Supplementary Materials

Kinetics of Carbon Mineralization of Biochars in Three Excessive Compost-Fertilized Soils: Effects of Feedstocks and Soil Properties

Chen-Chi Tsai*, Yu-Fang Chang

Department of Forestry and Natural Resources, National Ilan University, Ilan 26047, TAIWAN, ROC

Corresponding author, E-mail: cctsai@niu.edu.tw

Materials and Methods

Chemical functional groups were determined by Fourier transform infrared spectra (FTIR), and the biochar FTIR spectra were obtained from pressed pellets of 1:10 biochar/KBr mixtures using a PerkinElmer Pyris Diamond (PerkinElmer, Waltham, MA, USA). The pellets were then scanned in the reflectance mode in the range 4000~500 cm^{-1}. In addition, in this study the powdered biochar samples were placed into aluminum holders to obtain random powder X-ray diffraction (XRD) patterns. The scans were collected from 3 °to 75 °using a BRUKER AXS D8A (Bruker Corporation, Billerica, MA, USA) and Ni-filtered CuKα radiation (35 kV, 28.5 mA), with a step size of 0.02° 2θ and a scan speed of 1.0 ° 2θ/min. The minerals were identified by comparing the d-spacings in the diffraction patterns to the ICDD-PDF mineral database. Scanning electron microscopy (SEM) observations of biochar used powdered samples that were placed on aluminum stubs using carbon tape, and electron micrographs were obtained using FEI Inspect S (Thermo Fisher Scientific Inc., Waltham, MA, USA).

Results and Discussion

The Fourier-transform infrared spectroscopy (FTIR) spectrum of the high temperature-pyrolyzed (> 700°C) ash, bamboo and lead tree biochar all displayed similarly various low-intensity bands (Supplemental Fig. S1), corresponding to the stretching of OH in water, H-bonded hydroxyl groups (3500~3200 cm^{-1}), methyl CH asymmetric -CH_3 (2935 cm^{-1}), ester C=O bonds (1739 cm^{-1}) (no for bamboo biochar), aromatic C=C (1600 and 1440 cm^{-1}), O-H bending in plane bending of phenolic -OH (1375 cm^{-1}), C-O stretching in the guaiacyl ring (1270 cm^{-1}) (no for bamboo biochar), C-

O stretching in the O-CH_3 and C-OH groups (1100 and 1030 cm^{-1}), and the C-H bending (875 cm^{-1}) of aromatic CH out-of-plane deformation [1-3]. The total loss of the plant's amorphous structure would occur at 700 ℃, and resulted in the peaks between the 1500-1200 cm^{-1}, indicating the existence of lignin related functional groups, almost disappear [3]. These FTIR spectra results agree with the changes in elemental composition, indicating high temperature-pyrolyzed biochar with higher aromatic structure content and fewer polar functional groups.

The X-ray diffraction (XRD) patterns of three biochars shown similar broad hump (Supplemental Fig. S1), and Singh et al. [4] suggested that the broad hump in the XRD pattern indicated the poorly crystalline C-rich phase in a biochar sample. As has suggested in previous study [5], the major crystalline phase in the lead tree biochar was calcite ($CaCO_3$), and the biochar XRD pattern included a broad hump with a centroid at approximately 3.8 Å, in line with Singh et al. [4]. The XRD pattern of ash biochar shown weaker peak at approximately 3.8 Å, suggesting calcite formed. There is no obvious peak could be observed in the XRD pattern of bamboo biochar, indicating no crystalline phase formed. Scanning electron microscopy (SEM) showed that the cell structure of three biochars was mostly maintained after pyrolysis (Supplemental Fig. S1), however, there was more structural collapse in bamboo biochar. The porous structure examination of the resulting biochars can be clearly seen in the SEM photographs, revealing irregular and highly porous structures with tubular shapes, rough surface structures and sharp edges, and a variety of shapes in the macropores and mesopores. The honeycomb-like pore structures are clear in ash biochar and lead tree biochar. Although not quantitative, the surface shape of ash and lead tree biochar appears to be clearer and sharper than that of bamboo biochar and it generally shows a more active porous structure, with many small pores existing within or between big pores. The bamboo biochar developed high porosity, presenting longitudinal pores with sizes ranging from micro to macro pores (10-200 μm) [6].

