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Determination of carbonate-C in biochars

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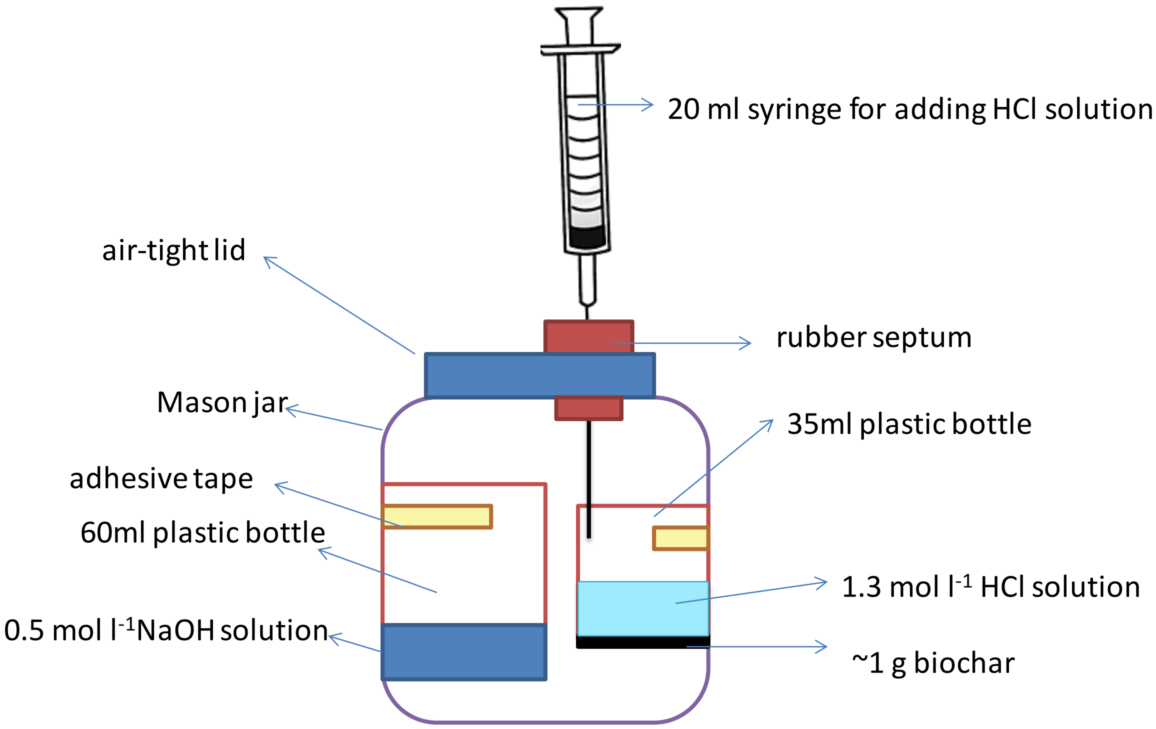

Fig. S1. An apparatus used for trapping CO_2 evolved from biochar after the addition of HCl solution. The setup was slightly modified from Bundy and Bremner (1972).

