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

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College of Sciences, Massey University
Palmerston North, New Zealand

Tao Wang

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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_2. 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_{org}) ratio, volatiles to (volatiles + fixed C) ratio, C mineralisation rate and % $K_2Cr_2O_7$ oxidisable C. According to the IBI Guidelines (IBI 2012), an upper H/C_{org}

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_{org}) and C_{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 $CaCO_3$ 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}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 $K_2Cr_2O_7$ 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 H_2SO_4-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_3 N
AAN	α-amino acid N
ASN	Amino sugar-N
BD	Bloch-decay
BSe	A mixture of biosolids and eucalyptus wood chips
C	Carbon
CaP	$Ca(H_2PO_4)_2$
C/N	C to N ratio (mass)
C_{org}	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_{org}	Organic H
H_2SO_4-P	0.5 M H_2SO_4 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_{ox}	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

CHAPTER 1. GENERAL INTRODUCTION

1.1 General background

Carbon (C) sequestration via conversion of biomass into a more durable form has been proposed as a strategy to combat global climate change (Lehmann et al. 2006; Macías and Camps Arbestain 2010), and the production of charcoal from biomass through slow-pyrolysis has received worldwide interest. Due to its predominantly aromatic structure, charcoal can be chemically and biologically stable in soil for hundreds to thousands of years compared with the biomass feedstock (Antal and Gronli 2003; McHenry 2009). When charcoal is added to soils to improve soil functions and reduce emissions from the organic materials that would otherwise naturally degrade to greenhouse gases (GHG), it is termed biochar (Lehmann and Joseph 2009).

The application of biochar has many benefits for environmental management (Lehmann and Joseph 2009). Briefly, when added to selected soils, biochar can contribute to (i) soil improvement, by increasing soil fertility, optimizing soil structure and microbial biodiversity, decreasing nutrient leaching and increasing fertiliser utilization efficiency, enhancing soil-water retention capacity, and further increasing crop production (Lehmann et al. 2006; Lehmann and Joseph 2009; Biederman and Harpole 2013); (ii) waste management, by greatly reducing the volume of organic wastes and decreasing the risks from pathogens, organic pollutants (Cantrell et al. 2007) and heavy metals (Inguanzo et al. 2002) associated with the feedstock; (iii) energy production, via producing biogas, biooil and biochar which can be used as promising sources of renewable energy; and (iv) GHG emission mitigation, as a result of formation of condensed aromatic C structure that is recalcitrant to natural degradation (Schimmelpfennig and Glaser 2012) and, in some cases, of the negative priming effect of biochar addition on soil native organic matter decomposition (Zimmerman et al.

2011; Singh et al. 2012) and other GHG emissions (Singh et al. 2010b; Zhang et al. 2010).

Economic viability of biochar production and application to land depends largely on (i) the costs of feedstock; (ii) the expenses of pyrolysis; (iii) the C offset credits; and (iv) the benefits in terms of soil improvement and agricultural productivity (Pratt and Moran 2010; Roberts et al. 2010). Through a life cycle assessment, Roberts et al (2010) concluded that, at present, producing biochar from organic waste streams has the largest potential to be financially feasible while still being net energy positive and mitigating GHG emissions. Meanwhile, management of wastes has become one of major environmental challenges worldwide and in New Zealand (Ministry for the Environment New Zealand 2007b). A 2004 survey in New Zealand (to my knowledge, it is the latest available data) estimated that organic waste (including food waste, animal and human sewage waste, and garden waste) comprises 23%, or 743,324 tonnes of the waste disposed to landfill (excluding paper, cardboard and timber and other biodegradable wastes) (Ministry for the Environment New Zealand 2007a). This large volume of waste necessitates an efficient system of disposal (Narayana 2009) and management with low negative impacts (Moberg et al. 2005), as it can otherwise pose a risk to human health and the environment (Ministry for the Environment New Zealand 2007b). Therefore, the combination of biochar technology and waste management may represent the sustainable solution that New Zealand needs.

However, one should note that benefits from biochar amendments on a specific soil are dependent on biochar characteristics, which further rely on the nature of feedstocks and pyrolysis conditions (Lehmann and Joseph 2009; Roberts et al. 2009; Sohi et al. 2009; Laird et al. 2010a; Laird et al. 2010b; Silber et al. 2010; Verheijen et al. 2010). This wide variety of feedstocks, process conditions and post-treatments leads

to large uncertainties in studies on the effects of biochar applications on the surrounding ecology, and the productivity of particular crops under specific pedoclimatic conditions (McHenry 2009). Thus it is essential to well-characterise biochar prior to its incorporation into soils. Previous publications on the characterisation of biochar have focused on the following aspects:

- Stability of biochar C (Calvelo Pereira et al. 2011; Harvey et al. 2012; Singh et al. 2012; Cross and Sohi 2013);
- Nutrient sources (Chan et al. 2007; Chan and Xu 2009; Silber et al. 2010; Hossain et al. 2011; Enders et al. 2012);
- Chemical properties, such as C structures (aromaticity and condensation) (Baldock and Smernik 2002; McBeath and Smernik 2009; Keiluweit et al. 2010; McBeath et al. 2011), bulk (volatiles, fixed C and ash) and elemental composition (Enders et al. 2012; Schimmelpfennig and Glaser 2012), and surface chemical properties (Singh et al. 2010a; Yao et al. 2010; Sun et al. 2011);
- Physical properties, such as surface morphology, surface area, porosity and other physical structures (Chen et al. 2008; Joseph et al. 2010; Chia et al. 2012a; Chia et al. 2012b; Lin et al. 2012);
- Health and environmental aspects, such as concentrations of toxic elements, PAHs and dioxins (Singh et al. 2010a; Fagernäs et al. 2012; Freddo et al. 2012; Hale et al. 2012; Hilber et al. 2012; Keiluweit et al. 2012; Schimmelpfennig and Glaser 2012) and toxicity (Free et al. 2010; Van Zwieten et al. 2010; Li et al. 2011; Rogovska et al. 2012);
- Potentially negative effects on soil C sequestration (positive priming effect on soil organic matter decomposition) (Wardle et al. 2008; Zimmerman et al.

2011), soil albedo (Meyer et al. 2012) and herbicide efficacy (Beesley et al. 2011; Graber et al. 2012).

In New Zealand, previous work pertaining to biochar research has been devoted to the characterisation of biochar C stability (Calvelo Pereira et al. 2011), toxic effects on seed germination and microbes (Free et al. 2010), surface chemical and physical properties (Hina et al. 2010; Joseph et al. 2010; Yao et al. 2010; Herath 2013), nutrient release pattern (Yao et al. 2010) and its influence on soil C dynamics and other properties (Taghizadeh-Toosi et al. 2012a; b; Herath 2013). Feedstocks used for producing biochars include corn stover (Herath 2013), biosolids (Yao et al. 2010), and wood from several tree species (such as willow, pine and eucalyptus) (Free et al. 2010; Hina et al. 2010; Yao et al. 2010; Calvelo Pereira et al. 2011; Taghizadeh-Toosi et al. 2012a; b). However, little information is available on the characteristics, especially the availability of nutrients (N and P) and the stability of C, of biochars produced from organic wastes from human and animal waste streams at different pyrolysis temperatures. Therefore, this thesis was aimed to fill in such gaps.

1.2 Research objectives

The main objectives of this thesis were to investigate the nutrient availability and C stability of biochars produced from organic waste streams, as well as to develop simple and robust methods for the characterisation of biochars in terms of these aspects. The specific objectives were:

- To study the stable organic C structures in biochars and establish one model to predict C aromaticity of biochars;
- To quantify the carbonate-C in biochars to understand the liming effect of biochars and its inorganic C, as it is also an integral fraction of biochar C;

- To investigate the N availability in biochars and develop chemical methods for measuring N availability in biochars;
- To investigate the availability of P in biochars and the transformation of biochar-P in a soil-plant system, and to develop fertiliser and soil tests for determination of biochar P availability so as to make biochar application recommendations.

1.3 Thesis outline

This thesis reports the current research progress in the characterisation of availability of nutrients and stability of C in biochars produced from alum-treated biosolids and cattle manure. It comprises 8 chapters in total. The first two chapters are general introduction and literature review respectively. Chapters 3-7 are research chapters and have been submitted or accepted as journal articles, which will be cited in each chapter. As these stand-alone chapters were written according to the format requirements from different journals, the structure of each chapter may differ slightly; and overlap and repetition between some sections occurs.

Chapter 1 gives a general introduction to the whole thesis and also provided some background information to the present research.

Chapter 2 provides a review of (i) current status of organic waste and its disposal in New Zealand, (ii) the feasibility of biochar production from organic waste, and (iii) research advances in the study of nutrient availability and C stability in biochars.

Chapter 3 presents a model which can be used to predict C aromaticity of biochars based on their elemental composition. As aromatic C is related to the stable C fraction, this model offers a simple approach to estimating stable C in biochars.

Chapter 4 compares different methods for quantification of carbonate-C in biochars. As many biochar samples were low in carbonate, we proposed to have the biochar samples screened for carbonates using a very simple methodology (e.g., effervescence after addition of diluted acid) prior to the determination of carbonate-C according to a coulometric titration method.

Chapter 5 reports the results of chemical and bioassay characterisation of N availability in biochars produced from dairy manure and biosolids. A 6 M HCl hydrolysis procedure was proposed to estimate the labile N fraction in biochars in the short term and a dichromate oxidation method to measure available N in a long run.

Chapter 6 studies the bioavailability of phosphorus in high-ash biochars. 2% formic acid extraction was recommended to predict the availability of P in ash-rich biochars.

Chapter 7 investigates the forms and release pattern of P from a biochar-amended sandy soil and the transformation of biochar P in a soil-plant system. We suggested available P (either soil or fertiliser tests) in biochars should be measured prior to its application to soil, so that dose, frequency and timing of application are correctly established.

Chapter 8 is a summary of the whole thesis concluding with some future research recommendations.

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CHAPTER 2. LITERATURE REVIEW

2.1 Organic wastes

2.1.1 Organic wastes and their treatment

Organic waste is defined as "any waste that is capable of undergoing anaerobic or aerobic decomposition through a biological treatment process" (DEHLG 2006). This includes animal manures, crop residues, garden waste (green waste), food processing wastes, municipal biosolids, and wastes from wood industries (Westerman and Bicudo 2005; Ministry for the Environment New Zealand 2007a). They are usually called "wastes" because they are not the primary product of a specific production process (Westerman and Bicudo 2005); indeed they can represent an inefficient use of valuable resources (Ministry for the Environment New Zealand 2007b).

Management of wastes has become a major environmental challenge (Odlare et al. 2011) as a consequence of the rapid population growth, urbanization and increasing rate of consumption of natural resources (Ministry for the Environment New Zealand 2007b; Narayana 2009; Odlare et al. 2011). It was estimated that around 8.7 million tons of municipal solid waste were generated in New Zealand in 2006 (Ministry for the Environment New Zealand 2007c). The Solid Waste Analysis Protocol of Waste to Landfill indicated that in 2004 organic waste comprises 23% of the waste disposed to landfill (excluding paper, cardboard and timber and other biodegradable wastes) (Ministry for the Environment New Zealand 2007a). This large volume of waste necessitates an efficient system of disposal (Narayana 2009) and management with low negative impacts (Moberg et al. 2005), as it can otherwise pose a risk to human health and the environment (Ministry for the Environment New Zealand 2007b). In an ideal world all organic waste would be converted to useful products by such processes as recycling of the nutrients, replenishment of soil organic matter, or generation of useful energy (Sims 1996). A waste management infrastructure should be based on a hierarchy

of the following principles: (i) waste prevention; (ii) recycling/re-use; (iii) the use of waste as a source of energy; and (iv) controlled final disposal. At present, the most common methods used to treat waste are the following: incineration, landfilling, composting and anaerobic digestion, and land application, with land filling being the least recommended.

2.1.1.1 Incineration

Incineration turns waste into gas (including SO_x, HCl, NO_x, CO, and organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and halogenated aromatic compounds) (Heger et al. 1998) and an ash residue (Narayana 2009), greatly reducing the waste volume and generating some energy (Bogner et al. 2008). However, this process can also represent a significant local source of air pollution in developing countries where the incinerators do not usually have post-combustion air pollution control systems (Diaz et al. 2005), constituting a health risk for nearby communities. Some products (such as polychlorinated dioxins/furans (PCDD/PCDF)) formed during incineration are far more difficult to deal with than the original waste (Narayana 2009). A few regions and nations, e.g. Ontario (Canada), the Philippines and Argentina, have banned or restricted waste incineration.

