Can Biochar Ameliorate Phosphorus Deficiency and Aluminium Phytotoxicity in Acid Soils?

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ABSTRACT

The use of biochar as soil amendment to enhance soil functionality is being increasingly investigated, with particular attention given to its effects on the sustainable increase of crop production and carbon (C) sequestration. To date, however, limited research has attempted to unravel the effect of biochar on either the chemical and/or biological mobilization of the residual fraction of phosphorus (P) in soil. This fraction tends to accumulate as a result of long–term P fertilization in soils rich in aluminium (Al) and iron (Fe) oxy–hydroxides and short–range ordered aluminosilicates (i.e. allophane). There is also scant information on (i) how the speciation of soluble Al changes when biochar is applied to acid soils, and (ii) whether this application alleviates Al toxicity on plant roots. My objective in this study is therefore to determine the effect of different biochars with contrasting fertilizer and liming values on the chemistry, biology and nutrient fertility of acid mineral soils.

Before studying the effect of different biochars on soil properties, several methodologies for measuring the liming properties and available nitrogen (N) in biochar were evaluated and modified where needed. For this, 19 biochars produced by pyrolysing a wide range of feedstocks under various production temperatures were used. Different pH–buffering capacity (pH–BC) methodologies – originally developed for soils (single vs multiple acid additions, short vs long equilibration times) – were tested, along with the methodology used to measure the liming equivalence. The methodologies were then validated by incubating over 10 d two acid soils (an Haplic Cambisol and an Andic Umbrisol) to which separated amendments of the 19 biochars were made at the rates estimated using both methodologies to target a final pH of 6.5.

The results indicated that the relationship established between the pH–BC of the 19 biochars under study after 30–min equilibration ($pH–BC_{30min}$) with a single addition of acid and that obtained after a 5–d equilibration ($pH–BC_{5d}$) (predicted $pH–BC_{5d} = 2.2 \times pH–BC_{30min} + 20.4$) allowed an adequate estimate of the liming potential of biochars. Similar results were found with the liming equivalent, and both methods were considered suitable to make the recommendation of the application rate. Acid hydrolysis using 6 M HCl has been proved adequate to determine available N in biochar. For this, hydrolysates of biochar are oxidized using potassium peroxodisulfate with a dilution factor of 600 so that chloride interferences are overcome and nitrate–N is then measured. This methodology, originally developed using biochars rich in N, proved not suitable for biochars with low N concentrations. Results obtained in this study have shown that a smaller dilution factor (242) is sufficiently adequate to overcome the chloride interferences while avoiding over–diluting the sample.

In this study, we hypothesized that biochar can increase P availability to plant by stimulating the growth of arbuscular mycorrhizal fungi (AMF) hyphae. Therefore, methodologies to (i) estimate the length of fungal hyphae in soil and (ii) evaluate the transfer of P by AMF hyphae needed to be tested and modified where necessary. In this part of the study, three different biochars and two soil types were used. Two biochars were produced from chipped pine (*Pinus radiata* D. Don) branches at 450^{o}C and 550°C (referred to as BP450 and BP550, respectively); and a third one from chipped weeping willow (*Salix matsudana* L.) branches at 550°C (referred to as BW550). The soils were two sil–andic Andosols of contrasting P status (Olsen P of 4.3 vs 33.3 mg kg^{-1}, referred to as LP and HP soil, respectively).

The traditional visual gridline intersection (VGI) method commonly used to measure the length of AMF hyphae distribution in soil was modified by (i) using a

digital photomicrography technique (referred to as "digital gridline intersection" (DGI) method), and (ii) processing the images using ImageJ software (referred to as the "photomicrography–ImageJ processing" (PIP) method). These methods were first tested with known lengths of possum fur and then applied to measuring the hyphal length in the LP and HP soils after a 32 wk experiment growing *Lotus pedunculatus cv* barsille. The study confirmed that the use of digital photomicrography in conjunction with either the grid–line intersection principle or image processing (with ImageJ software) is a suitable method for the measurement of AMF hyphal lengths in soils.