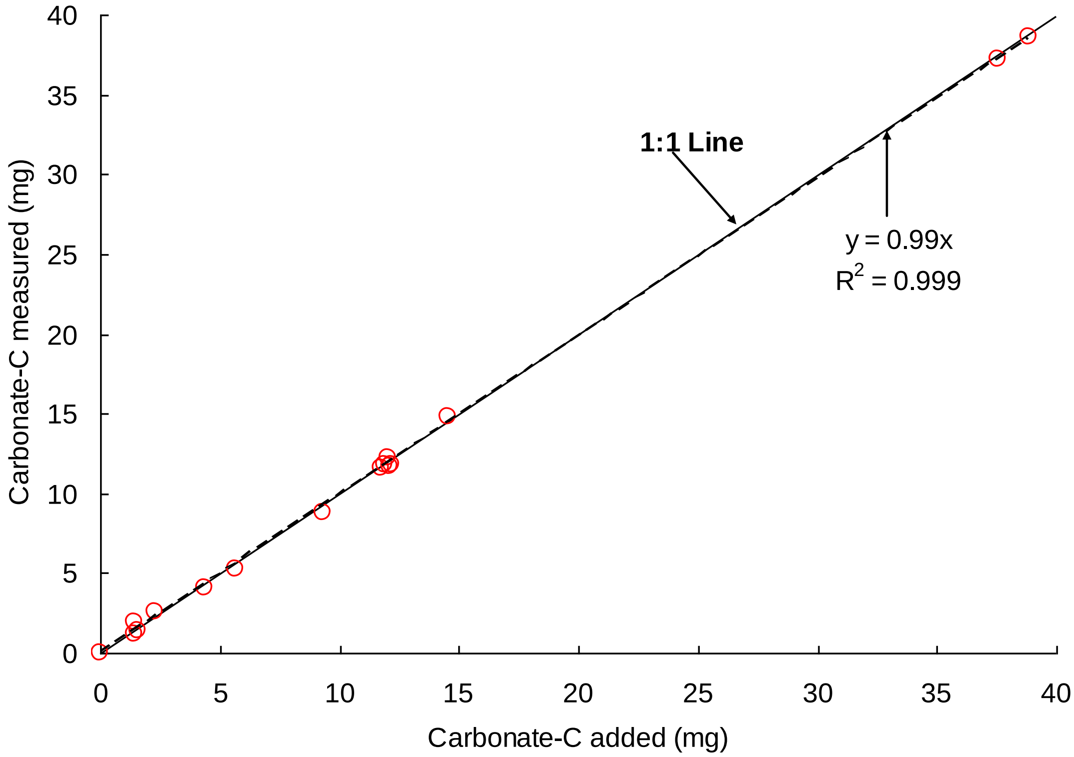

Fig. S2. The calibration curve used for correcting concentration of CO_3-C in biochars according to a titrimetric method. Oven-dried $CaCO_3$ was used as a standard.