2.1.1.2 Landfilling

A landfill is an area of land where waste is deposited onto, or, into the soil, aiming to avoid any contact between the waste and the surrounding environment, particularly the groundwater (Narayana 2009). Disposing of organic waste via landfill does not allow either the recycling of nutrients or the mitigation of GHG emission, and may generate toxic leachates and occupy a large landfill space; therefore it is considered an unsustainable option (Carey et al. 2008). Among all the waste treatment methods,

landfilling has the lowest priority (Moberg et al. 2005). However, landfilling still plays a major role in waste treatment all over the world. For example, in New Zealand, about 6.3 million tonnes out of total 8.7 million tonnes of solid waste are sent to landfill and cleanfill sites each year (Ministry for the Environment New Zealand 2007a). Diverting organic wastes from landfills is critical to reduce landfill emissions and their contribution to global warming and climate change (Carey et al. 2008) and, obviously, to minimize the risk of groundwater pollution.

2.1.1.3 Composting and anaerobic digestion

Composting and anaerobic digestion are biological methods that effectively reduce the amount of organic wastes (DEHLG 2006). Composting is the aerobically-controlled decomposition of organic waste through biological processes, resulting in products as CO_2, water, and an organic matter fraction (Bogner et al. 2008; Narayana 2009). It can reduce the bulk volume (Westerman and Bicudo 2005) and odour, kill pathogens and produce a stabilized product for transport. Compostable materials in developing countries accounted for 80–85% of that of organic wastes (Narayana 2009). However, composting is not a suitable option for sequestering C and recovering some nutrients such as N (Macías and Camps Arbestain 2010). Additionally, the quality of the end products strongly depends on the raw material and the operating conditions (Narayana 2009). Under poor management conditions, in which suboxic, or, anaerobic conditions are generated, CH_4 and N_2O form during composting (Bogner et al. 2008).

Anaerobic digestion produces biogas (CO_2 and CH_4) – used for energy generation – and biosolids (Bogner et al. 2008). It is strongly recommended by many governments as a method to reduce the C footprint of waste treatments (Odlare et al. 2011). However, the resulting biosolids still need to be disposed somewhere and these

can contain high amounts of heavy metals , organic contaminants and pathogens, and have a high risk of nitrate leaching (Cooke et al. 2001; Gove et al. 2002; Magesan and Wang 2003; Egiarte et al. 2006; Egiarte et al. 2009; Jalali and Arfania 2010).

2.1.1.4 Land application

For organic waste, biological treatments (composting and anaerobic digestion) are obviously preferable options compared with landfilling and incineration (Bogner et al. 2008). However, both composting and anaerobic digestion results in substantial amounts of leftover material, namely biosolids and composts (Odlare et al. 2011). A sustainable, economical and safe application of these products (Odlare et al. 2011) is needed to avoid the generation of new waste. Land application of organic wastes offers a promising approach. High quality organic waste can be used as fertiliser, contribute to the pool of soil organic carbon (Odlare et al. 2011), and improve soil physical, chemical and even biochemical properties and thus enhance crop growth (Westerman and Bicudo 2005; Diacono and Montemurro 2010). However, recommended application rates should be considered to avoid both excessive leaching of nitrate to groundwater, and excessive loading of heavy metals, organic pollutants and undesirable microorganisms in soils (Egiarte et al. 2005).

2.1.2 Greenhouse gas (GHG) emissions from organic waste streams

Carbon dioxide (CO_2), CH_4 and N_2O are the three primary GHGs from waste streams (Johnson et al. 2007; Smith et al. 2007; Bogner et al. 2008). Compared to CO_2, CH_4 and N_2O have lower emissions; however, their global warming potentials are much higher (24.5 times higher for CH_4 and 320 times for N_2O relative to CO_2) (IPCC 1995; Mosier 1998). Carbon dioxide is released largely from oxic and suboxic microbial decay and burning of organic waste; CH_4 is produced when organic materials are

decomposed under highly reduced conditions; N_2O is generated by the microbial transformation of nitrogen in wastes either through nitrification or denitrification pathways, the latter being dominant (de Klein et al. 2001; Saggar et al. 2004; Saggar et al. 2007; Smith et al. 2007; Saggar et al. 2008).

2.1.2.1 Municipal waste

In 2004, the municipal waste sector accounted for ~3% of the annual total global emission of GHG, including landfill CH_4 and N_2O, and incinerator CO_2 (Johnson et al. 2007; Bogner et al. 2008).

Methane from landfills and wastewater, which represented 18% of world anthropogenic CH_4 emissions in 2004, is the major contribution to GHG emissions from municipal wastes (Bogner et al. 2008). It was estimated that CH_4 emissions from global landfill are about 500–800 Mt CO_2-eq $year^{-1}$, accounting for about 90% of GHG emissions from the waste sector (Bogner et al. 2008). Methane emissions in Europe, the US and South Africa have been reported to range between 0.1 and 1.0 t CH_4 ha^{-1} day^{-1} (Bogner et al. 2008). Furthermore, landfill CH_4 emissions can continue for several decades after waste is buried.

The major sources of N_2O are human sewage and wastewater treatment (Bogner et al. 2008). Carbon dioxide from the non-biomass portion of incinerated waste is only a small source of GHG emissions (Bogner et al. 2008).

2.1.2.2 Agricultural wastes

Agricultural activities contribute directly to GHG emissions through many processes, including enteric fermentation in domestic livestock, livestock manure management, rice cultivation, agricultural soil management, and field burning of agricultural residues (US EPA 2011). The agricultural activities accounted for an

estimated 10–12% of total global anthropogenic emissions of GHGs (5.1 to 6.1 Gt CO_2-eq $year^{-1}$) in 2005, including about 60% of global N_2O emissions, about 50% of world CH_4 emissions and 0.04 Gt CO_2 $year^{-1}$ (Smith et al. 2007). Additionally, manure management (7%) and biomass burning (7%) accounted for over 14% of total non-CO_2 emissions in 2005 (Smith et al. 2007).

2.1.2.3 Current situation of GHG emissions from organic wastes in New Zealand

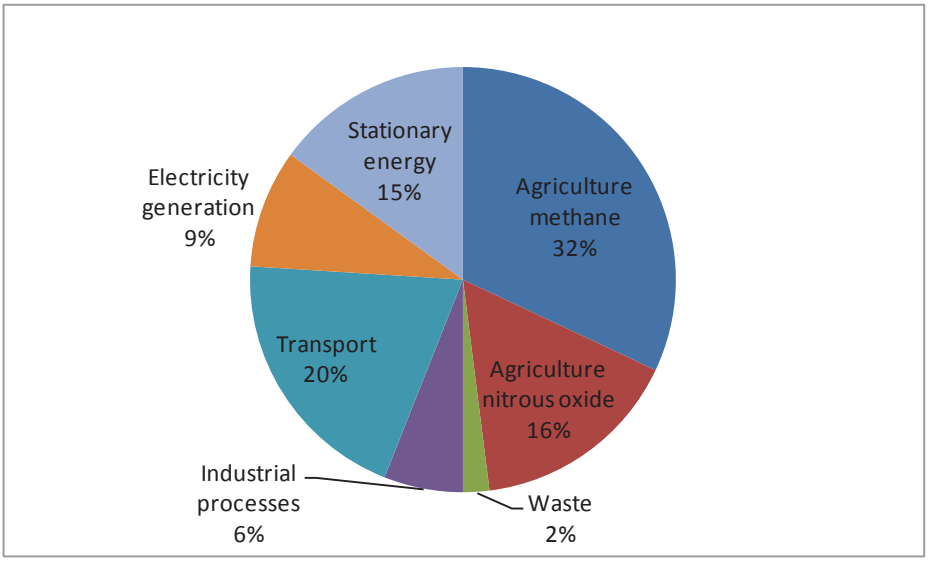

Figure 2-1. New Zealand's greenhouse gas emissions by sector: 2007. Source: Ministry for the Environment New Zealand (2009)

Agriculture is the sector with the highest total GHGs emissions in New Zealand; about half of (~49%) total GHGs were from this sector (Figure 2-1) (Sevenster and de Jong 2008; Ministry for the Environment New Zealand 2009). In 2008, the emissions from the manure management category comprised 776.3 Gg CO_2-eq (~2.2%) of the total emissions from the agriculture sector (Ministry for the Environment New Zealand 2008a). It has thus increased by 159.1 Gg CO_2-eq relative to the levels of reference (617.2 Gg CO_2-eq in 1990) (Ministry for the Environment New Zealand 2008a). The majority of animal waste in New Zealand is excreted directly onto pasture, including 95% of dairy and 100% of sheep, beef and deer (Ministry for the Environment New

Zealand 2011). It was estimated that, in 2009, pasture, range and paddock generated 5514.38 Gg CO_2-eq N_2O emissions (7.1% of total emissions from agriculture) (Ministry for the Environment New Zealand 2011), over 80% of which was from manure N (Ministry for the Environment New Zealand 2007d). Field burning of agricultural residues (barley, wheat and oats residue but not maize and other crop residues in New Zealand), produced 19.1 Gg CO_2-eq in 2008 (Ministry for the Environment New Zealand 2008a). Compared with agricultural waste, municipal waste contributed to another 2.2% of total GHGs emission in New Zealand (Ministry for the Environment New Zealand 2008b). In sum, organic wastes may contribute up to 11% of GHGs emissions in New Zealand.

2.1.2.4 Mitigation strategies from organic waste management

"Under the Kyoto Protocol, New Zealand will have to limit its levels of greenhouse gas emissions to 1990 levels during the period 2008 to 2012. If we cannot reach this target, we will have to take responsibility for any excess emissions."

— Ministry for the Environment New Zealand website

In 1990, New Zealand's total GHG emissions were 59,112.1 Gg CO_2-eq. In 2009, total GHG emissions had increased by 19.4% to 70,563.8 Gg CO_2-eq (Ministry for the Environment New Zealand 2011). The increase in total emissions has resulted from road transport, dairy enteric fermentation, public electricity and heat production, and agricultural soils (Ministry for the Environment New Zealand 2011). Specific forest management strategies (for example, afforestation and reforestation) resulted in long-term C sequestration in soils, which has been widely accepted (Moffat 1997; Jandl et al. 2007). In 2009, net removals from afforestation, reforestation and deforestation under the Kyoto Protocol were –17.3 Mt (–17,300 Gg) CO_2-eq in New Zealand (Ministry for

the Environment New Zealand 2011). However, it was estimated that annual emissions would increase a further 4.8% for the accounting period 2008–2012 compared with 1990, even with consideration of C sequestration from forest management (New Zealand Climate Change Research Institute 2010).

As above mentioned ~11% of New Zealand's GHG emissions were estimated to be derived from organic waste. A great potential exists to decrease the GHG emissions from this sector. Solid wastes disposed of to landfill decreased slightly from 3.180 Mt in 1995, to 3.156 Mt in 2006, and collection of methane gas used to generate energy has increased from 5% in 1998 to 23% in 2007 (Ministry for the Environment New Zealand 2007c). However, a step-change is needed in the technologies intended to reduce current GHG emissions from waste sector in New Zealand while managing wastes in a sustainable way.

2.2 Pyrolysis of organic waste to biochars

Pyrolysis is a thermal decomposition that occurs in the absence of oxygen. It can be divided into slow and fast pyrolysis, and both processes generate char, biogas, and biooils (Roberts et al. 2010). The relative amounts and characteristics of the products are controlled by pyrolysis conditions such as temperature, heating rate, residence time, pressure, and type of feedstock (Roberts et al. 2010). Slow pyrolysis is generally carried out at lower temperature (< 600 ^{o}C), slower heating rate, and longer residence time than fast pyrolysis (Roberts et al. 2010), and it generates more biochar and biogas than fast pyrolysis, which gives rise to more biooil (Brown et al. 2011). Pyrolysis has many advantages over the other waste treatment methods: (i) it can drastically reduce the volume of waste; (ii) it is able to decrease the risk of pathogens, organic pollutants (Cantrell et al. 2007) and heavy metal availability (Inguanzo et al. 2002); (iii) it gives rise to biogas, biooil and even biochar as potential fuels; (iv) it is carried out at lower

temperatures than in the case of incineration, so as to decrease the amount of pollutants released as gases (Inguanzo et al. 2002); and (v) it can, most importantly, generate biochars, which are made to be used in C negative strategies (causing atmospheric C concentration decline, cited from Johnson et al. 2007), as C stored as biochar uncouples the terrestrial C cycle (Fowles 2007; Lehmann 2007; Mathews 2008; Woolf et al. 2010).