Canonical discriminant analysis

Canonical discriminate functions (CDFs), which are the canonical weights of the original variables, provide information about the discriminatory power of each variable and are usually standardized to aid interpretation by plotting the standardized canonical scores of individuals in each group for each CDF [28]. In addition, the absolute values and signs of the standardized canonical coefficients are used to rank variables in order of their contribution and to characterize the function. However, when many groups are under study and visual discrimination is difficult, scores of dominant CDFs may undergo analysis of variance (ANOVA) followed by an independent multiple comparison test. Using correlations between CDFs and original variables enhances interpretation of CDFs, indicates how individual variables contribute to the CDF, and highlights the relationship between original variables and CDFs [28]. A distinction is made between interpreting each CDF and evaluating the contribution of each original variable to that CDF.

Figure S2 illustrates that the chemical behavior of the seven treatments for SAO, MAI, and SAI soils can be differentiated. A little overlap was observed between A2 and L2 treatments for the SAI soil. Can1 explained 94.1%, 87.7%, and 85.9% of the variability of the chemical behavior of the seven treatments in SAO, MAI, and SAI soils, respectively; Can 2 explained 4.67%, 7.46%, and 10.5%, respectively; and both functions together explained 98.8%, 95.2%, and 96.4%, respectively. In SAO and SAI soils, Can1 discriminated the treatments into five groups: B5, A5, B2 and L5, A2 and L2, and control; Can 2 discriminated the seven treatments to two groups: B5, B2, A2, and control, and A5, L2, and L5. A5 treatment was close to L5 treatment in SAI soil. The five groups discriminated in MAI soil by Can1 were B5; A5; L5; A2, B2, and L2; and control.

Both in MAI and SAI soils, Can2 discriminated the seven treatments to two groups: B5, B2, and control; and A2, A5, L2, and L5. Standardized canonical discrimination coefficient (SCC) and correlations between CDFs and original variables revealed that the available M3-K in three soils was the most important for the discrimination of the treatments based on Can1, especially for the SAO soil (Table S5). Except for M3-K, cumulative CO_2–C release and TC in SAO soil, TC and M3-Al in MAI soil, and TC and M3-Mn in SAI soil, respectively, were the most important parameters for Can1. For Can2, M3-Fe and TC in SAO soil; TC and M3-Cu, -Pb and -Zn in MAI soil; and M3-Ca, -Zn, cumulative CO_2-C release, and TP were the most important variables for the discrimination of the treatments. In general, the effect of biochar treatments, including feedstock and rate, was distinct in SAO soil, but it was less so in MAI and SAI soil. Ash and bamboo biochar applied at the high rate evidently influenced the soil, with SAO > MAI > SAI. The 2% bamboo biochar and 5% lead tree biochar, and 2% ash biochar and

2% lead tree biochar both produced similar effects on SAO and SAI soils. The 2% ash, bamboo, and lead tree biochar all had similar influences on MAI soil.

References

1. Keiluweit, M.; Nico, P.S.; Johnson, M.G.; Kleber, M. Dynamic Molecular Structure of Plant Biomass-Derived Black Carbon (Biochar). *Environ. Sci. Technol.* **2010,** *44*, 1247-1253. https://doi.org/10.1021/es9031419
2. Chen, D.; Yu, X.; Song, C.; Pang, X.; Huang, J.; Li, Y. Effect of pyrolysis temperature on the chemical oxidation stability of bamboo biochar. *Bioresour. Technol.* **2016**, *218*, 1303–1306. https://doi.org/10.1016/j.biortech.2016.07.112
3. Feng, Z., Zhu, L. Sorption of phenanthrene to biochar modified by base. *Front. Environ. Sci. Eng.* **2018**, *12*, 1. https://doi.org/10.1007/s11783-017-0978-7
4. Singh, B.; Singh, B.P.; Cowie, A.L. Characterisation and evaluation of biochars for their application as a soil amendment. *Aust. J. Soil Res.* **2010**, *48*, 516-525. https://doi.org/10.1071/SR10058
5. Tsai, C. C., & Chang, Y. F. (2016). Viability of biochar on reducing C mineralization and improving nutrients status in a compost-treated Oxisols. *Taiwanese J. Agric. Chem. Food Sci.* **2016**, *54*, 74-89. http://dx.doi.org/10.6578%2fTJACFS.2016.009
6. Hernández-Mena, L.; Pécora, A.; Beraldo, A. Slow pyrolysis of bamboo biomass: analysis of biochar properties. *Chem. Eng. Trans.* **2014**, *37*, 115-120. DOI: 10.3303/CET1437020