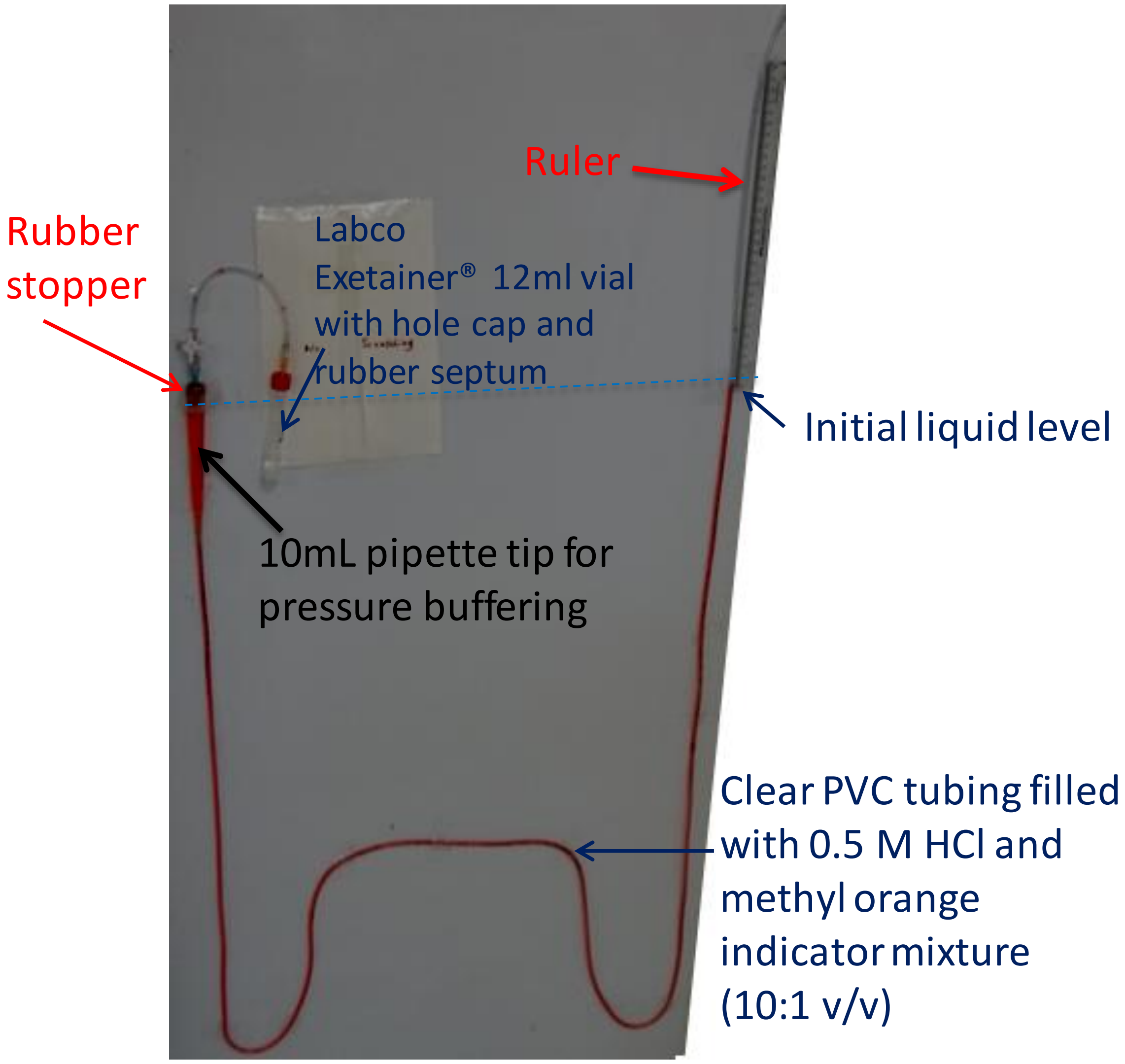

Fig. S3. A home-made manometer used for CO_2 volume measurement.

