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

A thesis presented in partial fulfilment of the requirements for the degree of

Doctor of Philosophy
(PhD)
in
Soil Science



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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 CO₂-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 δ^{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 N₂O 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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Other contributions

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- 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. http://www.biochar.co.nz/pdf/2012 Biochar Final programme for%20web.pdf
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- **4.** Marta Camps-Arbestain, M. Hedley, R. Calvelo Pereira, **Herath, H.M.S.K.**, T. Wang, E. Wisnubroto, 2012. Is biochar a suitable amendment for New Zealand soils? Results from three years of research at the NZBRC. The 4th International Biochar Congress, Bejing, China, 16 20th September, 2012:50.
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- **6. Herath, H.M.S.K.**, Marta Camps-Arbestain, Mike Hedley, 2011. Mineralisation of carbon from fresh and carbonised corn stover in two New Zealand soils. New Zealand 2011 Biochar Workshop, 10 11 February 2011. Massey University, New Zealand. http://www.biochar.co.nz/Files/2011_Biochar_Final_programme_low_res.pdf
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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)

 δ^{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_{nbl} 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