Figure Captions

Figure. S1. Spectra of FT-IR and XRD, and SEM images of three studied biochars derived from ash (A), bamboo (B), and lead tree (L).

Figure S2. Canonical scores of the first two canonical discriminant functions (Can) of seven treatments for SAO, MAI, and SAI soil.

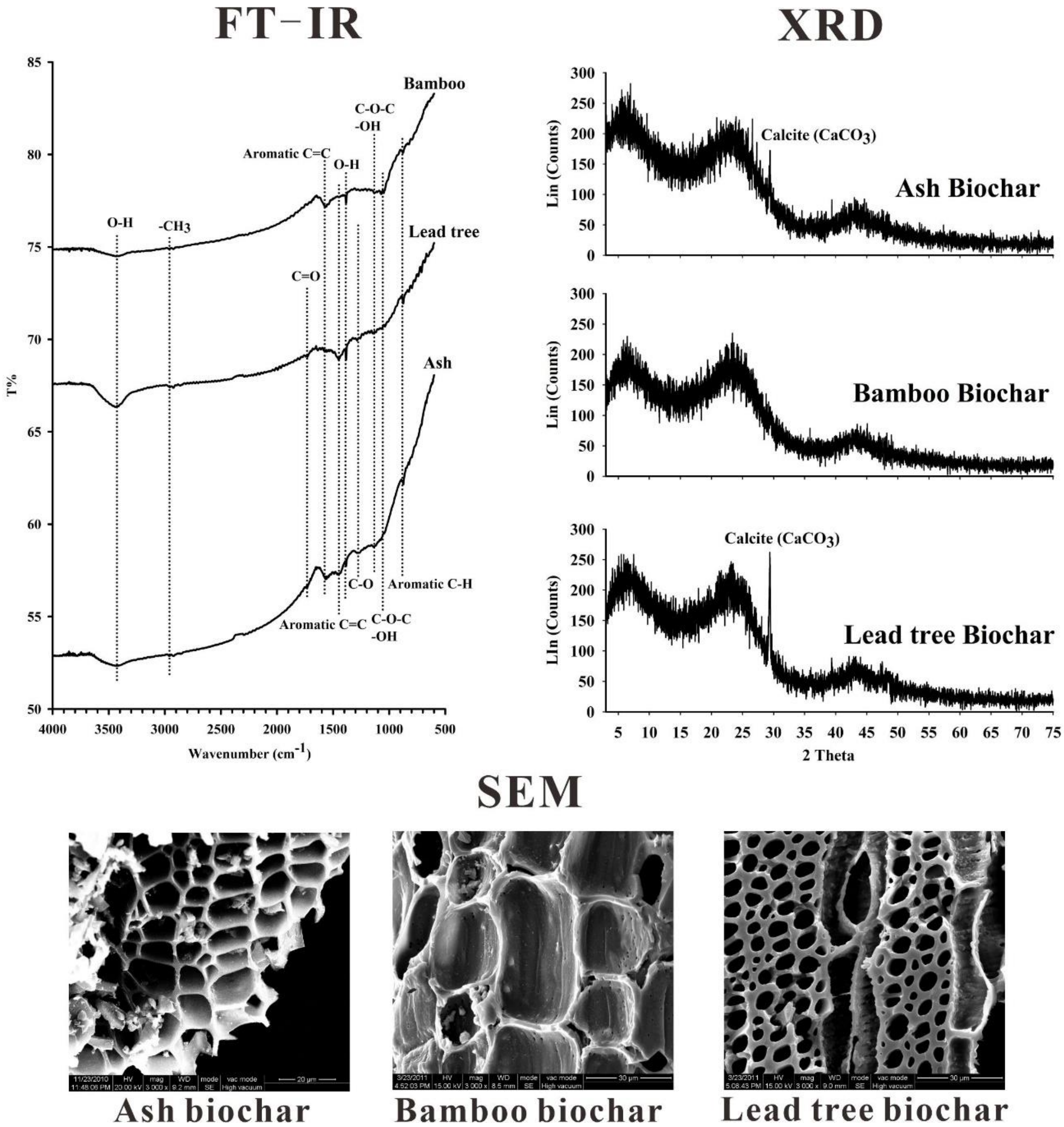

Figure S1. Spectra of FT-IR and XRD, and SEM images of three studied biochars derived from ash (A), bamboo (B), and lead tree (L).