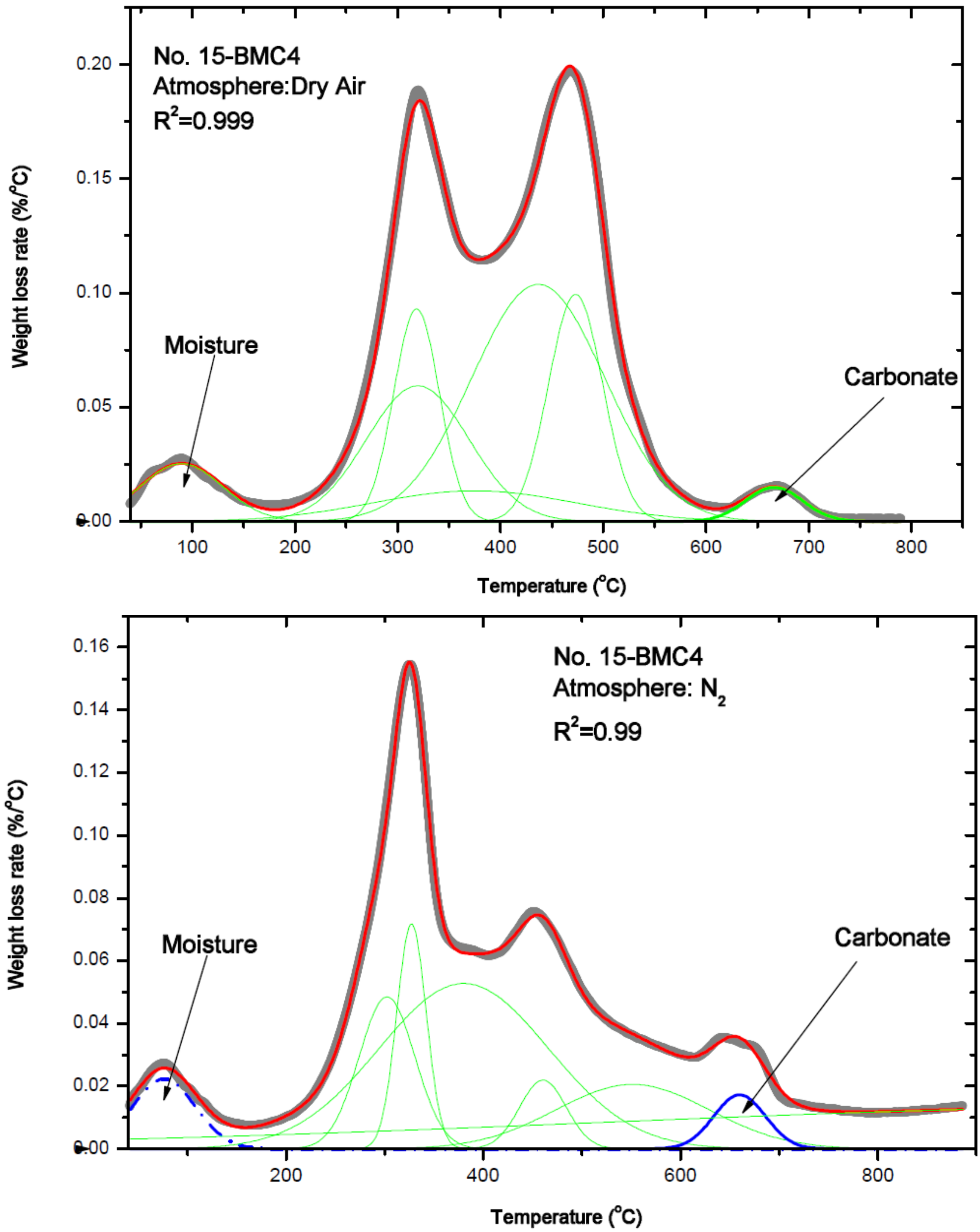

Fig. S4. Examples of deconvolution of peaks associated with carbonate decomposition.

