STABILITY OF BIOCHAR AND ITS INFLUENCE ON THE DYNAMICS OF SOIL PROPERTIES

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This Thesis is Dedicated to My

Father (Late Mr. H.M.S.P. Herath),

Mother (Mrs. W.M.P. Wijesinghe),

and All the Teachers Who Paved the

Way and Expected Me to Achieve

Such a Task One Day...............!!!

ABSTRACT

The overall objective of this PhD was to investigate the stability of specific biochars – produced from corn stover (*Zea mays* L.) at 350 °C (CS-350) and 550 °C (CS-550) – and their roles on the dynamics of native organic matter (NOM) and physical properties of a Typic Fragiaqualf (Tokomaru soil; TK soil) and a Typic Hapludand (Egmont soil; EG soil). Except for the controls, all other treatments received a 7.18 t C ha^{-1} application, either as fresh corn stover or as biochar. After 295 d, bulk density, saturated hydraulic conductivity (*Ks*), volumetric moisture content (θ_V), aggregate stability and soil water repellency were measured. At that sampling time, two undisturbed subsamples from each pot were taken: (i) in one subsample, lucerne (*Medicago sativa* L.) was seeded; (ii) in the other, the incubation was continued without plants. All pots were additionally incubated for 215 d. During the 510 d incubation, the CO_2-C efflux rate was determined for the selected 82 d, and samples for 19 d out of these 82 d were analysed for $\delta^{13}CO_2$. Soil samples at T0, T295 and T510 (with and without plants) were physically fractionated into coarse and fine free particulate organic matter (fPOM), silt+clay, and heavy fraction (HF), and analysed for $\delta^{13}C$ and total OC. Dichromate oxidation and acid hydrolysis were also conducted for the bulk soil and physical fractions.

Biochar application significantly increased (P<0.05) the aggregate stability of both soils (the effect of CS-550 biochar being more prominent in the TK soil than that in the EG soil, and the reverse pattern being observed for the CS-350 biochar), and the volumetric moisture content (θ_V). The latter effect was generally more evident in the TK soil than that in the EG soil, at both T0 and T295. Biochar addition significantly (P<0.05) increased the macroporosity in the TK soil and also the mesoporosity in the EG soil. Biochar also significantly increased (P<0.05) *Ks* of the TK soil but not that of the EG

soil. However, biochar was not found to increase water repellency of these soils. Overall, the results suggest that these biochars may facilitate drainage in the poorly drained TK soil and potentially reduce N_2O emissions.

Total accumulated CO_2-C evolved from the corn stover treatment was significantly higher ($P<0.05$) than that from rest of the treatments. No significant differences ($P<0.05$) were observed in the rate of CO_2-C evolution between the controls and biochar treatments. In both soils, fresh corn stover had a net positive priming effect on the NOM decomposition, while biochar had a net negative priming effect in the TK soil, but no effect in the EG soil. When a C balance was made considering the C lost during pyrolysis, the combination of CS-350 biochar and EG soil provided the greatest C saving of all treatments. When the different priming effects on NOM were also considered, differences among the two soils were balanced. The longer half-life (494 y) corresponded to the CS-550 biochar in the TK soil, while the half-lives of the other biochar-soil combinations were <200 y. It was estimated that 55 – 70 % of amended biochar-C would remain in soil after 100 y.

After 295 d, >78 % of biochar-C recovered in the TK soil and >64 % of biochar C in the EG soil ended in the coarse fPOM, >13 % (TK) and >21 % (EG) in the fine fPOM fraction, and the rest in the silt+clay fraction. The same pattern was observed after 510 d, both with and without plants. Most of the biochar particles thus concentrated into the "unprotected pool". The use of dichromate oxidation to distinguish the recalcitrant fraction of C in the "unprotected pool" is suggested. Finally, the presence of both biochar and plants induced an additional accumulation of total organic carbon (OC) in the TK-350 and EG-550 soils ($P<0.05$), compared with the treatments with plants but no biochar.

The use of biochars in these OC-rich soils was proven to be adequate to promote C sequestration, especially when compared to the direct application of the fresh feedstock. This enhanced C sequestration is suggested to occur through (i) the addition of a stable C source (*e.g.*, condensed aromatic C in biochar), (ii) the protection of NOM (especially in the TK soil), and (iii) the interaction of biochar with new OC inputs to soil (*e.g.*, root exudates). The results from this study also indicated that long-term incubations in the absence of a continuous fresh input of plant material may create artefacts such as reduced aggregate protection and an apparent loss of aggregate protected OC. Future research should be directed to investigate (i) the influence of these physicochemical changes on microbial activity, population and diversity; and (ii) the evolution of these interactions under field conditions.