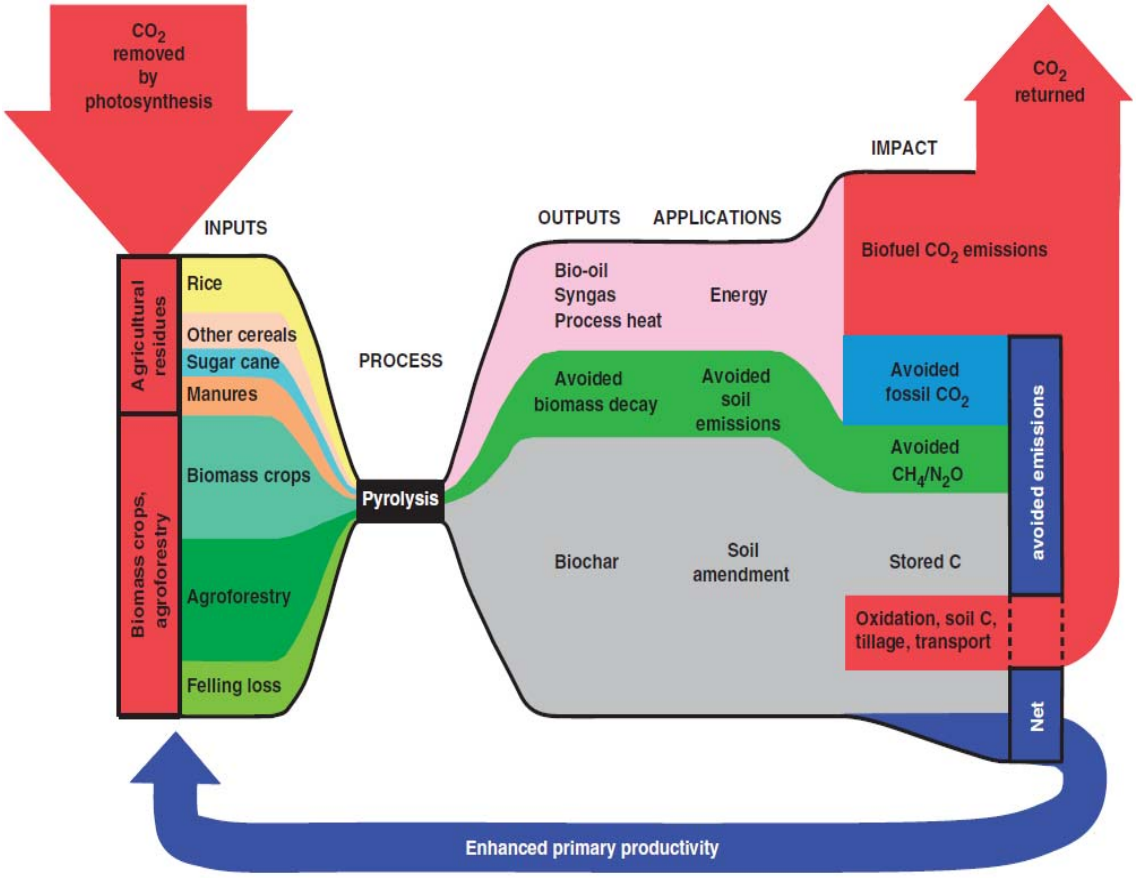

Figure 2-2. Overview of the sustainable biochar concept. Source: Woolf et al (2010)

2.2.1 A sustainable biochar concept

Woolf et al (2010) summarised the sustainable biochar concept (Figure 2-2). Organic wastes such as forest residues, mill residues, field crop residues, green waste, animal manures and biosolids (all these materials are originally from CO_2 assimilation by photosynthesis) could be a suitable and quantitatively important source of feedstock

for biochar production (Lehmann et al. 2006). Pyrolysis generates biogas and biooil as C neutral energies to offset fossil carbon emissions (Johnson et al. 2007; Woolf et al. 2010). Biochar can be used as a fuel; however, its land application can mitigate more GHG emissions than when it is used as a fossil fuel (Gaunt and Lehmann 2008; Laird 2008). As shown in Figure 2-3, biochar has a relatively high fraction of recalcitrant C, which can last for a significantly longer period than would have occurred if the original biomass had been left to natural decay (Woolf et al. 2010). Furthermore, biochar amendments to certain soils can decrease emissions of nitrous oxide and methane (Lehmann 2007; Zhang et al. 2010). In addition, biochar application to soil can enhance soil fertility and thus increase plant growth, which will thus sequester more C in plant tissues (Woolf et al. 2010).

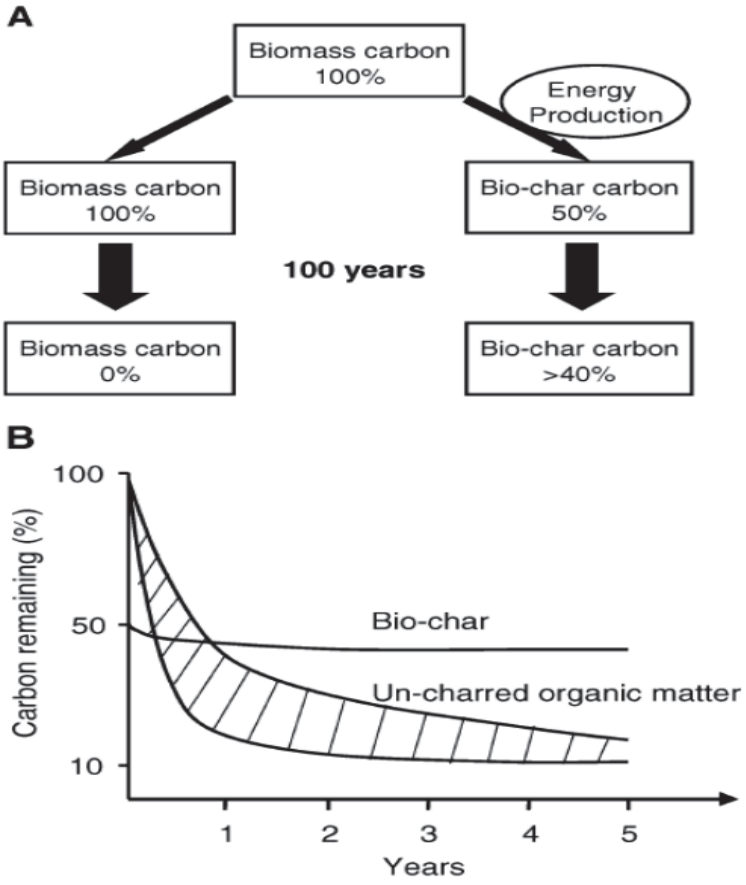

Figure 2-3. Schematics for biomass or biochar remaining after charring and decomposition in soil. Source: Lehmann et al (2006).

2.2.2 Indices for stability of C in biochar

Stability of biochars is of fundamental importance because it not only determines how long biochar C can be sequestered in soil but also how long biochars can benefit the soil environment. Theoretically, the stability of C in biochar can be predicted from modelling C mineralisation kinetics obtained from incubation studies. However, this method is very time-consuming, costly and labour intensive. Furthermore, both incubation conditions (e.g. temperature) and period (i.e. length of time) can interfere with the extrapolation of results to achieve a reliable prediction of C stability. In general, for instance, a long-term study at optimistic temperature of microbial growth (>5yr at >20°C) is preferred as short-term incubation at low temperature can only monitor mineralization of labile C components of biochar and thus underestimate its stability in soil (Singh et al, 2012). Questions thus arise over how long an incubation should be carried out so as to obtain a trustworthy result. As a consequence, Crombie et al (2013) believed that there was no globally established method for determination of absolute stability for biochar. Instead, only relative stability of different biochars can be established (Crombie et al., 2013) and many efforts have been made for this purpose.

Under the same pedoclimatic conditions, biochar is likely to be more stable to microbial attack than the feedstock from which it is produced because of its high content of condensed aromatic C (Schimmelpfennig and Glaser, 2012). Singh et al. (2012) found the existence of a strong negative relationship between the amount of CO_2 evolved during a long-term incubation of different types of biochar and their initial proportion of aromatic C. Therefore, measurement of C aromaticity in biochars can provide a simple and useful approach to evaluate stable C in biochars. Solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy associated with bloch-decay (BD) or

direct polarization (DP) techniques has been widely employed to quantitatively characterise aromatic C in various environmental matrixes (e.g. soil, coal and charcoal) (Preston, 1996; Kögel-Knabner, 1997; Smernik and Oades, 2000; Baldock and Smernik, 2002; Knicker *et al.*, 2005). However, these techniques are expensive and require high technical skills, and not always available. Cheap and robust alternatives are thus necessary to be developed to estimate the aromaticity of biochar C.

Biochar C structures are formed by heat-induced dehydration, decarboxylation, dehydrogenation, demethylation, and cyclization reactions, corresponding to the loss of volatiles and C, H, O and other elements (Almendros et al., 2003; Calvelo Pereira et al., 2011). The volatile content (Calvelo Pereira et al., 2011; Zimmerman et al., 2011), atomic H/C (IBI, 2012; Schimmelpfennig and Glaser, 2012) and O/C (Spokas, 2010) ratios have thus been used as indicators for the carbonisation grade and stability of biochars, with high values suggesting a large proportion of uncarbonised C and low stability. According to the incubation study of Zimmerman et al (2011), for example, the total degraded biochar C was most strongly directly related to the volatile content of the biochar. Furthermore, Spokas (2010) found a good correlation between the atomic O to organic C (O/C_{org}) ratio and the stability of biochars. Given that atomic H/C_{org} ratio closely correlated with O/C_{org} ratio (ash content<50%; Enders et al., 2012), a certain relationship between H/C_{org} and C stability should also exist. The upper atomic H/C_{org} ratio limit of 0.7 has thus been recommended to distinguish biochar from other carbonaceous organic matter based on a consideration of C stability (IBI, 2012). One should note that the use of C_{org} value instead of total C in this ratio is proposed by the IBI as inorganic C can represent a considerable amount of C in ash-rich biochar and this does not form part of the aromatic structure. For the same reason, H may need to be corrected if there is a contribution from inorganic H (e.g. metal silicates, hydroxides and

HCO_3^- and $H_2PO_4^-$ salts), as this does not belong to the aromatic structure. However, up to the present, no research has been carried on this.

Besides the abovementioned indices, other approaches evaluating biochar C stability by thermal oxidation and chemical oxidation have also been proposed. Harvey et al (2012) suggested a new recalcitrance index, R_{50}, calculated as the ratio of temperature values corresponding to 50% oxidation/volatilization of biochar and graphite (886°C). A direct link was found between R_{50} and biochar mineralised C acquired from 1 yr incubation study (at 32°C). Even though, the drawback of this method is also obvious, i.e. R_{50} does not provide any information on how much C is stable. Chemical oxidation by peroxide (H_2O_2, Crombie et al., 2013) or acid dichromate ($K_2Cr_2O_7$; Calvelo Pereira et al., 2011; Naisse et al., 2013), which are useful to assess labile C fraction (thus the recalcitrant C can be determined by difference), were developped to distinguish relative reactivity of biochar C. Nevertheless, variations arising from the complicated solution conditions (e.g. concentration of chemicals) and the lack of correlation between the oxidisable values and mineralisable data hindered the further use of these methods.

As discussed above, all the methods mentioned are not globally accepted either due to our limited understanding of the mechanisms behind which these methods work or lack of comparision among methods. Therefore, cross-validation between methods is necessary to be carried out in future research to improve our understanding about these methods so as to select an appropriate one for C stablitility classification.

2.3 Nutrients in biochars and their bioavailability

Besides mitigating GHG emissions, biochar application may have positive effects on soil functions (Chan and Xu 2009; Laird et al. 2010a; Laird et al. 2010b; Roberts et al. 2010; Silber et al. 2010; Sohi et al. 2010; Verheijen et al. 2010). However,

these benefits are dependent on soil conditions, and biochar characteristics which further rely on the nature of feedstocks and pyrolysis conditions (Lehmann and Joseph 2009a; Roberts et al. 2009; Sohi et al. 2009; Laird et al. 2010a; Laird et al. 2010b; Silber et al. 2010; Verheijen et al. 2010). As this thesis was aimed to develop methodologies to characterise biochars, here only the information on composition and availability of nutrients in biochars is reviewed, with a major emphasis paid to nitrogen (N) and phosphorus (P), given their large demands by plants.

2.3.1 Influencing factors of nutrient properties of biochar

Biochar properties are highly variable due to the variability of feedstock types and pyrolysis conditions under which biochars are produced. The nutrient contents of biochar depend largely on the type of feedstock (Gundale and DeLuca 2006; Chan et al. 2008). Under the same production conditions, biochar produced from nutrient-rich feedstock generally contains higher concentrations of nutrients. Pyrolysis conditions can be manipulated by changing temperature, heating rate, pressure, heating time, feedstock particle size, catalyst, and gas atmosphere conditions (Demirbas 2004; Chan and Xu 2009; Roberts et al. 2010; Brown et al. 2011). At different pyrolysis conditions, feedstock undergoes complex and varying changes, which further influence the chemical properties of the resulting biochars and their nutrient availability (Gaskin et al. 2008; Chan and Xu 2009).