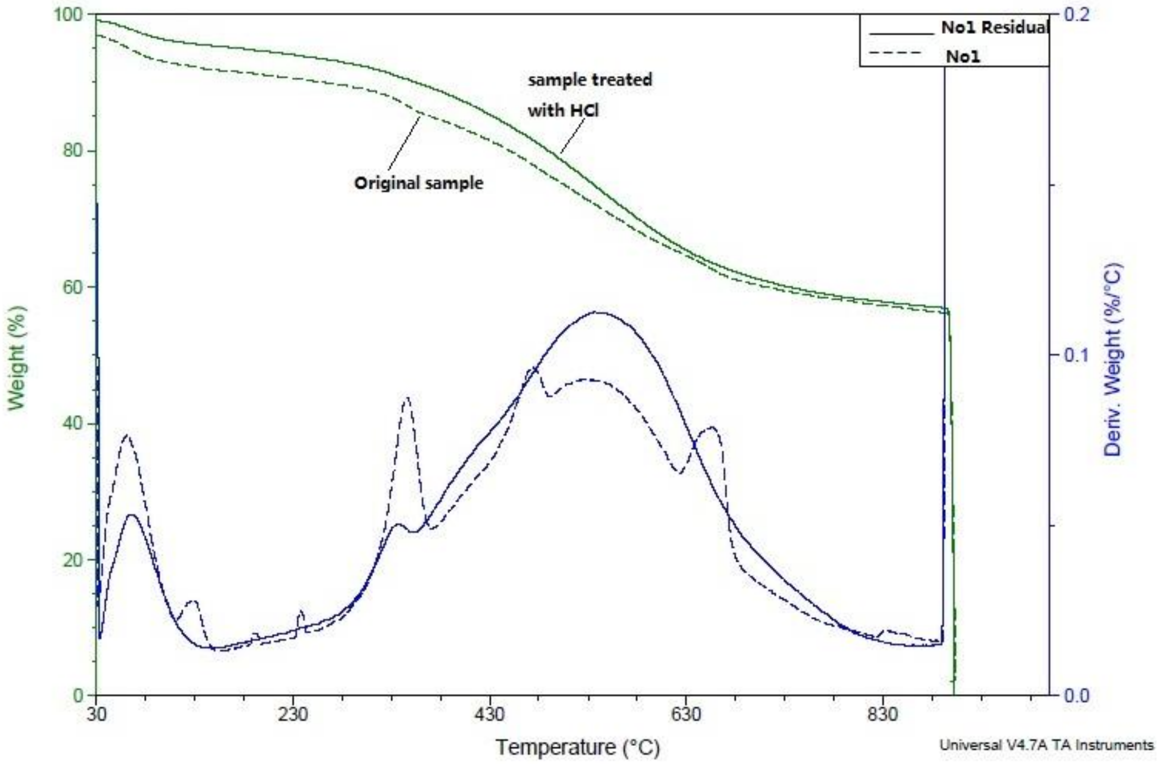

Fig. S5. TG/DTGA curves of sample No1 and its residual after acid treatment.

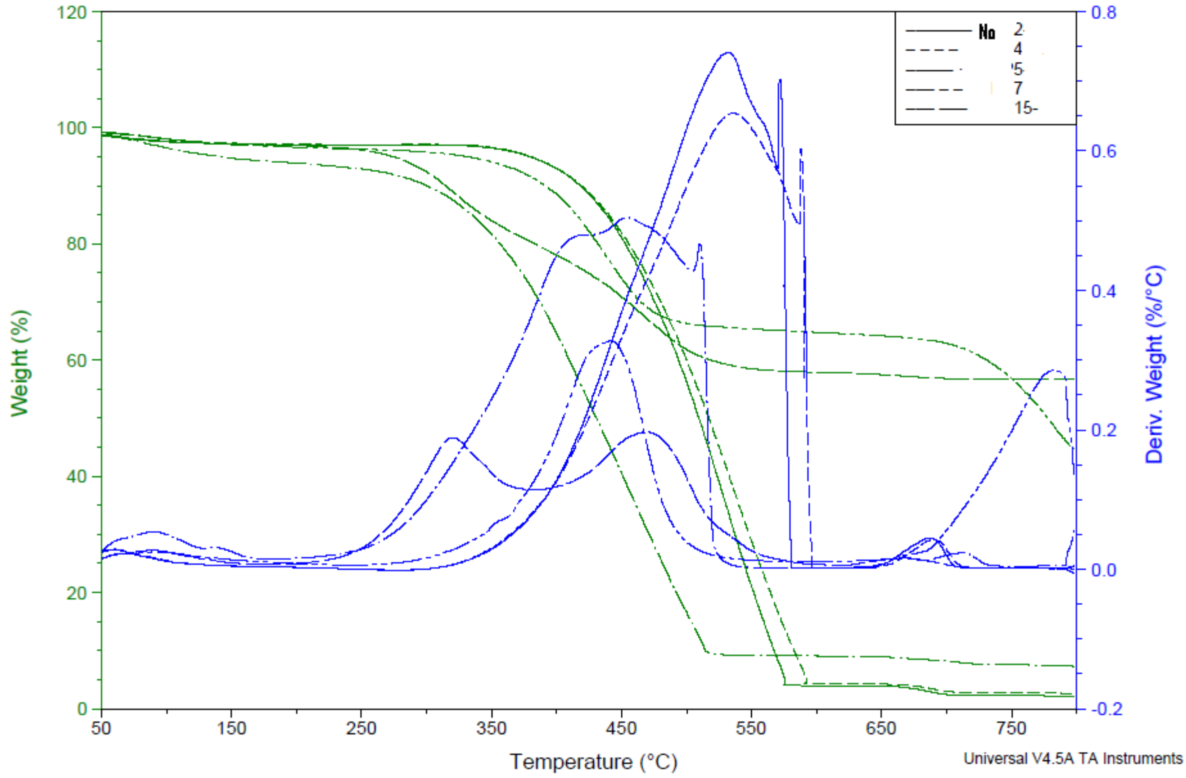

Fig. S6. TG/DTG curves of selected samples. Samples were run in an air atmosphere.