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PUBLICATIONS

Journal articles

1. **Herath, H.M.S.K.**, Marta Camps-Arbestain, Mike Hedley, 2012. Effect of biochar on soil physical properties in two contrasting soils: an Alfisol and an Andisol (*Submitted*, ***Geoderma***).

2. **Herath, H.M.S.K.**, Marta Camps-Arbestain, Mike Hedley, M.U.F. Kirschbaum, Robert van Hale, 2012. Experimental evidence for sequestering C by avoidance of CO_2 emission from feedstock and enhanced protection of native soil organic matter with the use of biochar (*To be submitted*).

3. **Herath, H.M.S.K.**, Marta Camps-Arbestain, Mike Hedley, Robert van Hale, 2012. Fate of biochar in chemically- and physically defined organic carbon pools (*To be submitted*).

Other contributions

1. **Herath, H.M.S.K.**, Marta Camps-Arbestain, Mike Hedley, 2012. Stability of biochar in soil and its effect on native organic matter. The 4th International Biochar Congress, Bejing, China, 16 – 20th September, 2012: 42.

2. **Herath, H.M.S.K.**, Marta Camps-Arbestain, Mike Hedley, 2012. Effect of biochar on the distribution of soil organic carbon in physical and chemical soil fractions. New Zealand 2012 Biochar Workshop, Massey University, New Zealand.
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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACRONYMS

AWC	available water content
BET	Brunauer, Emmett and Teller surface area
BC	black carbon
C	carbon
C_{dichro}	dichromate oxidisable C
C_{Net}	net C
C_{org}	organic carbon (biochar/feedstock)
CP	cross polarisation
CS	corn stover feedstock
CS-350	corn stover biochar produced at 350 °C
CS-550	corn stover biochar produced at 550 °C
Ctr	control
d	day(s)
ECEC	effective cation exchange capacity
EG	Egmont soil
EG-350	CS-350 biochar amended Egmont soil
EG-550	CS-550 biochar amended Egmont soil
EG-CS	corn stover amended Egmont soil
f_{OA}	fraction of C from organic amendment
fPOM	free particulate organic matter
f_{SOC}	fraction of C from soil organic carbon
GC/MS	gas chromatography mass spectroscopy
GHG	greenhouse gas
h	hour(s)
HF	heavy fraction

IBI	international biochar initiative
IPCC	Intergovernmental panel on climate change
iPOM	intra particulate organic matter
Ks	saturated hydraulic conductivity
MED	molarity of ethanol droplet
MWD	mean weight diameter
NOM	native organic matter
NOM-C	C from native organic matter
OA	organic amendment
OA-C	C from organic amendment
OC	organic carbon (soil)
OM	organic matter
OC_{hl}	hydrolysable organic carbon
OC_{nhl}	non-hydrolysable organic carbon
OC_{nox}	non-oxidisable organic carbon
OC_{ox}	oxidisable organic carbon
RAWC	readily available water content
S	supportive information
SEM	scanning electron microscopy
SOM	soil organic matter
SSB	spinning side bands
T0	time zero
$t_{1/2}$	half life
T295 (R)	after 295 d of soil respiration
T510 (P)	after 510 d in the presence of plants
T510 (R)	after 510 d of soil respiration

TK	Tokomaru soil
TK-350	CS-350 biochar amended Tokomaru soil
TK-550	CS-550 biochar amended Tokomaru soil
TK-CS	corn stover amended Tokomaru soil
TPV	total soil pore volume
VM	volatile matter
VPDB	Vienna Pee Dee Belemnite
WDPT	water droplet penetration test
WHC	water holding capacity
y	year(s)
$\delta^{13}C$	stable C isotopic ratio
$\delta^{13}C_{OA}$	stable C isotopic ratio of organic amendment
$\delta^{13}C_{SOC}$	stable C isotopic ratio of soil organic carbon
ΔOC	difference of OC content between the amended and unamended treatments
ΔOC_{hl}	difference of non-oxidisable OC content between the amended and unamended treatments
ΔOC_{nhl}	difference of oxidisable OC content between the amended and unamended treatments
ΔOC_{nox}	difference of non-oxidisable OC content between the amended and unamended treatments
ΔOC_{ox}	difference of oxidisable OC content between the amended and unamended treatments
θ_V	volumetric water content