In addition, the traditional root study container that divides the plant growth medium into two sections – (i) a *root zone* to which both root and AMF hyphae have access and (ii) an *hyphal zone* to which only AMF hyphae have access – by a layer of nylon mesh was further modified by including a 3–mm thickness of tephra under the nylon mesh between two sections. This layer of tephra was found to be adequate to halt P diffusion from the HP soil to the LP soil for a plant growth period of 32 wk. Under such circumstances, the increase in P uptake by plant growth in a combination of a *root zone* of LP soil and a *hyphal zone* of HP soil compared with that in which both *root* and *hyphal zones* were filled with LP soil was only ascribed to the transfer of P from HP soil to LP soil by AMF hyphae. This novel root study container allows the biochar to be added to either the *root zone* or the *hyphal zone* and separates the effect of biochar on AMF hyphae development and P uptake from that on P content and availability (i.e., biochar rich in P; changes in soil pH). This device can contribute to discern whether biochar can influence AMF development and enhance P bioavailability.

In order to investigate the feasibility of adding biochar to soils with high residual P so that this can become bioavailable, *Lotus pedunculatus cv* barsille was grown in LP and HP soils separately amended with BP450, BP550 and BW550 biochars

at an application rate of 10 t ha^{-1} using the novel root study container for 32 wk without any further P and N fertilization. We found that (i) none of the tested biochars conferred any specific advantage to the HP soil; (ii) the addition of BW550 biochar to the LP soil increased plant growth by 59% and P uptake by 73%, while the pine–based biochar (e.g., BP450 and BP550) provided no extra nutrient uptake and no plant growth increase. This was ascribed to supplemental nutrients (especially P) from the BW550 biochar along with its liming effect and associated increase in P availability; (iii) biochar produced from BP450 biochar caused a 70% P uptake increase (and 40% plant growth increase) by stimulating AMF growth and accessing a high–P area (HP soil) to which the plant root had no access. More research is needed to discern the underlying mechanism.

The liming effects of BW550 and BP550 biochars were further compared with those of lime chemicals (e.g., $Ca(OH)_2$ and NaOH) in a short–term (10–d) incubation using two soils with contrasting pH–BC (an Haplic Cambisol and an Andic Umbrisol) to which these amendments were added. The two soils were first amended with BW550, BP550, $Ca(OH)_2$ or NaOH at specific rates so that pH values of 5.4, 5.6, 5.8 and 6.4 were targeted and incubated at room temperature (25 ^{o}C) for 10 d. At the end of the incubation, a radical elongation bioassay using alfalfa (*Medicago sativa* L.) was carried out. Thereafter, soils were characterized with special attention to the Al chemistry, i.e. aqueous reactive Al fractionation and inorganic monomeric Al speciation. The final objective was to reveal the mechanisms through which these biochars alleviate Al toxicity on roots. Results showed that, for a specific soil, a smaller amount of BW550 biochar was required to increase the same unit of pH and reduce a similar amount of exchangeable Al compared with the amount required of BP550 biochar. The addition of BW550 biochar (at application rates < 9.1 %) and $Ca(OH)_2$ stimulated alfalfa (*Medicago sativa* L.) seedling growth, whereas that of BP550 (at application rates >

2.4 %) and NaOH caused inhibition. The distinct responses of the root growth to the presence of $Ca(OH)_2$ and BW550 biochar and to that of NaOH and BP550 biochar were explained by (i) a decrease in both inorganic monomeric Al (mainly in AlF^{2+} and Al^{3+}) and colloidal Al, and (ii) an increase in aqueous Ca^{2+}, in the former, as expected. In the latter there was (i) an increase in aqueous colloidal Al and Na^{+}, and (ii) a decrease in soluble Ca^{2+}. Thus, BW550 biochar was shown to be a more effective liming agent than was BP550 biochar.

The information obtained in this thesis supports the use of biochar to manage high P affinity Andosols and acid soils, which are abundant in New Zealand. The technology of producing biochar from willow woodchips or feedstock alike with resultant solid products of high nutrient status and liming potential may contribute to the recycle of nutrients while increasing soil pH. Pine woodchips produced at relatively low temperature (e.g., 450^{o}C) have been shown to enhance AMF abundance and functionality. Thus, biochar with specific environmental and agricultural purposes should be tailored accordingly. The root study container with a layer of "P diffusion break" and the measurement of AMF hyphal length using the photomicrography in conjunction with image software analysis (e.g., ImageJ) will advance studies of the responses of AMF to soil additives (e.g., biochar or green waste) and their associated enhancement of soil functions.