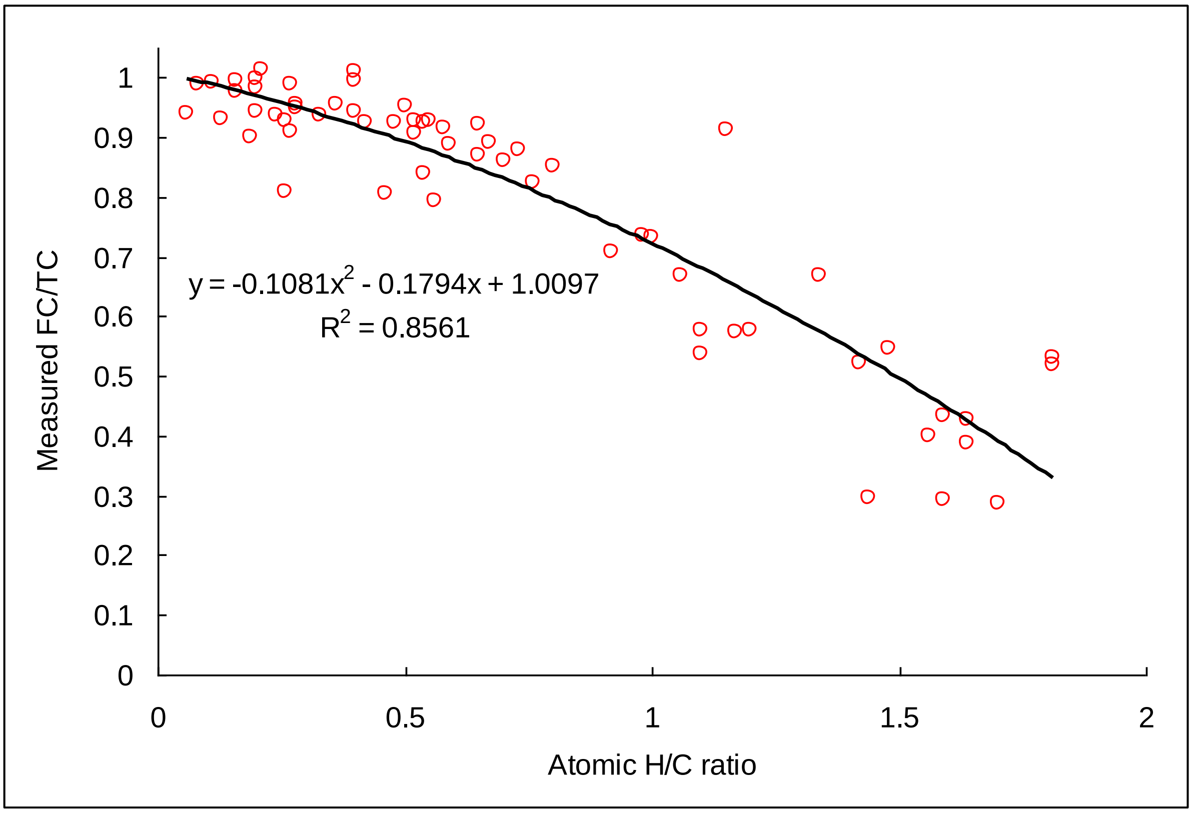

Fig. S7. Relationship between the measured fixed C to total C ratio (FC/TC) and molar H to total C ratio (H/C). Values were collected from literature as shown in Table S3. Therefore, FC/TC can be estimated according to the following equation (Equation 6 in the manuscript):