2.3.2 Nitrogen

Nitrogen is the nutrient element required by plants in largest quantities. During pyrolysis, N in feedstocks can undergo very complex reactions. On one hand, a large proportion of N is released as N_2, NH_3 (ammonia) and HCN (hydrogen cyanide) and other N-containing volatile matter (Kambara et al. 1993; Hossain et al. 2011). Table 2-1 is a summary of N release during pyrolysis from model compounds and biomass. As

shown in the table, both feedstock types and pyrolysis temperature can influence the production of N-containing gases. Functional forms of N in feedstocks play an important role in the N release characteristics during pyrolysis. Quaternary N converts finally to NH_3, and a fraction of the pyrrole- and pyridine-type N converts to HCN (Kambara et al. 1993). It should be noted that both NH_3 and HCN are NOx precursors (Becidan et al. 2007), which are air pollutants needing special attention.

Table 2-1. Nitrogen release during pyrolysis by model compounds and biomass. Source: Becidan et al (2007)

Pyrolysis products and influencing factors	amino acids and proteins	pyrrole- and pyridine-type N compounds	biomass
Released N-compounds	HCN, NH_3 and HNCO for all model compounds and biomass		
Fuel intrinsic properties influence	functional groups favours the formation of NH_3		no clear correlation
Fuel physical properties influence	higher heating rates appear to increase HCN/NH_3 ratio		
Mechanistic comments	main intermediates are cyclic amides	main intermediates are nitriles formed by ring opening	see model compounds; however, results are difficult to interpret because of the complex N-compounds makeup in biomass and their possible interactions with other biomass compounds (cellulose, hemicellulose and lignin)
Main N-component	HCN major compound for most compounds, else NH_3	HCN major product and almost only product at high temperature (>1000°C)	HCN or NH_3
Char production	compounds with side-chains or extra functional side groups produce char		significant amount of char produced
NH_3-HCN release vs. operating parameters	increasing N-release with increasing temperature and heating rates		increasing release with increasing temperature and heating rate for HCN but conflicting results for NH_3
NH_3 release	correlation between char and NH_3 production		char formation appears to be important for NH_3 formation

On the other hand, as a direct result of charring, heterocyclic N-containing structures are formed (Almendros et al. 1990; Almendros et al. 2003) and remain in the

biochar matrix. Not all the peptide-structures of the biomass are transformed simultaneously (Almendros et al. 2003; Knicker et al. 2005). Concentrations of aromatic C-types and heterocyclic N-forms increase with progressive heating (Knicker et al. 2005). It has been traditionally believed that heterocyclic N-forms make the biochar relatively recalcitrant against microbial decomposition (Knicker 2010), limiting the conversion of N to available forms for plant uptake (Almendros et al. 2003; Chan and Xu 2009; Yao et al. 2010). However, a recent study has shown that N-heterocyclic forms can be degraded in 28 month incubation (Hilscher and Knicker 2011). Therefore, an in-depth study on N availability in biochars is needed.

2.3.3 Phosphorus

Compared with the knowledge available on thermal transformation of N, less information is available on what changes occur to P during pyrolysis (Chan and Xu 2009). However, reactions of P during pyrolysis are expected to be relatively simple, because P has fewer chemical forms than N. Phosphorus in biosolids and manure is predominantly in inorganic form (Hedley and McLaughlin 2005) and tends to be concentrated in the ash fraction of biochars during pyrolysis (Gaskin et al. 2008; Chan and Xu 2009; Hossain et al. 2011). If organic P is present, the organic P bonds can be cleaved by thermal treatment and result in an increase of acid soluble P salts (De Luca et al. 2009). If pyrolysis is conducted at temperature >700 °C, P is likely to volatize. However, biochars are generally produced at a temperature < 600 °C, and it is expected that feedstock P will be fully recovered in biochars (Bridle and Pritchard 2004; Hossain et al. 2011).

Given the full recovery of feedstock P after pyrolysis, it is necessary to investigate whether the availability of this element changes with the thermal treatment, as this may have strong implications on the fertility value of biochar. Previous studies

arbitrarily concluded that P availability in biochars decreases with increasing pyrolysis temperature based on limited information (Bridle and Pritchard 2004; Hossain et al. 2011). Doubt arises when considering the fact that thermal treatment (calcination, a similar process to pyrolysis except for the presence of air) generally increases neutral ammonium citrate solubility and bioavailability of P in phosphate rocks (Gilkes and Palmer 1979; Bolland and Bowden 1982). Therefore, more studies are needed to examine the changes in P availability of biochars as a function of pyrolysis temperature.

2.3.4 Methodologies used for characterisation of available N and P in biochars

Few studies have been carried to determine the available N and P in biochars, especially for N. As N is also an integral part of organic structure of high temperature biochar (Knicker, 2010), it may follow a similar pattern that of C. Therefore, future studies are needed to find out the relationship between N dynamics and C turnover before N availability in biochar can be measured. As absolute stable C is likely impossible to be obtained at this stage as above mentioned, quantification of absolute available N value is also a challenge; instead, we would suggest that relative availability of N is a more accurate expression. If thermally survived proteinaceous material and ester-bound biopolymers are the only available N sources in biochars, acid hydrolysis using 6 M HCl (Kelley and Stevenson, 1995) can be an appropriate method to characterise available N in biochars (Kaal and Rumpel, 2009). However, recent studies showed that a part of heterocyclic N in biochar was also bioavailable to both soil microorganisms and plants (Hilscher and Knicker, 2011). For this, methods for evaluating labile/stable C, such as chemical oxidation, may be more useful to characterise available N in biochars.

A few studies investigated P availability using those methods originally developed for soil available P tests (e.g. Olsen P by Hossain et al., 2011). Doubt is thus

created over their suitability as the characteristics of biochars and soils are very different. In this sense, fertiliser P tests may be more appropriate. A relatively thorough review of these methodologies can be found in Chapter 6.

2.3.5 Other nutrient elements

Sulphur (S) in feedstocks exists as either protein forms (50−40% of total S in straw) or inorganic forms (60–50%) correspondingly (Knudsen et al. 2004). Figure 2-4 is a summary of possible reactions of S during thermal treatments. Decomposition of organically associated S starts from below 200 °C to form SO_2, H_2S and carbonyl sulfide (COS) (Knudsen et al. 2004; Wang et al. 2010). Most of the C bonded S (especially from sulfonates) in corn stalks can be decomposed at 450°C (Churka Blum et al. 2013) and almost all the organic S in feedstock can be released at temperatures below 500 °C (Johansen et al. 2011).

The decomposition of inorganic sulphate is complicated by the complex interactions between S, Ca, K, and Si (Lang et al. 2006). If there is small amount of Ca and K and high concentration of Si in the feedstock, SO_2 starts to be released to the gas phase from 500 °C and up to 85% of total S can be lost at 950 °C (Knudsen et al. 2004). Sulphur may also be captured by charred materials (Knudsen et al. 2004). Therefore, it is concluded that half of the feedstock S is expected to be recovered in the biochar if biochar is produced below 600°C.

Sulfur in biochars can be readily available. Biochars made from broiler litter manure (Uchimiya et al. 2010) and corn stalks (Churka Blum et al. 2013) have been found to increase soil soluble S, which probably results from the dissolution of sulphate and degradation of ester-S in biochars (Churka Blum et al. 2013). Yao et al. (2010) found that 20 – 28% of S in sewage sludge biochar could be released into solution during 300 h weathering in a modified Soxhlet reactor. However, it is still not clear how

much S is available in biochars produced at different pyrolysis conditions, since no bioassay test has yet been conducted in this regards.

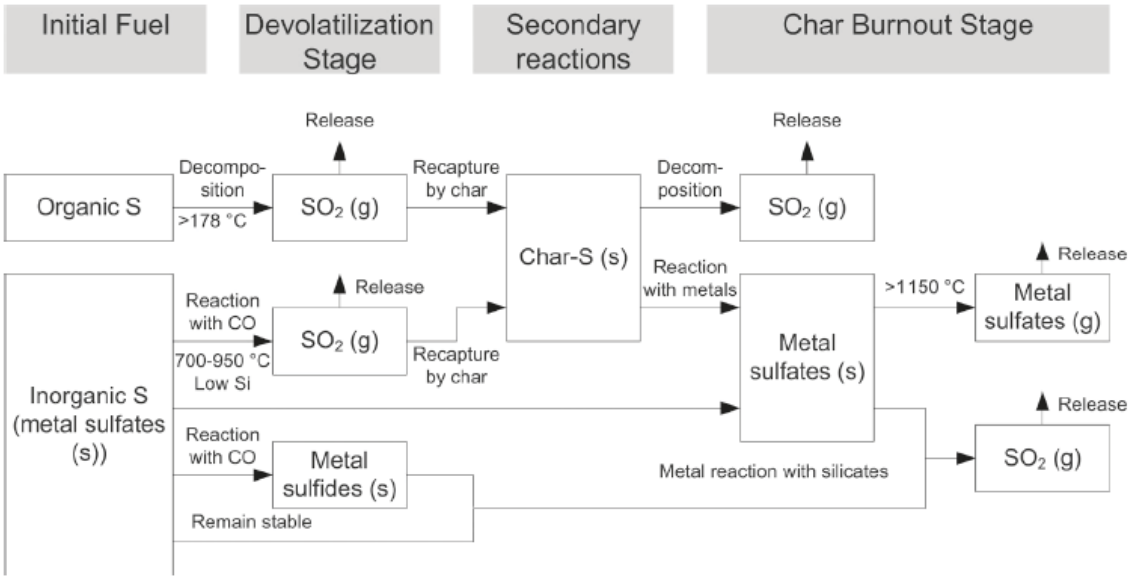

Figure 2-4. Possible reaction paths and release mechanisms of S during devolatilization and combustion with special emphasis on combustion of annual. Source: Johansen et al (2011)

Potassium (K) and sodium (Na) can be lost by vaporization during pyrolysis at 473-673 °C (Yu et al. 2005) (cited in Chan and Xu, 2009). The fraction remaining in the biochar tends to be highly soluble and thus readily available (Yu et al. 2005; Yao et al. 2010). Other metal elements such as calcium (Ca), magnesium (Mg), iron (Fe), and zinc (Zn) are likely to be enriched in the biochars (Hossain et al. 2011), and their availability will be highly depended on the solubility of their salts (pH-dependent) (Silber et al. 2010), as well as their redox status (for Fe).

2.4 Pollutants in biochars and their bioavailability

Before any large-scale application of biochar to soils, it is critical to know its potential environmental risks. Contaminants, such as heavy metals, polyaromatic hydrocarbons (PAHs) and dioxins, may exist in some biochars. The concentrations and

composition of pollutants in biochar depend on the feedstock type and pyrolysis conditions (Thies and Rillig 2009).

Heavy metals are not easily vaporized during pyrolysis, but tend to be enriched in the ash fraction if biochar is produced below 600 °C (Hossain et al. 2011), with the exception of Cd and Hg, and the metalloid As (Yoshida and Antal 2009). Therefore, biochars will contain considerable amount of heavy metals if it is produced from heavy metals containing materials. High contents of heavy metals have been reported in biochars produced from sewage sludge and tannery wastes (Bridle and Pritchard 2004; Hospido et al. 2005). However, very little experimental evidence is available on the bioavailability of heavy metals in biochar and biochar-enriched soil (Verheijen et al. 2010).

Polyaromatic hydrocarbons are recognized as important environmental pollutants resulting from both natural and anthropogenic sources (Wilson and Jones 1993). Some PAHs are inherently carcinogenic and mutagenic (Garcia-Perez 2008), posing threats to human and animal health. PAHs are formed in large quantities as the result of secondary thermo-chemical reactions at temperatures over 700 °C, whereas very small amounts of these compounds are formed between 350 ^{o}C and 600 °C (Garcia-Perez 2008). PAHs are probably not a problem for the biochar application to soil (Singh et al. 2010) as biochar is generally produced at lower temperature than 600°C. However, the total amount and composition of PAHs strongly depend on feedstock type and pyrolysis temperature (Keiluweit et al. 2012). Further tests need to be carried out on a wide range of biochars produced from different types of feedstock under various pyrolysis conditions.

Polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs), two groups of organic compounds that are ubiquitous in the environment at ultra-trace levels, have

aroused considerable concern among scientists and policy makers because of their environmental persistence, high risk of bioaccumulation through the food chain, and high toxicity. PCDD/Fs are not produced intentionally but are released into the environment in ultra-trace amounts from various chlorinated feedstocks at high temperature (McLachlan et al. 1996; Evans and Dellinger 2003; 2004). Most feedstocks used in the production of biochars have low levels of chlorinated compounds (Tosine et al. 1985), which make it less likely to have high dioxins concentrations in biochars.

Furthermore, flash carbonizing and some low temperature pyrolysis conditions may condense bio-oils and other re-condensed derivatives on the biochar surfaces (Thies and Rillig 2009), which can be toxic to plants and soil microorganisms (Gell et al. 2011). Other environmental health concerns associated with the production of biochar is the possible presence of crystalline silica in rice husk biochars which are produced at temperatures above 550 °C. These crystals (cristobalite and tridymite) can cause lung diseases (Lehmann and Joseph 2009b).