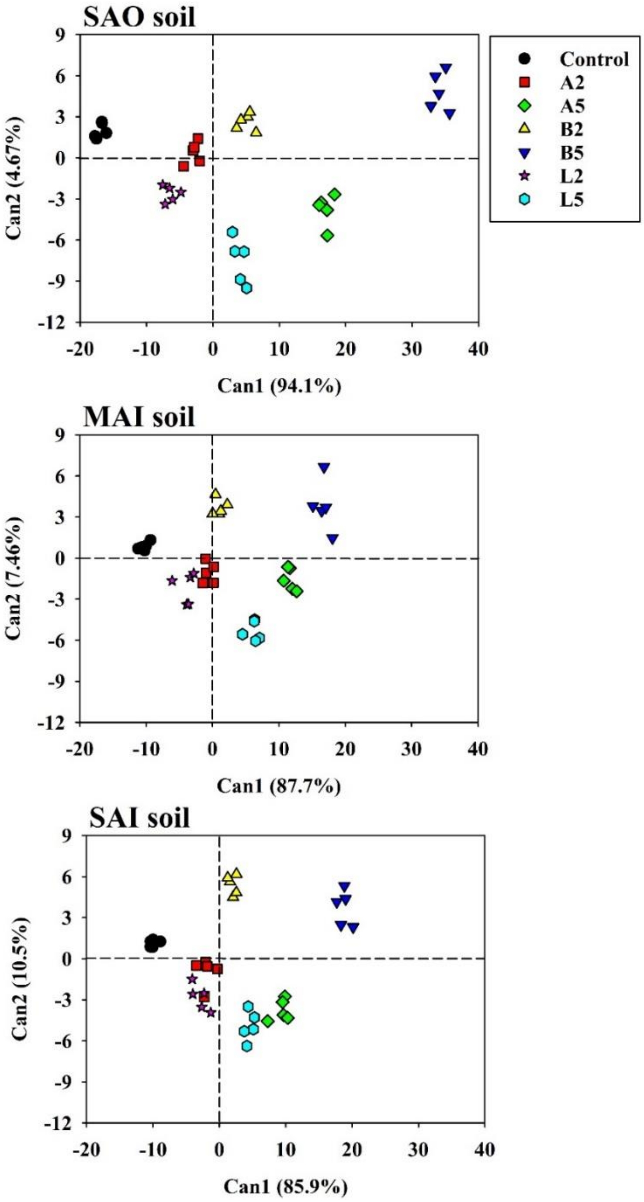

Figure S2. Canonical scores of the first two canonical discriminant functions (Can) of seven treatments for SAO, MAI, and SAI soil. (A2 & A5 = 2% & 5% ash biochar; B2 & B5 = 2% & 5% bamboo biochar; L2 & L5 = 2% & 5% lead tree biochar).

Table S1. Characteristics of studied compost and three soils.