$$FC/TC= -0.1081(H/C)^2 - 0.1794(H/C) + 1.0097$$

where H/C is the molar ratio of H to total C of biochar. As >90% of the literature values used to obtain this equation corresponded to biochar samples low in ash (<20%) and therefore low in carbonate-C and inorganic H, the predicted data should reflect the ratios of FC/TC of low-ash biochars. Furthermore, the predictive accuracy of this model is apparently low for charred materials with a molar H/C ratio >1.

Table S1. Decomposition temperature zones of common carbonate minerals at atmospheric CO_2 pressure

Minerals	Decomposition temperature zones (°C)	Reference
dolomite	two steps peaked at 772 and 834°C	(Samtani et al. 2002; Gunasekaran and Anbalagan 2007)
magnesite	500-650	
calcite	600-800	
synthetic calcite	520-595	(Frost et al. 2009)
ankerite	two steps peaked at 657 and 857°C	(Milodowski et al. 1989; Vassileva and Vassilev 2005)
siderite	500-600	

Table S2. Correlation matrix of carbonate-C in biochars determined by various methods (including No 7)

with No 7	acid wash	acid fumigation	titrimetric	TGA-N_2	TGA-air
acid wash	1.00*				
acid fumigation	0.93*	1.00*			
titrimetric	0.93*	0.98*	1.00*		
TGA-N_2	0.95*	0.96*	0.98*	1.00*	
TGA-air	0.94*	0.96*	0.99*	0.99*	1.00*

*Significant at $\alpha = 0.05$.

Table S3. An overview of selected chemical compositions of biochars

Biochar	C^A	H^A	O^A	Fixed C (%)^A	H/C^B	O/C^B	Molar Fixed C/C^C	Reference
Pine wood100 (W100)	50.60	6.68	42.70	21.96	1.59	0.63	0.43	
W200	50.90	6.95	42.20	21.73	1.64	0.62	0.43	
W300	54.80	6.50	38.70	28.63	1.42	0.53	0.52	
W400	74.10	4.95	20.90	63.08	0.80	0.21	0.85	
W500	81.90	3.54	14.50	74.26	0.52	0.13	0.91	
W600	89.00	2.99	8.00	88.47	0.40	0.07	0.99	
W700	92.30	1.62	6.00	93.59	0.21	0.05	1.01	Keiluweit *et al.*, 2010
Fescue straw100 (G100)	48.60	7.25	44.10	25.24	1.81	0.69	0.52	
G200	47.20	7.11	45.10	25.03	1.81	0.72	0.53	
G300	59.70	6.64	32.70	39.96	1.34	0.41	0.67	
G400	77.30	4.70	16.70	67.98	0.73	0.16	0.88	
G500	82.20	3.32	13.40	76.00	0.48	0.12	0.92	
G600	89.00	2.47	7.60	83.35	0.33	0.06	0.94	

G700	94.20	1.53	3.60	88.72	0.20	0.03	0.94	
Mallee wood-RB (MW-RB)	49.00	6.70	44.10	18.98	1.64	0.68	0.39	
MW-LB	49.10	5.90	44.60	14.51	1.44	0.68	0.30	
MW-R300	59.10	5.90	34.70	34.01	1.20	0.44	0.58	
MW-L300	59.60	5.80	34.30	34.14	1.17	0.43	0.57	
MW-R500	84.20	3.80	11.50	77.93	0.54	0.10	0.93	
MW-R500	85.10	3.90	10.50	79.02	0.55	0.09	0.93	
MW-R750	89.70	1.50	8.20	89.58	0.20	0.07	1.00	
MW-L750	92.30	2.10	5.10	91.22	0.27	0.04	0.99	Wu *et al.*, 2011
Mallee leaf-RB (ML-RB)	56.00	7.30	34.90	22.45	1.56	0.47	0.40	
ML-LB	56.70	7.50	33.70	16.63	1.59	0.45	0.29	
ML-R300	68.60	6.30	22.80	36.79	1.10	0.25	0.54	
ML-L300	68.50	6.30	23.00	39.50	1.10	0.25	0.58	
ML-R500	81.60	4.00	11.80	72.47	0.59	0.11	0.89	
ML-L500	81.30	3.90	12.30	74.48	0.58	0.11	0.92	
ML-R750	87.30	2.00	8.30	79.49	0.27	0.07	0.91	

