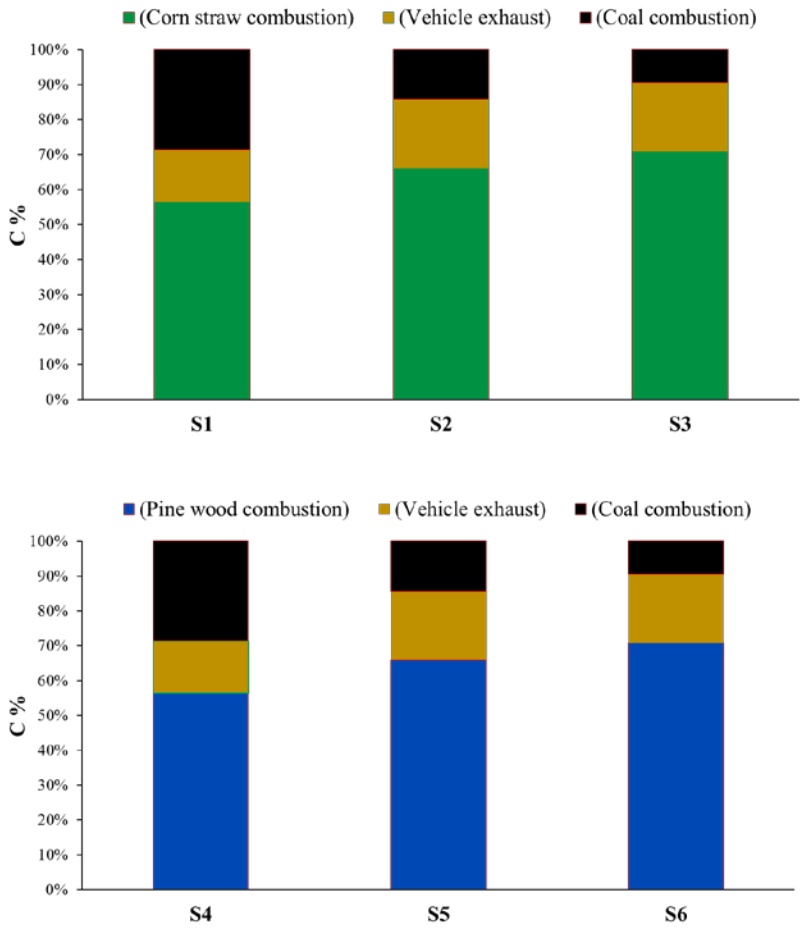


Figure S1. Composition ratio information (C% weight) of the six synthetic known samples.