Biochar incorporation into soil can enhance the sorption capacity of soils for many soil pollutants, either hydrophobic or hydrophilic (Chen et al. 2008; Cao et al. 2009; Chen and Chen 2009; Cao and Harris 2010). This behaviour may greatly mitigate toxicity and transport of common pollutants in soils through reducing their bioavailability; however, it may also result in their localised accumulation, although the extent and implications of this have not been fully assessed experimentally (Verheijen et al. 2010). The possibility of biochar being a carrier of contaminants to soil needs to be evaluated on a case-by-case basis (Verheijen et al. 2010). Full and careful risk assessment in this context is required in order to relate the bioavailability and toxicity of the contaminants to the biochar type, 'safe' application rates, feedstock, pyrolysis

conditions, and the sorption capacity to pollutants of biochar, as well as soil type and environmental conditions (Verheijen et al. 2010).

2.5 Current research demand for the characterisation of biochars produced from organic waste streams in New Zealand

According to the literature review, current research gaps in the characterisation of biochars produced from organic wastes in New Zealand can be summarised as following.

- Stability of C in biochars is one of the research priorities in biochar studies, given that biochar is intentionally made to sequester C in soils. However, little information is available on the stability of biochars produced from organic wastes. Simple tests are also needed to substitute the costly and time-consuming incubation method to predict C stability in biochars.
- Transformations of nutrient elements (mainly N and P) during pyrolysis are still not well studied.
- The bioavailability of N and P in biochars is not fully understood and robust chemical methods are needed to be put in place so that the biochar fertility values can be determined.
- An in-depth understanding of the potential formation of pollutants (e.g., PAH) during pyrolysis and bioavailability of pollutants (including heavy metals) in biochars – produced with different feedstock types and under different pyrolysis conditions – is required to fully estimate the risk of biochar application to soil. However, previous results suggest that environmental impacts attributable to metals, metalloids and PAHs associated with biochar following its application to soil are likely to be minimal (Freddo et al. 2012). Therefore, this thesis will not consider this topic.

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CHAPTER 3. PREDICTING C AROMATICITY OF BIOCHARS BASED ON THEIR ELEMENTAL COMPOSITION

Stability of biochar is of fundamental importance because it not only determines how long biochar C can be sequestered in soil but also how long biochar can benefit the soil environment. As indicated in Chapter 2, knowledge of the aromatic C fraction in biochar can be extremely useful for understanding its C stability. However, previous methods used for quantifying C aromaticity based on NMR techniques were expensive and required high technical skills. Simple and robust methods are thus proposed to predict C aromaticity in biochars in this chapter.

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Abstract

Three models were examined to predict C aromaticity (f_a) of biochars based on either their elemental composition (C, H, N and O) or fixed C (FC) content. Values of f_a from solid state ^{13}C nuclear magnetic resonance (NMR) analysis with bloch-decay (BD) or direct polarization (DP) techniques, concentrations of total C, H, N, and organic O, and contents of FC of 60 biochars were either compiled from the literature (dataset 1, n=52) or generated in this study (dataset 2, n=8). Models were first calibrated with dataset 1 and then validated with dataset 2. All models were able to fit dataset 1 when atomic H to C ratio (H/C) <1(except two ash rich biochars) and to estimate f_a of HF treated biochars (H/C<1). Model 1, which was based on values of H/C only and calibrated with a root mean square of error (RMSE) of 0.04 f_a–unit (n=41), could predict the experimental data with a RMSE=0.02 f_a–unit (n=6). Model 2, which was based on biochar elemental composition data, showed the most accurate prediction, with a RMSE of 0.03 f_a-unit (n=41) for the calibration data, and of 0.02 f_a-unit (n=6, H/C<1) for the validation data. Model 3, which was based on contents of FC and C, and modified with a correction factor of 0.96, displayed the highest RMSE (0.06 f_a -unit, n=19) among the three models. Models 1 and 2 did not work properly for samples having either an H/C ratio>1, high concentrations of carbonate or high inorganic H. These models needs to be further tested with a wider range of biochars before they can be recommended for classification of biochar stability.

Keywords

Aromatic C; fixed C; atomic H/C ratio; pyrolysis; char

3.1 Introduction

Biochar is charcoal made from waste biomass and intended to be added to soils to improve soil functions and increase C sequestration (Lehmann *et al.*, 2006). Stability of biochars is of fundamental importance because it not only determines how long biochar C can be sequestered in soil but also how long biochars can benefit the soil environment. Under the same pedoclimatic conditions, biochar is likely to be more stable to microbial attack than the feedstock from which it is produced because of its high content of condensed aromatic C (Schimmelpfennig and Glaser, 2012). Singh *et al.* (2012) described the existence of a strong negative relationship between the amount of CO_2 evolved during a long term incubation of different types of biochar and their initial proportion of aromatic C. Furthermore, the degree of aromaticity has been shown to influence the adsorption of organic pollutants onto biochars (Sun *et al.*, 2011). Therefore, quantification of the aromaticity of biochar C can be extremely useful not only for the prediction of the mean residence time (MRT) of biochar C in soils but also for the understanding of the interactions between hydrophobic organic pollutants and biochars.

Solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy associated with bloch-decay (BD) or direct polarization (DP) techniques has been widely employed to quantitatively characterise aromatic C in various environmental matrixes (e.g. soil, coal and charcoal) (Preston, 1996; Kögel-Knabner, 1997; Smernik and Oades, 2000; Baldock and Smernik, 2002; Knicker *et al.*, 2005). However, these techniques are costly and time consuming, and not always available. Therefore, simple, cheap and robust alternatives are needed to estimate the aromaticity of biochar C.

Biochar C structures are formed by heat induced dehydration, decarboxylation, dehydrogenation, demethylation and cyclisation reactions (Baldock and Smernik, 2002;

Almendros *et al.*, 2003; Schimmelpfennig and Glaser, 2012). With increasing degree of thermal modification, biomass loses functional groups and C, H, O, N and other elements, progressively aromatises and then polycondenses into a polyaromatic network (Kaal *et al.*, 2012). The H/C and O/C ratios have thus been used as indicators for the degree of condensation (Calvelo Pereira *et al.*, 2011; Schimmelpfennig and Glaser, 2012), with high values suggesting a large proportion of uncarbonised C. However, very few studies have attempted to establish a mathematic model to predict C aromaticity of so-called 'black C continuum' using their elemental composition. Some efforts in this regard have been carried out in coal samples. For example, Maroto-Valer *et al.* (1998) developed a linear relationship between atomic H/C ratio and C aromaticity. Later on, Mazumdar (1999) successfully developed a series of equations, based on a revised densimetric approach, to precisely estimate the aromaticity of coals using their elemental composition data. Given the spectral and thermogravimetric similarity of coal and biochars (Reeves, 2012; Yi *et al.*, 2012), especially when produced from woody materials and at high pyrolysis temperatures, certain correlation between elemental composition and C aromaticity are also expected to occur in biochars. Therefore, the objective of this study was to examine models originated from coal chemistry to estimate the C aromaticity of biochar based on its elemental composition.

3.2 Materials and methods

3.2.1 Biochar preparation and characterisation

Eight biochars were used in this study. Their production and characteristics were reported in Wang *et al.* (2012) (also can be seen in Chapters 5 and 6). Briefly, two feedstock were used: (i) one (BSe) was a mixture of alum treated biosolids (from anaerobic digestion of sewage sludge (containing ~5 dry wt% of Al) and eucalyptus wood chips, and (ii) the other (MAe) was a mixture of cattle manure (from a dairy farm)

and eucalyptus wood chips. Both mixtures were made up to a 1:1 dry wt% basis ratio. Biochar was produced by slow pyrolysis in a well closed, gas fired rotating drum kiln (Calvelo Pereira *et al.*, 2011) at four final heating temperatures (250, 350, 450, and 550 °C). Biochar samples from different final temperatures were referred to as MAe-250, MAe-350, MAe-450, MAe-550, BSe-250, BSe-350, BSe-450, and BSe-550. Samples were treated with 10% HF solution, for 4 times with a solid to liquid ratio of 1:20 followed by a thorough rinse with deionised (DI) water (4 times) to remove residual acid (more details in the Appendix I Supporting Information SI), to eliminate the inorganic H and paramagnetic or ferromagnetic minerals (Gonçalves *et al.*, 2003). Then both treated and untreated samples were analysed for their elemental C, H, N and S composition (Elementar, Vario MACRO, Germany). Moisture, volatile matter (VM), fixed C (FC) and ash contents (wt%) of samples were determined using a thermogravimetric analyser (SDT Q600, TA Instruments, Melbourne, Australia) according to Calvelo Pereira *et al.* (2011) (more details in the Chapter 5). Thereafter elemental composition was recalculated on a dry ash free (*daf*) basis. Concentration of O (% *daf*) was then estimated by difference (100%-C%-N%-H%-S%).

Samples treated with 10% HF were subjected to solid state ^{13}C magic angle spinning (MAS) NMR analysis. Such treatment has been shown to have barely any effect on the NMR spectra and thus on the estimation of aromaticity of samples (Schmidt *et al.*, 1997; Rumpel *et al.*, 2006). NMR spectra were obtained at a ^{13}C frequency of 50.3 MHz on a Bruker DRX 200 Mhz spectrometer (Rheinstetten, Germany). Samples were packed in 7 mm diameter cylindrical zirconia rotors with Kel-F end-caps and spun at 5.0 ± 0.2 kHz in a Doty Scientific MAS probe. During acquisition the sample temperature was maintained at 20 ºC. Proton decoupled direct polarised magic angle spinning (DP-MAS) ^{13}C spectra free induction decays (FIDs)

were acquired with a ^{1}H 90° pulse of 5.5 μs, a sweep width of 16 kHz; 960 data points were collected over an acquisition time of 28 ms with 42 kHz proton decoupling, a relaxation time of 10 sec, and 2 k scans. All spectra were zero filled to 4 k data points and processed with a 0.005 s Gaussian broadening. Chemical shifts were externally referenced with glycine.

Quantification of aromatic C was carried out using a deconvolution procedure following McBeath *et al.* (2011). The chemical shifts of different C structures were following Baldock and Smernik (2002). The chemical shift limits >210 ppm were used for signal intensity in spinning side band (SSB) and it was assumed that the two SSBs associated with a given parent signal were of approximately equal intensity (Baldock and Smernik, 2002). Deconvolution and integration of NMR spectra were carried out by the best fits of Gaussian peaks using Origin 7.0 software with a Peak Fitting 7.0 module (OriginLab, Northampton, USA). The initial position, centre and width of each peak (except that of aryl C centred at ~128 ppm) were constrained within the range of chemical shifts of certain functional groups proposed by Baldock and Smernik (2002). Furthermore, peaks should be always non-negative. Figure S3-1 contains two examples of deconvolution components of biochar DP/NMR spectra. 100% of aromaticity was set as 1 f_a-unit.

3.2.2 Data collection and modelling

3.2.2.1 Model 1

Maroto-Valer *et al.* (1998) found a linear relationship between f_a and H/C ratio for bituminous coals with an H/C ratio ranging from 0.5–0.8 (f_a=1.22-0.58H/C). Concerns thus arise over the reliability of extrapolation of the relationship towards lower H/C ratios than 0.5. Therefore, a more general form is written as:

Table 3-1. Elemental composition (dry-ash free basis, *daf*) and predicted aromaticity ($f_{a\text{-}pre}$) of biochars treated and untreated (original) with 10% HF solution. $f_{a\text{-}exp}$ is the measured f_a by DP/NMR techniques. Data were presented as mean±standard deviation (n=2). 100% of aromaticity was set as 1 f_a-unit. RMSE was calculated after excluding BSe-250 and MAe-250. M denotes model and n/a not applicable.