Characteristics	Compost	Pc Soil (SAO)	Eh Soil (MAI)	An Soil (SAI)
pH	8.41 [1]	6.1/5.0 [2]	7.5/7.2 [2]	6.5/6.2 [2]
Electrical conductivity (dS m^{-1})	3.79 [1]	0.45	2.21	0.81
Sand (%)		11	24	33
Silt (%)		30	36	33
Clay (%)		59	39	34
Soil Texture		Clay	Clay loam	Clay loam
Total C (%)	23.3	2.03	1.11 (0.81) [3]	0.94
Total N (g/kg)	22.6	2.71	2.32	1.58
Total P (g/kg)	10.2	1.16	0.98	0.77
Exchangeable K (cmol(+) $kg^{-1}soil^{-1}$)	6.43	0.32	0.29	0.21
Exchangeable Na(cmol(+) $kg^{-1}soil^{-1}$)	1.09	0.31	0.26	0.37
Exchangeable Ca (cmol(+) $kg^{-1}soil^{-1}$)	2.70	4.85	2.94	2.24
Exchangeable Mg (cmol(+) $kg^{-1}soil^{-1}$)	2.72	0.64	0.80	0.36
Cation exchange capacity (cmol(+) $kg^{-1}soil^{-1}$)	19.7	8.58	11.5	14.2
Base saturation (%)	69	71	37	22
Mehlich 3-P (mg kg^{-1})	6874	163	236	94.0
Mehlich 3-K (mg kg^{-1})	8911	68.4	108	94.1
Mehlich 3-Ca (g kg^{-1})	14.5	2.03	8.22	2.99
Mehlich 3-Mg (mg kg^{-1})	3972	143	344	401
Mehlich 3-Fe (mg kg^{-1})	396	524	589	1199
Mehlich 3-Mn (mg kg^{-1})	188	29.0	213	185
Mehlich 3-Cu (mg kg^{-1})	6.22	9.77	9.95	3.17
Mehlich 3-Pb (mg kg^{-1})	1.23	10.8	11.7	1.54
Mehlich 3-Zn (mg kg^{-1})	62.4	20.4	7.98	5.28

[1] The pH and electrical conductivity (EC) of biochar and compost were measured using 1:5 solid: solution ratio after shaking for 30 min in deionized water; [2] Soil pH was determined in soil-to-deionized water ratio of 1:1 (g mL^{-1}) and in soil-to-1N KCl ratio of 1:1 (g mL^{-1}); [3] carbonate content; [4] ND = not detected. (**Data from Tsai and Chang [10]).**

Table S2. Significance (P value) of repeated-measures MANOVA results on CO_2-C release after 400 days of incubation.

Source of variation	**df**[1]	**CO_2-C release**[2]
Between subject effect		
Soil	2	**
Biochar	2	*
Rate	2	***
Soil × Biochar	4	ns
Biochar × Rate	4	ns
Soil × Rate	4	ns
Within subject effect		
Time	9	***
Time × Soil	18	***
Time × Biochar	18	***
Time × Rate	18	***
Time × Soil × Biochar	36	**
Time × Soil × Rate	36	***
Time × Biochar × Rate	36	ns

[1]: df = degree of freedom; [2] *: significant at $p < 0.01$, ** $p < 0.001$, *** $p < 0.0001$, ns = not significant.

Table S3. Mean values of soil total carbon (TC), total nitrogen (TN), total phosphorus (TP), and Mehlich-3 extractable nutrients of biochar treatments of three soils after 400-day C mineralization incubation[1].

