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# **DEVELOPMENT OF METHODOLOGIES FOR THE CHARACTERISATION OF BIOCHARS PRODUCED FROM HUMAN AND ANIMAL WASTES**

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A thesis presented in partial fulfilment of the requirements for the  
degree of  
Doctor of Philosophy in Soil Science



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## ABSTRACT

Biochar is charcoal made from waste biomass and intended to be added to soil to improve soil function and reduce emissions from the biomass caused by natural degradation to CO<sub>2</sub>. Biochar technology has many environmental benefits, such as carbon (C) sequestration, waste management, soil improvement and energy production. High quality biosolids (e.g., low in heavy metals) and animal wastes represent an adequate feedstock for production of biochars. Wide variation in biochar properties, dependent on feedstocks, process conditions and post-treatments, lead to large uncertainties in predicting the effects of biochar application on the surrounding ecology, and the productivity of particular crops under specific pedoclimatic conditions. It is essential to well-characterise biochars prior to its incorporation into soils. Therefore, the aims of this thesis were (i) to investigate the C stability and nitrogen (N) and phosphorus (P) availability in biochars produced from municipal and animal organic wastes at different pyrolysis temperatures; and (ii) to develop simple and robust methods for characterisation of C stability and nutrient availability in biochars.

Two types of feedstock, (i) a mixture (1:1 dry wt. basis ratio) of alum-treated biosolids (from anaerobic digestion of sewage, ~5% dry wt. of Al) and eucalyptus wood chips (BSe), and (ii) a mixture (1:1 dry wt. basis ratio) of cattle manure (from a dairy farm) and eucalyptus wood chips (MAe), were used to produce biochars at four different pyrolysis temperatures (highest heating temperature: 250, 350, 450, and 550°C).

The stability of C in charred materials increased as pyrolysis temperature increased, as proved by the increase of aromaticity and the decrease of atomic H to organic C (H/C<sub>org</sub>) ratio, volatiles to (volatiles + fixed C) ratio, C mineralisation rate and % K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> oxidisable C. According to the IBI Guidelines (IBI 2012), an upper H/C<sub>org</sub>

ratio limit of 0.7 is used to distinguish biochar samples from other carbonaceous biomass based on the consideration of C stability. According to this classification system, MAe-450 and MAe-550 biochars complied with this specific C stability requirement; this was also the case of BSe-450 and BSe-550 when their H values were corrected to eliminate the contribution of inorganic H from Al oxy-hydroxides. Both organic H ( $H_{\text{org}}$ ) and  $C_{\text{org}}$  forms were used in the calculation of this index instead of their total amounts, as the latter would also include their inorganic C or H forms – which can represent a considerable amount of C or H in ash-rich biochars – and these do not form part of the aromatic structure. Therefore, various methods, including titration, thermogravimetric analysis (TGA), acid fumigation and acid treatment with separation by filtration, were compared to quantify the carbonate-C in biochars. Overall, the titration approach gave the most reliable results as tested by using a  $\text{CaCO}_3$  standard (average recovery >96% with a relative experimental error <10% of carbonate-C). To assist in the prediction of the mean residence time (MRT) of biochar C in soils, simple models, based on their elemental composition and fixed C content, were established to calculate C aromaticity of biochars. This was able to replace methods using more costly solid state  $^{13}\text{C}$  NMR spectroscopy.

Biochar samples produced from MAe and BSe feedstocks were hydrolysed with a 6 M HCl to extract labile N (hydrolysable), which was considered the fraction of N that would be available in short term; and with 0.167 M  $\text{K}_2\text{Cr}_2\text{O}_7$  acid solution (dichromate) to determine potentially available N in the long term. An incubation study of biochars mixed with acid washed sand was also conducted at 32 °C for 81 d to study short-term N turnover pattern. Results showed that fractionation of biochar N into ammonia N (AN), amino acid N (AAN), amino sugar N (ASN), and uncharacterisable hydrolysable N (UHN) revealed the progressive structural rearrangement of N with

pyrolysis temperature. Hydrolysable- and dichromate oxidisable-N decreased as pyrolysis temperature increased from 250 to 550 °C, suggesting N in biochar becomes more stable as pyrolysis temperature increased. Organic N was an integral part of the biochar structure, and the availability of this N also depended on the stability of biochar C. The ratio of volatile C (representing labile C) to total hydrolysable N (THN) was proposed as a useful indicator of whether net N mineralisation or immobilisation of N in biochar occurred.