Samples	C (%*daf*)		H (%*daf*)		O (%*daf*)		N (%*daf*)		$f_{a\text{-}exp}$	$f_{a\text{-}pre}$ HF-treated			$f_{a\text{-}pre}$ Untreated		
	Original	HF	Original	HF	Original	HF	Original	HF	DP/NMR	M1	M2	M3’	M1	M2	M3’
BSe-250	53.4±0.7	56.7±0.9	6.4±0.1	6.0±0.0	37.9±2.0	35.3±1.4	2.3±0.1	2.0±0.1	0.48	0.40	0.30	0.52	0.12	0.11	0.45
BSe-350	60.6±0.7	66.1±0.9	5.9±0.2	5.0±0.2	30.4±1.8	25.7±1.1	3.1±0.1	3.2±0.1	0.66	0.69	0.67	0.77	0.41	0.45	0.70
BSe-450	66.5±1.5	70.8±0.8	5.3±0.2	4.0±0.2	24.8±2.1	21.9±0.9	3.4±0.2	3.3±0.0	0.86	0.83	0.81	0.86	0.59	0.64	0.81
BSe-550	71.2±1.4	74.0±0.9	4.5±0.4	3.4±0.1	20.8±2.0	19.2±0.5	3.5±0.2	3.4±0.0	0.87	0.89	0.87	0.90	0.74	0.78	0.93
MAe-250	57.0±0.3	54.1±0.7	6.3±0.1	5.9±0.1	35.0±2.1	38.7±0.7	1.7±0.1	1.4±0.0	0.44	0.36	0.21	0.52	0.25	0.24	0.46
MAe-350	71.1±0.9	70.4±0.9	5.4±0.1	4.8±0.1	21.2±0.3	22.5±0.7	2.3±0.1	2.3±0.0	0.72	0.74	0.73	0.79	0.63	0.68	0.70
MAe-450	77.5±0.2	73.9±0.9	4.4±0.2	3.7±0.0	15.6±1.0	20.0±0.6	2.5±0.1	2.4±0.1	0.84	0.86	0.85	0.85	0.79	0.83	0.74
MAe-550	84.8±0.9	82.3±0.1	3.3±0.4	3.0±0.2	9.4±0.2	12.2±0.6	2.6±0.1	2.5±0.0	0.93	0.92	0.93	0.92	0.89	0.92	0.82
RMSE	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.02	0.02	0.06	0.16	0.13	0.07

$$f_a = g(H/C) \tag{3-1}$$

where g is a symbol of function, and not necessarily a linear one, which can be solved as the best-fitted trend line.

3.2.2.2 Model 2

Mazumdar (1999) suggested a revised densimetric approach to precisely estimate the f_a of polyaromatic hydrocarbons (PAH, consisting only C and H) as shown in Equation (3-2):

$$f_a = (1 - {}^{H'}\!/_{C'}) + \alpha({}^{Mc}\!/_{d} - 5.34) \tag{3-2}$$

where *H'/C'* is the atomic ratio of H and C; *Mc/d* is the average molar volume of C-atom, decreasing as the condensation degree of PAH increases; 5.34 is the average molar volume of graphite C-atom and is considered as the lower *Mc/d* limit of C; α is a modification coefficient, which ranges from 0.115 to 0.125 for coal samples, increasing with increasing f_a values. *Mc/d* can be estimated (Mazumdar, 1999) by Equation (3-3):

$${}^{Mc}\!/_{d} = 5.34 + 9.15\,{}^{H'}\!/_{C'} - 2.9({}^{H'}\!/_{C'})^2 \tag{3-3}$$

However, one should note that the C structure of biochar does not only consist of C and H (i.e. hydrocarbon) but also of O, N and S and other elements, which can also influence *Mc/d* and hence the estimation of f_a of biochars. Therefore, a correction is needed to account for the presence of heteroatom groups (O and N). One CO double (*C=O*) bond can be replaced by 2 *C-H* bonds and one N atom can be simply replaced by a C atom (only applicable for compounds with high C/N ratios). So,

$${}^{H'}\!/_{C'} = (H\%/1 + 2\theta * O\%/16)/(C\%/12 + N\%/14) \tag{3-4}$$

where θ is the ratio of *C=O* bond to *CO* bonds (including aliphatic and O-aryl C *C-O* single bond and *C=O* double bond); *H%/1, C%/12, O%/16* and *N%/14* are the concentrations of corresponding elements divided by their molecular weight.

3.2.2.3 Model 3

Brewer *et al.* (2011) recently proposed the use of FC (*daf*) as a proxy for mass based f_a ($f_{a\text{-}mass}$), given that the determination of FC is also used in routine analysis for biochar characterisation (sometimes referred to as proximate analysis). Since f_a is generally estimated from ^{13}C NMR spectra on a molar basis, a correction to transform f_a (default on a molar basis) into $f_{a\text{-}mass}$ is needed. The relationship between $f_{a\text{-}mass}$ and f_a can be written as:

$$f_{a-mass} = f_a \times C_{org}(daf) \approx FC(daf) \tag{3-5}$$

Therefore,

$$f_a \approx FC(daf) / C_{org}(daf) \tag{3-6}$$

where C_{org} is the organic C content in biochar, which approximates to total C when carbonate content is low.

In order to calibrate the above models for f_a estimation, an additional dataset (dataset 1) was generated by compiling contents of C, H, N, O, ash, FC and f_a of 52 biochars from the literature (listed in SI Table S3-1). Data of elemental composition and FC content were calculated on a *daf* basis. Aromaticity was estimated from DP/MAS-NMR analysis, by deconvoluting peaks centred ~128 ppm (aryl-C) and ~150 ppm (O-aryl-C) (McBeath *et al.*, 2011; Singh *et al.*, 2012) or calculating aromatic C area from a wider chemical shift range (90–165 ppm) (Brewer *et al.*, 2011; Cao *et al.*, 2012). Due to the low contents (<2% of total NMR signal) of di-O-alkyl (90-110 ppm) and carboxyl

(165–184 ppm) groups in fresh biochars having a H/C<1 (Cao *et al.*, 2012), the results from these two methods were comparable for the quantification of f_a.

For Model 1, the 52 data from literature (Appendix I Table S3-1) were used to establish an equation which gave the best fit; while only data with an H/C ratio<1 (Table S3-1, non-grey-shaded ones) were adopted to calibrate Model 2. Model 3 was calibrated with only 19 data of which both FC and f_a were available (Table S3-1). After calibrating, the models were validated with our dataset of HF treated samples (dataset 2).

Excel's Solver (Microsoft Office 2007) was employed to obtain the best solutions of the parameters through minimising the residual sum of squares (RSS), which can be written as:

$$RSS = \sum_{i=1}^{n} (f_{a-\exp} - f_{a-pre})^2 \quad (3\text{-}7)$$

The prediction accuracy of the model was tested by both the root mean square of error (RMSE, Equation 3-8) and the Pearson's correlation coefficient (r) between $f_{a\text{-}pre}$ and $f_{a\text{-}exp}$. The best prediction is shown by the largest r and the smallest RMSE.

$$RMSE = \sqrt{\frac{RSS}{n}} \quad (3\text{-}8)$$

3.3 Results and discussion

3.3.1 General description of biochars

Elemental composition (daf) of samples before and after HF treatment is reported in Table 3-1. Total C in original samples ranged from 53–85%, total H from 3.3–6.4%, O from 12–38%, and N from 1.7–3.5%. Except total C in BSe samples and O in MAe samples, the concentrations of all elements decreased after 10% HF treatment. Total C recovery after HF treatment was 83% for BSe250 and 96% for MAe350 and

BSe550, with other biochars having recovery values in between (data not shown). The decrease in atomic H/C ratio after the HF treatment was greater in BSe than in MAe samples, indicating the existence of considerable amount of inorganic H in BSe biochars [mainly as inorganic OH, as determined by 1M NaF-titration according to Bracewell et al. (1970), data not shown]. The increase in total C of BSe biochars after treatment was due to the underestimation of the ash content in the original sample, which was caused by the loss of inorganic OH (e.g. 1% of inorganic H being equivalent with 19% of inorganic OH on a mass basis) during heating (Kloprogge et al., 2002).

The change in peak intensity and chemical shifts of NMR spectra as the pyrolysis temperature increased is displayed in Figure 3-1. Substantial differences were found for biochars from both feedstocks as pyrolysis temperature increased. For MAe-250 and BSe-250, the major signal in the O-alkyl region (64, 74 and 84 ppm) and the presence of a di-O-alkyl resonance peak at 105 ppm could be assigned to cellulose (Baldock and Smernik, 2002). The peaks around 23 and 173 ppm might be from the acetate and carboxyl structures of hemicellulose (Baldock and Smernik, 2002). Resonances at 56, 131, 148 and 168 ppm likely arose from the NCH and methoxyl, aryl, O-aryl C and COO/N-C=O groups, respectively, which were related to structures of lignin and proteins or peptides (Baldock and Smernik, 2002; Cao et al., 2010). As pyrolysis temperature increased, the resonances associated with hemicellulose, cellulose, lignin and proteins decreased. For 450 °C and 550 °C biochars no distinctive peaks for these compounds were observed in the spectra. This result was consistent with previous findings that hemicellulose degradation mainly occurred at 220–315 °C, cellulose decomposition at 315–400 °C (Yang et al., 2007), lignin within 250–450 °C (a small fraction of lignin can be stable at higher temperature, Raveendran et al., 1996) and protein at 300–400 °C (Thipkhunthod et al., 2007). The peak maximum of the aromatic

signal shifted with pyrolysis temperature from 131 ppm (BSe-250 and MAe-250) to 126 ppm (BSe-550) and 127 ppm (MAe-550), indicating the progressive formation of condensed aromatic structures (Baldock and Smernik, 2002; Knicker et al., 2005). The f_a of BSe biochars increased from 0.48 f_a unit (BSe-250) to 0.87 f_a unit (BSe-550), and that of MAe biochars increased from 0.44 f_a unit (MAe-250) to 0.93 f_a unit (MAe-250) (Table 3-1). These results were comparable with those of samples produced at similar pyrolysis temperature in previous studies (Appendix I Table S3-1).

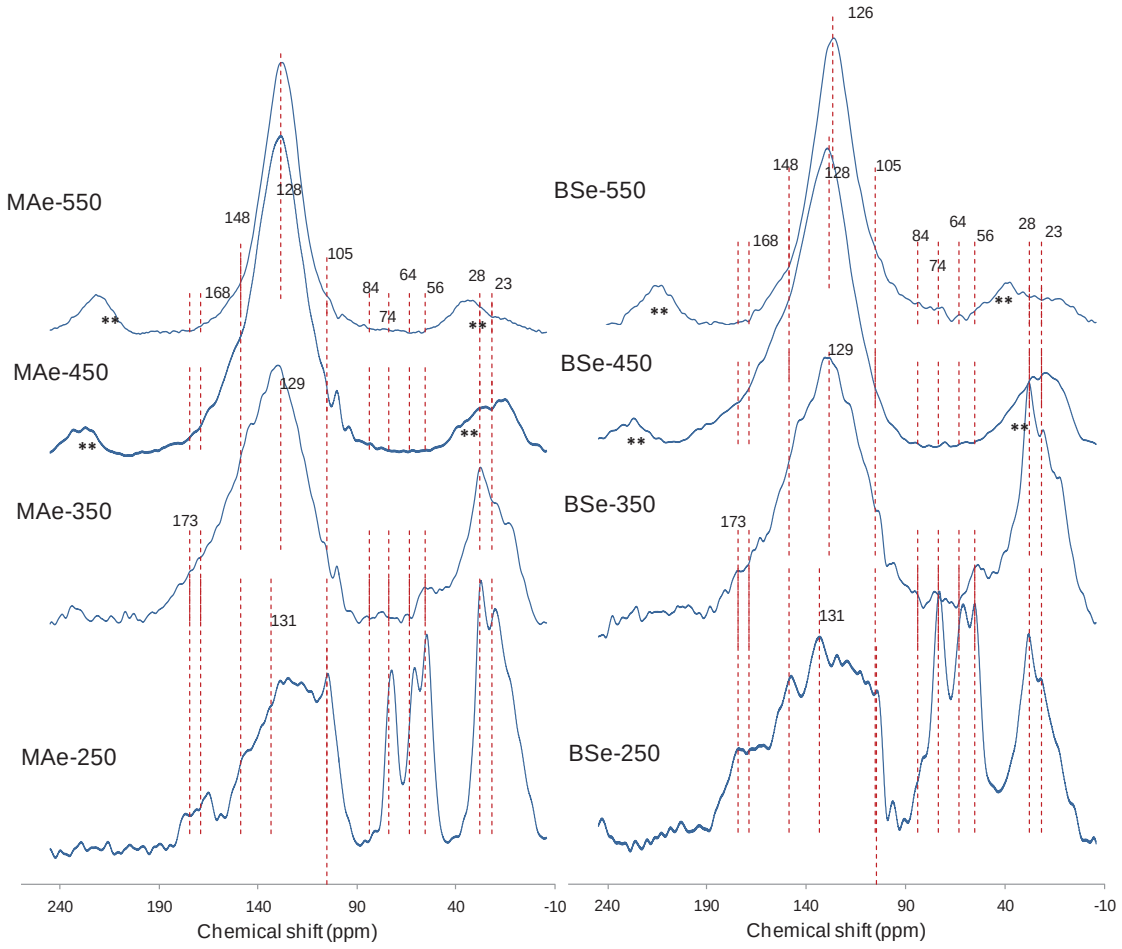

Figure 3-1. Solid state ^{13}C DP-MAS-NMR spectra of biochars produced from biosolids-eucalyptus wood mixture (BSe) and cattle manure-eucalyptus wood mixture (MAe). (**) refers to spinning side bands.