Soil	Treats[2]	TC	TN	TP	P	K	Ca	Mg	Fe	Al	Mn	Cu	Pb	Zn	Sum
		%	g kg^{-1}	g kg^{-1}	-------------	-------------	-------------	-------------	-------------	mg kg^{-1}	-------------	-------------	-------------	-------------	cmol(+) kg^{-1} $soil^{-1}$
SAO	Control	2.71 d	4.32 ab	2.56 bcd	590 b	350 f	2745 ab	466 ab	642 ab	1561 bc	30.7 b	14.2 a	19.6 a	49.3 abc	7.88 c
	A2	4.37 c	4.01 d	3.13 a	635 a	414 d	2707 ab	472 a	656 a	1516 cd	32.6 a	13.8 a	19.6 a	51.2 a	7.97 c
	A5	7.11 a	4.05 cd	2.86 ab	605 ab	511 b	2630 b	463 ab	620 bc	1481 de	32.0 ab	13.6 ab	18.9 b	49.5 abc	8.02 c
	B2	4.37 c	4.49 a	2.81 abc	577 b	454 c	3144 a	456 ab	618 bc	1618 a	30.9 b	14.2 a	19.8 a	50.7 ab	8.68 ab
	B5	5.95 b	4.30 abc	2.60 bcd	573 b	608 a	2974 ab	447 b	625 abc	1591 ab	32.0 ab	14.0 a	19.5 a	50.7 ab	8.81 a
	L2	3.94 c	4.22 bcd	2.31 d	595 b	375 e	2778 ab	460 ab	605 cd	1513 cde	32.0 ab	13.6 ab	18.9 b	48.0 bc	7.88 c
	L5	6.40 b	4.11 bcd	2.37 cd	579 b	413 d	3008 ab	447 b	585 d	1458 e	31.8 ab	13.1 b	18.5 b	47.1 c	8.15 bc
MAI	Control	2.03 e	3.96 bc	2.41 ab	686 b	419 f	7073 a	630 a	538 b	303 a	244 b	11.3 bc	15.6 bc	25.8 bc	12.3 ab
	A2	3.56 c	3.69 c	2.15 bc	728 a	482 d	5722 b	637 a	569 a	295 ab	255 a	10.8 de	15.2 cd	25.8 bc	10.9 c
	A5	5.83 a	3.82 c	2.23 abc	732 a	551 b	6763 ab	615 a	533 b	269 d	242 b	10.8 d	14.8 d	26.0 b	12.2 abc
	B2	3.01 d	4.09 ab	2.48 a	678 b	509 c	7000 a	612 a	511 bc	282 bcd	240 b	11.8 a	16.3 a	28.0 a	12.4 ab
	B5	5.33 b	4.14 ab	2.50 a	684 b	647 a	7358 a	613 a	497 c	287 bc	235 b	11.6 ab	15.8 ab	27.8 a	13.2 a
	L2	3.55 c	4.25 a	2.43 ab	673 b	461 e	6379 ab	636 a	526 bc	289 abc	244 b	11.1 cd	15.0 d	24.0 cd	11.6 bc
	L5	5.95 a	4.18 ab	2.09 c	633 c	508 c	6370 ab	612 a	520 bc	276 cd	238 b	10.4 e	14.2 e	22.3 d	11.6 bc
SAI	Control	1.68 c	3.23 c	2.40 a	504 b	355 e	3491 b	677 ab	903 a	495 a	150 c	3.78 c	1.56 b	18.0 bc	8.25 b
	A2	3.21 b	3.07 c	2.29 ab	523 b	401 d	3387 b	644 b	885 a	475 ab	148 c	3.65 c	1.49 b	17.4 c	8.13 b
	A5	5.39 a	3.17 c	2.02 b	535 ab	497 b	3021 b	647 b	898 a	429 c	153 bc	4.09 ab	1.92 a	17.7 bc	7.89 b
	B2	2.90 b	3.31 bc	2.52 a	569 a	468 c	4122 a	699 a	927 a	468 b	159 ab	4.11 ab	2.04 a	21.0 a	9.38 a
	B5	5.48 a	3.20 c	2.39 a	536 ab	589 a	3139 b	670 ab	923 a	468 b	163 a	3.90 bc	2.09 a	20.5 a	8.39 b
	L2	3.16 b	3.49 ab	2.20 ab	503 b	412 d	3261 b	669 ab	887 a	484 ab	151 bc	4.12 ab	1.78 ab	17.9 bc	8.07 b
	L5	5.29 a	3.64 a	2.19 ab	531 b	466 c	3082 b	671 ab	883 a	475 ab	152 bc	4.24 a	2.01 a	18.6 b	7.97 b

[1] Means (n = 5) compared within a column of the same soil followed by a different lowercase letter are significantly different at $p < 0.05$ using a one-way ANOVA. Sum = (K+Ca+Mg+Fe+Al+Mn+Cu+Pb+Zn).

[2] A = ash biochar, B = bamboo biochar, L = lead tree biochar, 2 = 2% addition, 5 = 5% addition.