ML-L750	90.70	2.00	4.70	84.24	0.26	0.04	0.93	
Mallee bark-RB (MB-RB)	52.00	6.40	40.90	28.36	1.48	0.59	0.55	
MB-LB	49.30	7.00	42.10	14.19	1.70	0.64	0.29	
MB-R300	62.30	4.80	31.40	44.08	0.92	0.38	0.71	
MB-L300	63.90	5.20	29.30	47.09	0.98	0.34	0.74	
MB-R500	88.50	3.40	6.30	71.44	0.46	0.05	0.81	
MB-L500	82.20	3.40	12.70	78.40	0.50	0.12	0.95	
MB-R750	84.40	1.70	12.90	79.20	0.24	0.11	0.94	
MB-L750	87.00	2.00	9.90	83.14	0.28	0.09	0.96	
Corn stover	74.36	4.03	19.91	64.62	0.65	0.20	0.87	
Corn stover	72.55	4.62	21.26	59.76	0.76	0.22	0.82	
Corn stover	67.83	5.97	25.14	45.40	1.06	0.28	0.67	
Corn stover	66.59	5.53	26.52	48.73	1.00	0.30	0.73	Brewer *et al.*, 2011
Corn stover	84.97	0.39	13.25	79.92	0.06	0.12	0.94	
Corn stover	87.28	2.87	7.58	82.37	0.40	0.07	0.94	
Switchgrass	76.41	4.48	18.14	65.69	0.70	0.18	0.86	

Switchgrass	92.17	4.30	2.26	73.09	0.56	0.02	0.79	
Switchgrass	85.19	3.84	9.89	71.52	0.54	0.09	0.84	
Switchgrass	83.23	1.31	14.75	75.00	0.19	0.13	0.90	
Switchgrass	83.23	0.94	14.65	77.53	0.13	0.13	0.93	
Switchgrass	79.89	1.74	17.72	64.69	0.26	0.17	0.81	
Switchgrass	83.79	2.76	11.91	84.76	0.40	0.11	1.01	
Red oak	81.50	3.55	14.20	75.54	0.52	0.13	0.93	
Mixed hardwood	85.12	2.58	11.82	81.27	0.36	0.10	0.95	
Wood waste	92.73	1.57	5.08	91.05	0.20	0.04	0.98	
Eastern hemlock	79.24	4.40	15.91	70.54	0.67	0.15	0.89	
Cotton stalk-250 (CS-250)	59.56	5.70	33.66	54.43	1.15	0.42	0.91	Chen *et al.*, 2012
CS-350	77.55	4.19	16.74	71.37	0.65	0.16	0.92	
CS-450	86.10	3.03	9.40	79.61	0.42	0.08	0.92	
CS-550	90.26	2.14	6.12	85.69	0.28	0.05	0.95	
CS-650	91.62	1.19	5.84	89.63	0.16	0.05	0.98	
CS-750	91.88	1.20	5.39	91.42	0.16	0.04	1.00	

CS-850	92.14	0.86	5.66	91.38	0.11	0.05	0.99
CS-950	92.85	0.63	5.24	91.90	0.08	0.04	0.99

[A]All the selected parameters are recalculated on a dried ash-free (daf) basis;

[B]H/C and O/C are molar ratios;

[C]Fixed C/C is the ratio of fixed C to total C content.

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