3.3.2 Calibration of the models

3.3.2.1 Model 1

The f_a values of 52 biochars were plotted against their atomic H/C ratios as shown in Figure 3-2. When only considering biochars with an atomic H/C ratio between 0.5 and 0.8, a linear adjustment gave a good fit, in agreement with Maroto-Valer et al. (1998). However, a linear model was not adequate to fit all the data. Instead, a quadratic equation (Equation 3-9) was found to give a satisfactory fit with r^2=0.93 and RMSE=0.06 f_a unit (n=52). When taking a close look at the data, it was apparent that the model did not work well when the H/C ratio was >1 and for specific samples from Brewer et al. (2011) (Figure 3-3a; grey-shaded in Table S3-1). After excluding these samples, the RMSE of Model 1 decreased to 0.04 f_a unit (n=41).

$$f_a = -0.3864(\mathrm{H/C})^2 - 0.0292(\mathrm{H/C}) + 0.9929 \qquad (3\text{-}9)$$

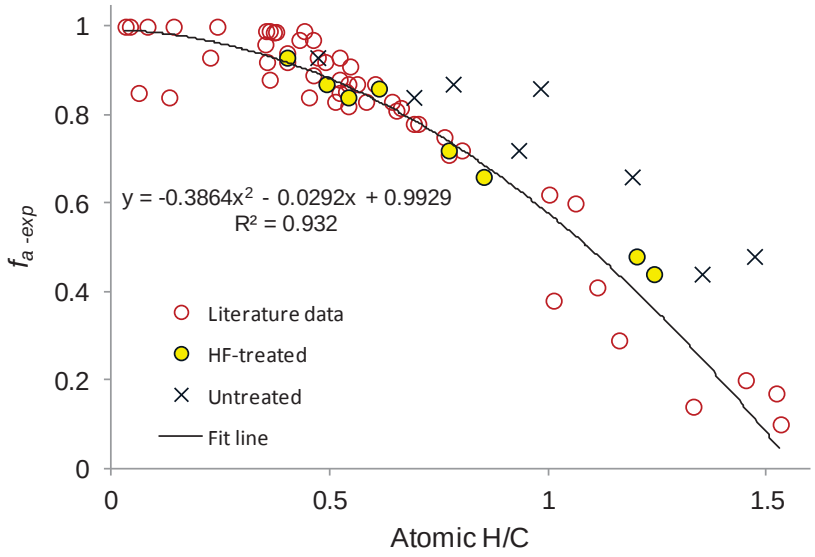

Figure 3-2. Plot of f_a-measured ($f_{a\text{-}exp}$) against atomic H/C ratios. Data were from literature (Table S3-1) and this study. 100% of aromaticity was set as 1 f_a-unit.

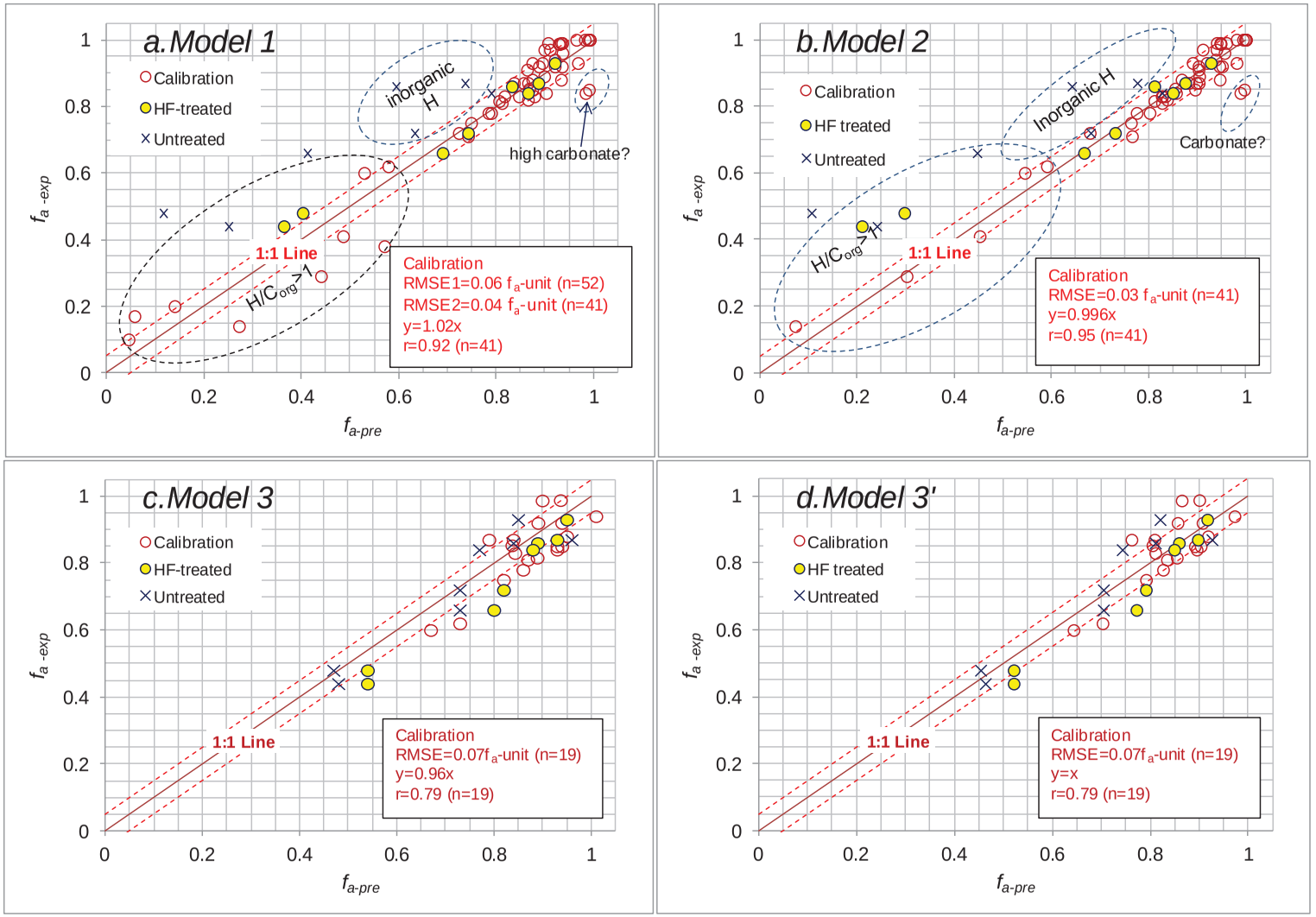

Figure 3-3. Comparison between f_a-measured ($f_{a\text{-}exp}$) and f_a-predicted ($f_{a\text{-}pre}$) obtained from different models.

3.3.2.2 Model 2

Model 2 was used by combining Equations (3-2)-(3-4) and calibrated using a dataset of 41 biochars, which included all data in Table S3-1 except those that had a H/C ratio>1 and two samples from Brewer et al. (2011) that, as mentioned above, were out of general trend (grey-shaded data in Table S3-1). With this model, the RMSE was minimised to 0.03 f_a unit (n=41, Figure 3-3b), suggesting a better prediction capacity of Model 2 compared to Model 1.The modification coefficient of Equation (3-2), α=0.110, was found to be very similar to that derived from models of coals (α ranging from 0.115 to 0.125 and increasing with coal aromaticity; Mazumdar, 1998, 1999). This indicates that biochar and coal are somewhat similar in C structures. Therefore, previous studies on coal chemistry may help to understand biochar in terms of its chemical properties. The derived ratio of C=O double bond to total CO bonds (sum of C-O single bonds and C=O double bonds) (Equation 3-4), θ= 0.290, was found to be close to the average value (θ=0.291±0.053) of biochars obtained from NMR data of Brewer et al. (2011) (calculation details can be found in Appendix I Table S3-2). It should be noted that θ actually is not constant but varies with biochars, and usually decreases as the atomic H/C ratio increases. Biochars produced at low temperature have a higher fraction of organic O as C-O single bond (accounting for ~100% of total CO bonds when θ=0), while those produced at high temperature have a larger fraction of organic O existing as C=O double bond (up to θ=1). However, θ could be fixed as a constant (0.290) when using Model 2 for predicting f_a of biochars with an atomic H/C< 0.7. It should be noted that this is the threshold value proposed by the International Biochar Initiative (2012) to define biochar. For biochars with H/C>1, θ varies to a large extent with type of biomass and thus Model 2 is considered not adequate.

3.3.2.3 Model 3

The relationship between $f_{a\text{-exp}}$ and $f_{a\text{-}pre}$ obtained by Model 3 is shown in Figure 3-3c. Model 3 showed a higher RMSE (0.07 f_a -unit) value than the other two models. As shown in Equation (3-10), Model 3 seemed to overestimate the f_a of biochars. Therefore, a correction factor of 0.964 was needed (hereafter referred to as Model 3', Figure 3-3d). Interestingly, this factor is extremely close to that for coals (Equation 3-11) obtained by Wang et al. (2010), further implying the similarity in C structure of biochars and coals.

$$f_{a-\exp} = 0.964\,FC(daf)/C_{org}(daf) \tag{3-10}$$

$$f_a = \frac{1200}{1240}\frac{(100\% - VM(daf))}{C(daf)} = 0.967\,\frac{FC(daf)}{C(daf)} \tag{3-11}$$

3.3.3 Comparison and validation of models

Among the three models (Models 1-2 and 3', Fig. 3), Model 2 showed the highest Pearson's correlation coefficient (r=0.95), followed by Model 1 (r=0.92), and Model 3' came the last (r=0.79). Moreover, Model 3' gave the highest RMSE (0.07, n=19), followed by Model 1 (0.04, n=41) and Model 2 (0.03, n=41). Therefore, Model 2 exhibited the best fit to the calibration data. This thus suggests that a correction with considering heteroatoms is necessary to establish an accurate model to estimate f_a of biochars from their atomic H/C ratios.

The models were validated with data of our biochars (Table 3-1). Results indicated that Models 1 and 2 could accurately estimate the f_a of the HF treated samples, except for BSe-250 and MAe-250 biochars (Table 3-1), with a RMSE of 0.02 (n=6, after excluding BSe-250 and MAe-250 as both samples had H/C>1 which caused large deviation, Table 3-1). Model 3' could predict f_a of all samples, but having the largest

RMSE (0.06, n=6), as expected. Therefore, Models 1 and 2 are proposed to predict the f_a of biochars, whereas Model 3' is suggested to be used as an alternative if no elemental composition data are available.

3.3.4 Notes for future users of Models 1 and 2 and suggestions to future research

Two ash-rich biochars (Brewer 5 and 11) had a much higher $f_{a\text{-}pre}$ than $f_{a\text{-}exp}$ when using either Models 1 or 2 (Figures 3-3a and 3-3b). The possible reasons for this disparity are the following: (i) the fact that those samples were produced in the presence of oxygen (Brewer et al., 2011) thus leading to more highly oxidised C compounds (Brewer et al., 2011) than those produced by pyrolysis (absence in oxygen); (ii) the presence of non-negligible amount of inorganic C that could significantly over estimate $f_{a\text{-}pre}$; and (iii) experimental errors associated with analytical measurements. However, the interference of carbonate C was believed to be largest source of this deviation for these ash-rich biochars.

In the case of untreated BSe biochars produced from alum-treated biosolids, the presence of inorganic H seemed to be the major cause for the underestimation of f_a by the Models 1 and 2 (Table 3-1); whilst these models worked well for the corresponding HF-treated samples and the MAe biochars which contain less inorganic H (if any).

Compared with Model 3 (derived from Brewer et al., 2011), Models 1-2 and 3' in this study represent a significant improvement in the prediction of aromaticity of C biochars. However, it should be noted that the prediction accuracy of models also depend on the quality and quantity of the data used for modelling. Additionally, as shown in this study, samples containing high carbonate and inorganic H will need a pre-treatment to remove carbonate and inorganic H if their elemental data are to be used in the models.

Given that all these models were originally derived from coal chemistry and values of some parameters in the models (e.g. α in Equation 3-3 and 0.96 in Equation 3-10) of coals were surprisingly applicable to biochars, future research is needed to clarify to what extent biochars and coals are similar in chemical structure. Model 2 considered the contribution of heteroatoms to the C structure and showed better prediction accuracy than Model 1, which just used H/C ratio for modelling. This suggests that a correction with considering heteroatoms is necessary to establish or improve models for estimating f_a from elemental composition. The average molar volume of C-atom (Equation 3-4), Mc/d, is likely to be an important parameter to estimate the condensation degree and stability of biochars and thus also deserves special attention.

3.4 Conclusion

Three models were examined to predict C aromaticity (f_a) of biochars using data from literature and that generated from this study. All models were found able to successfully fit the literature data when their atomic H/C ratio was below 1, and valid to estimate f_a of HF treated BSe and MAe biochars (H/C<1). Model 1, based on the H/C ratio of biochar, demonstrated a good fit to literature data (RMSE=0.04, n=41) and an accurate estimation to our experimental data (RMSE=0.02, n=6). Model 2, which was based on biochar elemental composition (C, H, N and O) data, showed the most accurate prediction, with a RMSE of 0.03 f_a -unit (n=41) for literature data and 0.02 f_a -unit (n=6, H/C<1) for HF treated BSe and MAe biochars. Model 3', which was based on contents of FC and C, and modified with a correction factor of 0.96, displayed the highest RMSE (0.06 f_a -unit, n=19) among the three models. Models 1 and 2 did not work properly for samples having an H/C ratio>1 and for those containing high concentrations of carbonate and inorganic H. The accuracy of model depends on the accuracy and precision of the data used for modelling. Future research on a wider range

of biochars is required before these models can be recommended for classification of biochar stability.