Table S4. Percentage (%) of mean relative value of soil fertility after 400-day C mineralization incubation[1].

Treats	TC[2]	TN[2]	TP[2]	P	K	Ca	Mg	Fe	Al	Mn	Cu	Pb	Zn	Sum
SAO														
A2	61.2 c[3]	-7.0 c	22 a	7.6 a	19 d	-1.4 a	1.5 a	1.7 a	-2.9 b	6.2 a	-2.1 ab	0.3 a	3.9 a	1.1 bc
A5	162 a	-6.0 c	12 ab	2.4 a	46 b	-4.2 a	-0.4 ab	-3.1 b	-5.3 bc	4.3 ab	-4.0 b	-3.6 b	0.56 ab	1.9 bc
B2	61 c	3.9 a	10 ab	-2.3 b	30 c	3.3 a	-2.1 ab	-3.2 b	3.8 a	0.7 b	0.04 a	0.6 a	2.9 a	10 ab
B5	119 b	-0.5 ab	1.5 ab	-2.9 b	74 a	8.3 a	-4.0 b	-2.4 b	1.9 a	4.3 ab	-1.36 ab	0.1 a	2.9 a	12 a
L2	45 c	-2.3 bc	-10 b	0.7 b	7.4 e	1.2 a	-1.2 ab	-5.6 bc	-3.1 b	4.1 ab	-3.7 b	-3.3 b	-2.6 bc	0.04 c
L5	136 ab	-4.7 bc	-7 b	-1.9 b	18 d	9.5 a	-3.8 b	-8.9 c	-6.6 c	3.6 ab	-7.3 c	-5.8 c	-4.5 a	3.4 abc
MAI														
A2	75 b	-6.8 b	-11 c	6.1 a	15 d	-19 b	1.1 a	6.1 a	-2.4 a	4.74 a	-5.4 c	-2.5 c	0.1 bc	-12 c
A5	187 a	-3.4 b	-7.4 bc	6.7 a	32 b	-4.4 a	-2.3 a	-1.5 b	-11 c	-0.5 b	-4.8 bc	-4.8 d	0.8 abc	-1.0 ab
B2	48 b	3.4 a	3.0 a	-1.2 bc	22 c	-1.0 a	-2.9 a	-4.7 b	-6.9 abc	-1.3 b	3.6 a	4.3 a	8.6 a	0.4 ab
B5	162 a	4.5 a	3.8 a	-0.3 b	55 a	4.0 a	-2.6 a	-7.6 b	-5.1 ab	-3.6 b	2 a	1.7 b	7.8 ab	6.8 a
L2	75 b	7.3 a	1.1 ab	-2.0 bc	10 e	-10 ab	1.0 a	-2.2 b	-4.5 ab	0.2 ab	-2.14 bc	-4.0 cd	-7.0 cd	-6.3 bc
L5	193 a	5.6 a	-13 c	-7.7 c	21 c	-10 ab	-2.8 a	-3.3 b	-8.9 bc	-2.1 b	-8.4 d	-8.7 e	-14 d	-6.0 bc
SAI														
A2	91 b	-4.8 d	-4.7 abc	3.7 bc	13 d	-3.0 b	-4.9 b	-1.7 bc	-3.7 a	-0.9 c	-3.6 c	-4.4 b	-3.3 c	-1.4 b
A5	220 a	-1.8 cd	-16 c	6.2 b	40 b	-13 b	-4.3 b	-0.4 abc	-13 b	2.3 bc	8.2 ab	23 a	-1.4 c	-4.4 b
B2	72 b	2.4 bc	4.7 a	13 a	32 c	18 a	3.3 a	2.9 a	-5.5 a	6.3 ab	8.4 ab	31 a	17 a	14 a
B5	226 a	-0.7 cd	-0.9 ab	6.3 b	66 a	-10 b	-1.1 b	2.1 ab	-5.4 a	9.0 a	3.0 b	34 a	14 a	1.7 b
L2	88 b	8.0 ab	-8.4 abc	-0.2 c	16 d	-7 b	-1.4 b	-1.8 bc	-2.1 a	0.7 c	8.9 ab	15 a	-0.5 bc	-2.3 b
L5	214 a	13 a	-8.9 c	5.3 bc	31 c	-12 b	-1.0 b	-2.0 c	-3.8 a	1.7 c	12 a	29 a	3.5 b	-3.4 b

[1] Percentage expressed as the difference between biochar amended treatments and un-amended control treatment; 0% indicates as No change in amount of those properties due to biochar addition.