Phosphorus in feedstock was fully recovered and enriched in the biochars under study. Various methodologies were employed to investigate the bioavailability of P in biochars, including (i) a bioassay test using rye-grass grown in a sandy soil fertilised with biochars; (ii) soluble P extractions (resin extraction and Olsen extraction) from biochar amended soils; and (iii) successive resin P extractions of soils treated with biochars. The results obtained with the different methods confirmed that P bioavailability diminished following the order of dihydrogen phosphate (CaP) > MAe biochars > BSe biochars > Sechura phosphate rocks (SPR). Plant availability of P in biochars could be predicted from the amount of P extracted in 2% formic acid extractable P (FA-P). In addition, resin-P was considered as a useful test for characterising P bioavailability in soils fertilised with P-rich biochars. However, more investigations with a wider range of soils and biochars are needed to confirm this. Pyrolysis temperature played a minor role on P availability in biochars produced below 450°C compared to the influence of the type of feedstock. This was supported by the results on (i) plant P uptake, (ii) 2% formic acid extraction, and (iii) successive resin P extractions. The availability of P in biochars produced at 550°C decreased noticeably compared with that in lower temperature biochars. The Hedley P fractionation procedure was also carried out to examine the forms and transformation of P in biochar

after its application into soils under the influence of plant growth. Generally, biochar P contributed to the readily available resin-P and moderately available NaOH-Pi fractions, and some equilibrium likely existed between these two fractions, both of which provided P for plant uptake. In a plant-sandy soil system, depletion of P in resin-P and NaOH-Pi fractions was attributed to plant uptake rather than conversion into less available P forms (e.g. from NaOH-Pi to  $\text{H}_2\text{SO}_4\text{-P}$ ). High-ash biochars with high P concentrations could be potential slow-release P sources with high-agronomic values. To determine appropriate agronomically effective rates of application and avoid the risk of eutrophication associated with biochar application, it is recommended to determine available P using 2% formic acid extraction in biochars, so that dose, frequency and timing of application are correctly established.

All the information obtained in this thesis will support the future use of the biochar technology to recycle nutrients and stabilise carbon from agricultural and municipal organic wastes of good quality.

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## ACRONYMS

AN	NH <sub>3</sub> N
AAN	$\alpha$ -amino acid N
ASN	Amino sugar-N
BD	Bloch-decay
BSe	A mixture of biosolids and eucalyptus wood chips
C	Carbon
CaP	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>
C/N	C to N ratio (mass)
C <sub>org</sub>	Organic C
DP/MAS	Direct polarization/magic angle spinning
$F_a$	C aromaticity
FC	Fixed C
DTG	Derivative thermogravimetric analysis
FC	Fixed carbon
H/C	An atomic H to C ratio
H <sub>org</sub>	Organic H
H <sub>2</sub> SO <sub>4</sub> -P	0.5 M H <sub>2</sub> SO <sub>4</sub> extractable P
MAe	A mixture of dairy manure and eucalyptus wood chips
NaOH-Pi	0.1 M NaOH extractable inorganic P fraction
NaOH-Po	0.1 M NaOH extractable organic P fraction
NaOH-Pt	total 0.1 M NaOH extractable P fraction
N	Nitrogen
NMR	Nuclear magnetic resonance
P	Phosphorus
P <sub>ox</sub>	Acid ammonium oxalate extractable P
PSO	Pseudo-second-order kinetic model
PR or SPR	Sechura phosphate rock
SD	Standard deviation
TGA	Thermogravimetric analysis
THN	Total hydrolysable nitrogen
UHN	uncharacterisable hydrolysable N
VC	Carbon in volatile matter
VM	Volatile matter