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PUBLICATIONS AND PRESENTATIONS

Publication under review/to be submitted

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2. **Qinhua Shen**, Mike J. Hedley, Marta Camps–Arbestain, Miko U.F. Kirschbaum. A novel technique for evaluating the phosphorus transferred by arbuscular mycorrhizal fungi hyphae. *Soil Research* (To be submitted).

3. **Qinhua Shen**, Mike J. Hedley, Marta Camps–Arbestain, Miko U.F. Kirschbaum. Can biochar increase the bioavailability of phosphorus? *Journal of Soil Science and Plant Nutrition* (Accepted)

4. **Qinhua Shen**, Marta Camps–Arbestain, Mike J. Hedley, Miko U.F. Kirschbaum, Peter Bishop. Can Biochar Ameliorate Aluminium Phytotoxicity? *Geoderma* (To be submitted)

5. Huo–Yan Wang, **Qin-Hua Shen**, Jian–Min Zhou et al. (2011). Plants use alternative strategies to utilize non–exchangeable potassium in minerals. *Plant and soil* 343: 209–220

Book chapters

1. Balwant Singh, Michaela Mei Dolk, **Qinhua Shen,** Marta Camps–Arbestain (2015). Chapter 3 Biochar pH, electrical conductivity and liming potential. In: Balwant Singh, Marta Camps–Arbestain, Johannes Lehmann (Eds.), Methods of Biochar Analysis for Environmental Applications. CSIRO Publishing, Melbourne

2. Marta Camps–Arbestain, **Qinhua Shen**, Tao Wang (2015). Chapter 24 Biochar Available nutrients. In: Balwant Singh, Marta Camps–Arbestain, Johannes Lehmann (Eds.), Methods of Biochar Analysis for Environmental Applications. CSIRO Publishing, Melbourne

Abstracts/proceedings and posters/presentations in Conference/Worshop

1. **Qinhua Shen**, Marta Camps–Arbestain, Mike J. Hedley (2014). Use of Biochar to Reduce Soil Acidity and Ameliorate Aluminum Phytotoxicity. In "Proceedings of NZ Society of Soil Science Conference "Soil Science for Future Generations" (NZSSS: Halmiton, New Zealand).

2. **Qinhua Shen**, Mike J. Hedley, Marta Camps–Arbestain (2014). Can Biochar be Used to Increase the Bioavailability of Phosphorus Immobilized in Andisols? IDS 5. Biochar Soil Amendment for Environmental and Agronomic Benefits. In 'Proceedings of the 20th World Congress of Soil Science; Soils Embrace Life & Universe' (IUSS: Jeju, Korea).

3. **Qinhua Shen**, Mike J. Hedley, Marta Camps–Arbestain (2014). Can Biochar be Used to Increase the Bioavailability of Phosphorus Immobilized in Andisols? Nutrient Management for the Farm, Catchment and Community (Eds. L D Currie and C L Christensen). (FLRC, Massey University, Palmerston North, New Zealand).

4. **Qinhua Shen**, Marta Camps–Arbestain, Mike J. Hedley (2013). Influence of Biochar Application on the Availability of Phosphorus in Volcanic Ash soils. In "Proceedings of New Zealand 2013 Biochar Workshop of The Final Answer? (New Zealand Biochar Research Center:Palmerston North, New Zealand)

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LIST OF ABBREVIATIONS

Al	Aluminium
Alox	Acid ammonium oxalate extractable aluminium
Alpy	Sodium pyrophosphate extractable aluminium
AMF	Arbuscular mycorrhizal fungi
C	Carbon
Ca	Calcium
Ca(OH)2	Calcium hydroxide
CaCO3	Calcium carbonate
CEC	Cation exchange capacity
Cl	Chloride
d	days
DGI	digital gridline intersection method
DM	dry matter
EC	Electrical conductivity
Fe	Iron
Feox	Acid ammonium oxalate extractable iron
Fepy	Sodium pyrophosphate extractable iron
FTIR	Fourier–transform infrared spectroscopy
GHG	Greenhouse gas
h	hours
H+	Hydrogen ions
HCl	Hydrogen chloride
K	Potassium
Mg	Magnesium
min	minutes
N	Nitrogen
Na	Sodium
NaHCO3	Sodium bicarbonate
NaOH	Sodium hydroxide
pH–BC	pH buffering capacity
PIP	photomicrography–ImageJ processing method
P	Phosphorus
RMSE	root mean square errors
VGI	visual gridline intersection method
wk	weeks
XPS	X–ray photoelectron spectroscopy