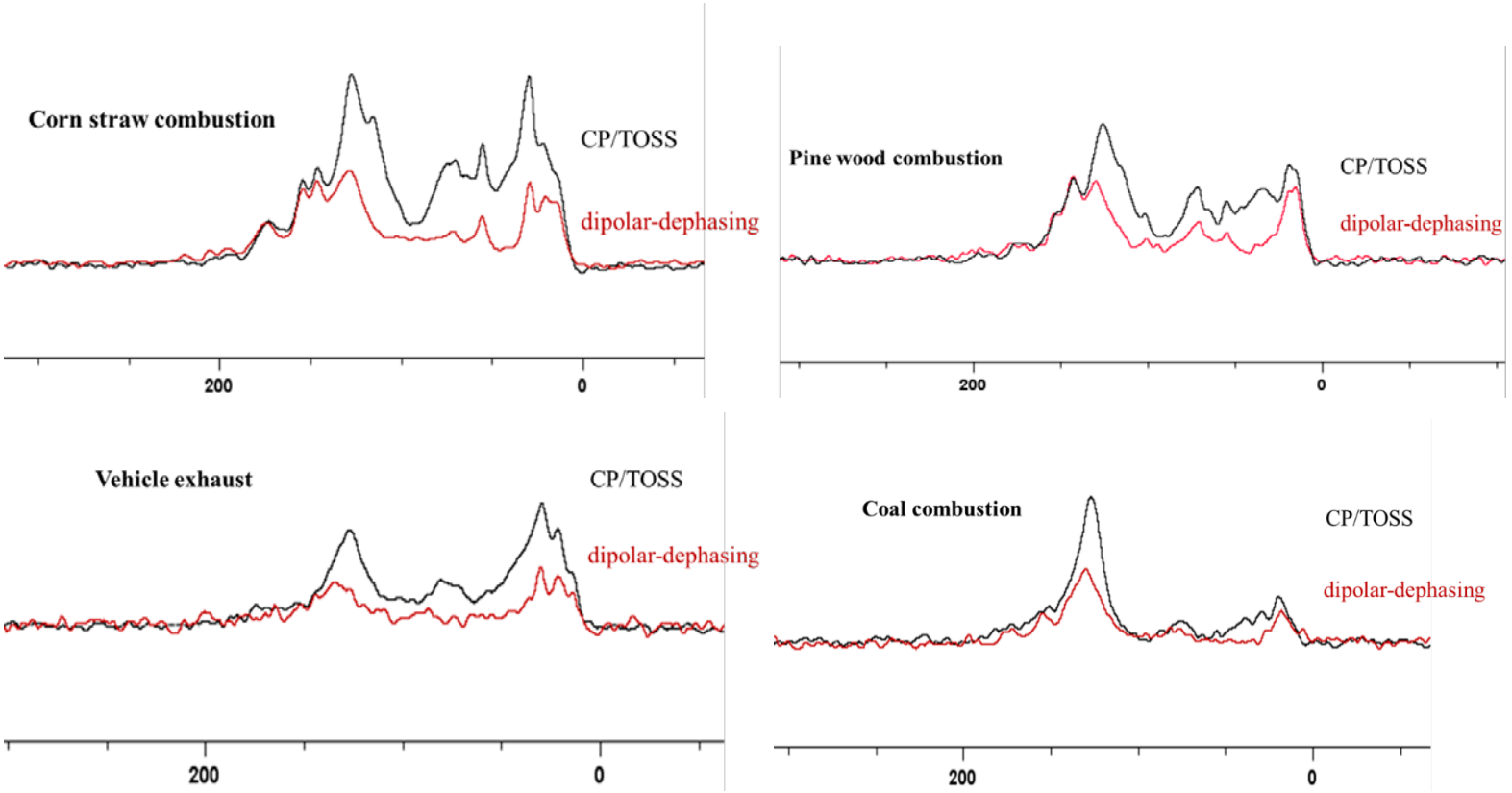
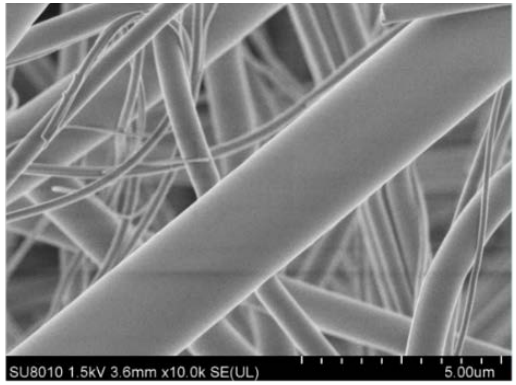


Figure S2. Solid-state ^{13}C NMR spectrum of Corn straw combustion, Pine wood combustion, Vehicle exhaust and Coal combustion.

^{13}C CP/TOSS and CP/TOSS/DD NMR for the identification of functional groups in the samples. Black lines: CP/TOSS/DD NMR, unselective CP/TOSS spectra. Red lines: CP/TOSS/DD NMR, CP/TOSS with dipolar dephasing to select non-protonated carbons and mobile groups.