[2] TC = total C; TN = total N; TP = total P.

[3] Means ($n = 5$) compared within a column of the same soil followed by a different lowercase letter are significantly different at $p < 0.05$ using a one-way ANOVA.

Table S5. Standardized canonical coefficients (SCC) and correlation coefficients (*r*) between the first two canonical discriminant functions (Can) and variables on three soils and of seven treatments on each soil.

	Soils				SAO				MAI				SAI			
	Can1		Can2		Can1		Can2		Can1		Can2		Can1		Can2	
Variables	**SCC**	***r***	**SCC**	***r***	**SCC**	***r***	**SCC**	***r***	**SCC**	***r***	**SCC**	***r***	**SCC**	***r***	**SCC**	***r***
Cumulative CO_2-C	0.02	0.08	0.26	0.26*	-0.80	0.47*	-0.87	-0.22	-0.05	0.44*	-0.20	-0.12	-0.17	0.57***	-0.51	-0.42*
TC	-0.81	-0.24*[1]	0.50	0.13	0.36	0.82***	-0.94	-0.51**	0.69	0.89***	-0.58	-0.42*	0.67	0.89***	-0.54	-0.37
TN	0.33	-0.44***	-0.12	0.74***	-0.36	-0.11	0.21	0.43*	-0.54	0.09	-0.46	0.02	-0.25	0.03	-0.70	-0.32
TP	0.07	-0.41***	-0.02	0.13	0.11	0.12	0.36	0.16	0.09	-0.11	0.09	0.48**	0.38	-0.17	0.41	0.49**
M3-P	-0.38	0.27*	0.41	0.84***	0.19	-0.12	-0.47	-0.08	0.32	0.06	-0.14	0.17	-0.11	0.40*	-0.62	0.22
M3-K	0.37	0.27*	-0.61	0.23*	2.09	0.98***	0.58	0.15	1.32	0.96***	0.45	0.22	1.71	0.98***	0.68	0.09
M3-Ca	0.23	0.72***	0.15	0.60***	-0.20	0.16	0.18	0.04	-0.33	0.005	0.44	0.37	0.14	-0.27	0.93	0.50**
M3-Mg	-0.40	0.88***	0.05	-0.41***	-1.39	-0.36	0.23	0.09	-1.26	-0.35	-0.22	-0.08	-1.35	-0.12	0.08	0.35
M3-Fe	-0.14	0.04	-1.14	-0.98***	-0.98	-0.25	1.17	0.53**	-0.02	-0.37	0.34	-0.24	-0.34	0.14	1.71	0.37
M3-Al	-0.86	-0.99***	0.42	0.09	-0.11	-0.01	-0.48	0.74***	-0.56	-0.59***	-0.15	0.26	-0.10	-0.57***	0.23	0.20
M3-Mn	1.13	0.98***	0.76	0.21	2.11	0.27	-0.81	-0.25	0.06	-0.26	-0.48	-0.14	0.81	0.50**	-2.06	0.35
M3-Cu	0.22	-0.53***	-0.23	0.84***	0.40	-0.20	0.37	0.58***	0.22	-0.13	0.30	0.80***	-0.03	0.30	-0.78	-0.27
M3-Pb	-0.47	-0.49***	1.38	0.87***	-0.19	-0.13	0.02	0.69***	-0.39	-0.16	0.36	087***	-0.28	0.60***	0.60	0.04
M3-Zn	0.08	-0.89***	-0.71	0.42***	-0.52	0.18	0.18	0.42*	0.12	0.13	0.32	0.78***	0.01	0.43*	1.14	0.59***

[1] * $p < 0.01$; ** $p < 0.001$; *** $p < 0.0001$.