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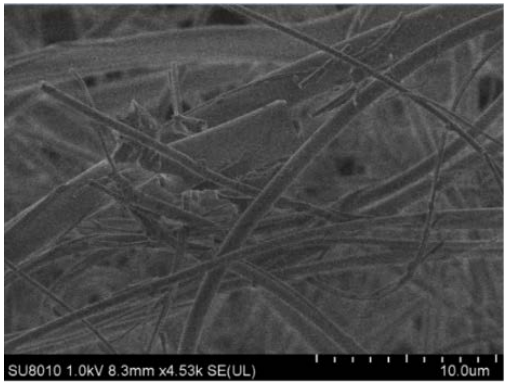
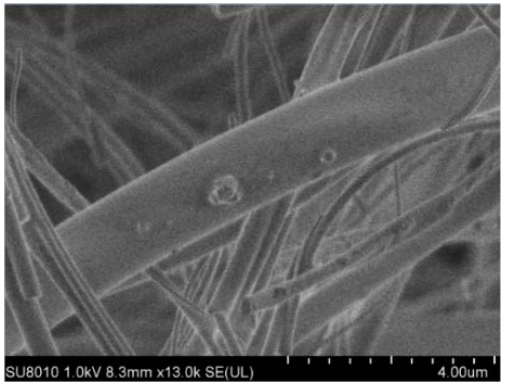
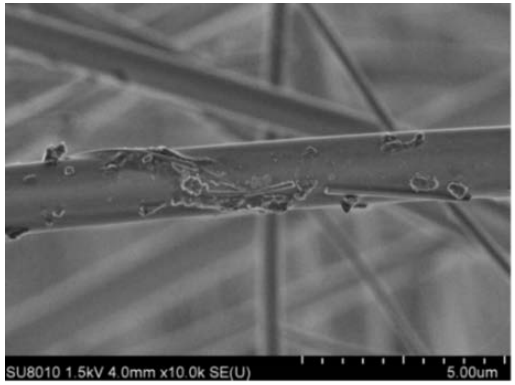
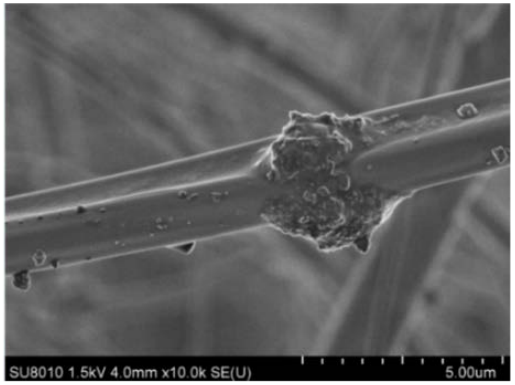


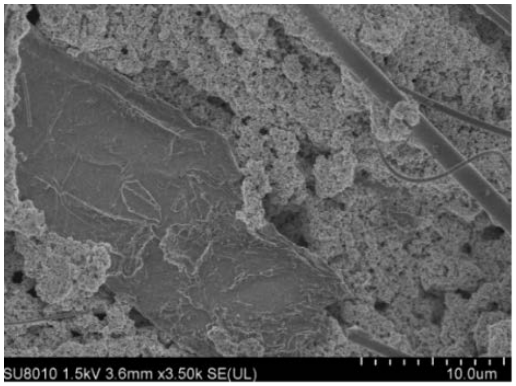


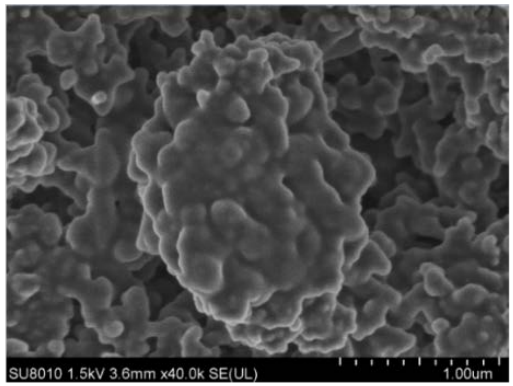
Corn stem combustion



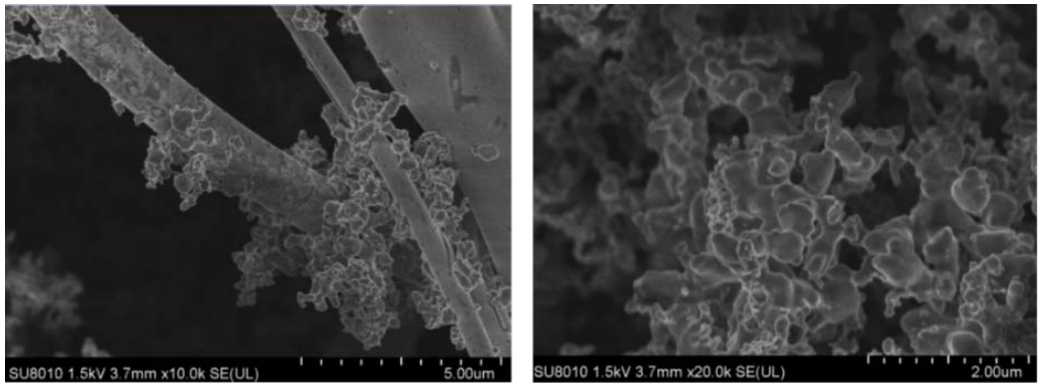


Pine wood combustion





Vehicle exhaust



Coal combustion

Figure S3. The field emission scanning electron microscopy (FESEM) results of Corn straw combustion, Pine wood combustion, Vehicle exhaust and Coal combustion.

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