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CHAPTER 4. DETERMINATION OF CARBONATE-C IN BIOCHARS

As discussed in Chapter 3, a high content of carbonate-C, which does not form part of the organic structure, can interfere with the prediction of C aromaticity in biochar. Therefore, it is essential to determine the carbonate-C content in biochar so that organic C content can be accurately obtained for a reliable prediction of aromaticity and stability of biochar C. Different methods for determination of carbonate-C in biochar are examined in this chapter.

A paper from this study has been submitted for publication:

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Abstract

Carbonate-C is an integral part of biochar C. It contributes to the liming properties of this material yet interferes with the estimation of its stable C fraction. In this study various methods, including two direct methods —titration and thermogravimetric analysis (TGA); and two indirect methods — acid treatment with separation by filtration and acid fumigation, were compared to quantify the carbonate-C in biochars. Overall, the titration approach gave the most reliable results as tested by using a $CaCO_3$ standard (average recovery>96% with a relative experimental error <10% of carbonate-C). The acid treatment with a filtration step over-estimated the carbonate-C content (on average by a 4-fold increment) due to the loss of dissolved/fine particulate organic C during the filtration. The acid fumigation method was suitable for biochars containing high amount of carbonate-C (>0.3% wt) and when the isotopic signatures are to be determined. TGA methods were reliable when calcite was the main carbonate form in biochars, but were found to be inadequate for samples containing considerable amount of whewellite and other carbonate-bearing minerals that decompose < 600°C. As more than half of the samples studied (58%) contained< 0.4 % carbonate-C (and 38 % of these contained no detectable carbonate C), a low-cost screening method was developed in order to identify the biochars in need for carbonate-C analysis. For this purpose, two methods were proposed: (i) an effervescence test using a 20% ethanol-1 M HCl water solution; and (ii) a graphic method by plotting fixed C to organic C ratio (fixed C/C_{org}) vs. H/C_{org} . A decision tree, including 2 steps— a screening step and a titration step, could be used to determine the carbonate-C in biochars.

Keywords

Inorganic C; organic C; total C; method development

4.1 Introduction

Biochar is charcoal produced from pyrolysis of waste biomass. Its proposed use as a soil amendment, to enhance C storage in soils due to its relative recalcitrance to natural degradation, and it may offer benefits to soil fertility and other ecological functions, depending on its characteristics (Lehmann et al. 2006). The characteristics of biochar can vary widely as a result of differences in the types of feedstock and pyrolysis conditions (Schimmelpfennig and Glaser 2012). Numerous publications have documented the characterisation of biochars, with respect to C stability, elemental composition, nutrient- and pollutant- concentrations (Singh et al. 2010; Schimmelpfennig and Glaser 2012; Singh et al. 2012; Wang et al. 2012a). However, very limited information is available regarding the liming value and the measurement of carbonate-C in biochars.

Carbonate-C in biochars can be derived from either the mineral fraction of the original feedstock or CO_2 (e.g., evolved from organic C during pyrolysis) trapped in the alkaline charred material (Singh et al. 2010; Yuan et al. 2011). Knowledge on the amount of carbonates present in biochar is essential to understanding both the liming effect and C stability of biochars as: (i) carbonates contribute to the liming properties of biochars as one of the major alkaline components of high temperature biochars (Yuan et al. 2011); (ii) the dissolution of carbonate-C from biochars, under the influence of microbiotic crusts and acidic rain (Monger and Martinez-Rios 2001), can overestimate the mineralisation of biochar C and thus induce an under-estimation of its C stability (Calvelo Pereira et al. 2011); (iii) when present in large amounts, they can interfere with the determination of the organic ^{13}C isotope signature (Harris et al. 2001) of biochars and therefore hamper the use of ^{13}C natural abundance ($\delta^{13}C$) to monitor organic C decomposition; and iv) carbonate-C in biochars may represent a possible C sink if

applied to xeric or aridic soils (Macías and Camps Arbestain, 2010), although carbonate-C is not considered in the IPCC accounting system.

Generally, there are two groups of methods to measure carbonate C in solid samples, i.e., direct and indirect approaches (Bisutti et al. 2004). Direct methods involve the determination of the CO_2 evolution after acid or thermal treatments through (i) a titration method, in which evolved CO_2 trapped in a NaOH solution after treating the sample with acid is determined (Bundy and Bremner 1972; Yuan et al. 2011); and (ii) loss of ignition/pyrolysis methods, gauging the weight loss of the sample at specific temperature regions (e.g. calcium carbonate decomposes around 650-800°C) (Dean 1974; Heiri et al. 2001; Calvelo Pereira et al. 2011; Wang et al. 2011). Indirect methods, in contrast, determine the difference in total C before and after the removal of inorganic C by acid (Enders et al. 2012). These methods have been proven effective when working with soil samples (Harris et al. 2001). Biochar, however, is usually more hydrophobic and richer in organic C than soil samples. Moreover carbonate-C content in biochar is low compared to that present in carbonate-rich soils, which are common under xeric and aridic types of moisture regime. Therefore, it is necessary to assess the accuracy of the above methods when determining carbonate C in biochar and modify them if needed so that this property is correctly determined.

The objectives of the present study were: (i) to obtain a simple, economic and robust method for determination of carbonate-C in biochars, and (ii) to develop a screening test to determine whether a specific biochar needs to be characterised for carbonate-C, as a considerable amount of biochars have negligible amounts of carbonate-C.

4.2 Materials and methods

4.2.1 Biochars

Twenty-four biochars produced from slow pyrolysis were used in this study. Information regarding the production and selected characteristics of these biochars have been provided in previous publications (Singh et al. 2010; Keith et al. 2011; Lin et al. 2012; Singh et al. 2012; Wang et al. 2012a; Wang et al. 2012b). A brief summary of the details can be also found in Table 4-1. Briefly, samples 1 to 13 were produced in a Daisy Reactor (Pacific Pyrolysis, Australia) at a heating rate of 5–10 °C min^{-1}, with 40 min residence time in the reactor at the highest heating temperature (HHT, 400-550°C) from eucalyptus wood, eucalyptus leaves, papermill sludge, poultry litter and cow manure (Keith et al. 2011; Singh et al. 2012). Samples 14 to 16 (biochar mineral complex: BMC) were *Terra Preta* (black earth)-like particles composed of biochar made from woody waste (400°C) mixed with manure and other sludges, clay and minerals such as calcium carbonate, rock phosphate, dolomite, crushed granite, and biomass ash. The mixtures were heated at 220 °C for 2 h to form a stable organo-mineral biochar micro-aggregate (Singh and Joseph 2011). Samples 17 to 24 were made in a gas-fired rotating drum kiln under four temperature regimes (HHT at 250, 350, 450 and 550°C) with a heating rate of 15-20 °C/min without holding at HHT, using two feedstocks: (i) a mixture of alum-treated biosolids (from anaerobic digestion of sewage) and eucalyptus wood chips, and (ii) a mixture of cattle manure (from a dairy farm) and eucalyptus wood chips (details see Chapters 5 and 6). All biochar samples were dried at 60 °C and ground to below 100 μm before further analysis.

4.2.2 Determination of carbonate-C via a coulometric titration

The procedure used was modified after Bundy and Bremner (1972) (Appendix II SI Figure S4-1). Briefly, one g of biochar sample was weighed in a 35 ml polypropylene

(PE) Urine Specimen container. Five ml deionised (DI) water was then added into the container to wet the sample thoroughly. Thereafter, the container was placed into a Mason jar (0.5 l) fitted with an airtight lid equipped with rubber septum. An 60 ml PE container with 20 ml of 0.5 M NaOH solution was also placed into the jar. Subsequently, both bottles were attached to the jar wall with adhesive tapes. The Mason jar was then tightly sealed with a lid and 10 ml of 2 M HCl was added with a syringe through the septum into the biochar slurry. The jar was then kept for 5 d at room temperature and gently shaken by hand several times. The CO_2 evolved from the dissolved carbonate-C and trapped in the NaOH solution was determined by titrating this solution with a standardised 0.2 M HCl solution using an Auto-titrator (TIM 865 Titration Manager, Radiometer 267Analytical). A standard calibration curve was made by using $CaCO_3$ (oven-dried at 105°C for overnight before use) at different concentrations (0-100.0 mg $CaCO_3$, Figure 4-1) in place of biochar.

For samples1to 16, the residues remaining after HCl treatment were collected through a Whatman 542 filter paper and oven-dried at 60 °C following rinsed with DI water to remove the extra acid (hereinafter called "acid wash treatment"). The recorded weight of the residue was used to calculate the mass and C recovery. The C, H, N and S content in biochars and their residual samples were determined using an elemental analyser (Elementar, Vario MACRO, Germany). All the analyses were conducted in duplicates.

4.2.3 Thermogravimetric and derivative thermogravimetric (TG/DTG) analysis

TG/DTG scanning of samples was conducted using a thermogravimetric analyser (SDT Q600, TA Instruments, Melbourne, Australia) in either (i) a N_2+air atmosphere according to Calvelo Pereira et al (2011), and (ii) an air atmosphere following Harvey et al (2012). For procedure (i), a sample (~20 mg) was placed in a

small Al_2O_3 crucible and heated from room temperature to 900 °C (at 5 °C min^{-1}) under a N_2 atmosphere; then air was provided and the sample was burnt for 30-40 min until it reached a constant minimum weight. The weight loss and weight loss rate (recorded as wt.%) were recorded. Moisture, volatile matter (VM), fixed C (FC) and ash content (wt. %) were calculated according to Donahue and Rais (2009). For procedure (ii), the temperature was increased up to 800 °C (isothermal time: 10 min) at a rate of 10 °C min^{-1} under a constant dry air flow. Procedure (i) was carried out in duplicates and procedure (ii) was run once.

4.2.4 Carbonate-C removal with acid fumigation

Carbonate-C in biochars was indirectly determined after its removal using acid and estimated by difference after Walthert et al (2010). In brief, ~50 mg of biochar (samples 1 to 16) was weighed into a silver foil boat (6 x 6 x 12 mm) and the boat was placed in the well of a titre plate (both silver boat and titre plate were purchased from Elementar, Vario MACRO, Germany). Then 100 µl of 0.5 M HCl was added into the boat to wet the sample as well as avoid excessive foaming. Afterwards, the samples on the titre plate were exposed to vapour produced by 100 ml of 32% HCl solution in a closed desiccator for 3 d. After that, the sample titre plate were taken out from the desiccator and placed in a fume hood for 2 d to accelerate the release of HCl vapour. Subsequently, samples were dried at 105°C for another 2 d to remove extra HCl. Finally, samples as well as the boat were re-packed into a larger tin boat and analysed on the Elementar (Elementar, Vario MACRO, Germany).

4.2.5 A bubble test for the selection of carbonate-rich biochars

About 50 mg of biochar was weighed in a 2 ml colourless glass vial (Grace Discovery Sciences, US). Then 200 µL of 20 % ethanol-1 M HCl water solution was

added to the vial. Bubbles were formed and released at a rate dependent on the total amount of carbonate-C presented in the sample.

4.2.6 Data analysis

Temperatures at which various carbonate compounds/minerals degrade are shown in Appendix II SI Table S4-1. At temperature < 600°C, there is an almost complete overlap of the peaks at which carbonates and organic matter thermally degrade. Therefore, only the peaks that appeared above this temperature region (generally between 600-800°C) were considered for carbonate-C calculation. Peaks were deconvoluted and integrated via the best fits of Gaussian peaks using Origin 7.0 software with a Peak Fitting 7.0 module (OriginLab, Northampton, USA) (examples are shown in Figure 4-2 and SI Figure S4-2). As the peak area corresponds to the mass loss of CO_2, a correction factor of 0.27 (the molecular weight ratio of C to CO_2) was used to determine the carbonate-C content.

Carbonate-C concentration was also calculated as the difference between samples before and after acid treatments (both acid fumigation and acid wash-titration procedure). For samples treated with acid fumigation, carbonate-C can be calculated according to:

$$IC = TC - OC \tag{4-1}$$

where IC is carbonate-C content, TC is total C, and OC total C of residues obtained after treatment.

However, for samples treated with acid wash, Equation (4-2) should be used;

$$IC = TC - OC * \eta \tag{4-2}$$

where η is the weight recovery after acid wash.

According to the rules of error propagation, the standard deviation (SD) of carbonate-C can be calculated by;

$$SD_{IC} = \sqrt{(SD_{TC}{}^2 + SD_{OC}{}^2)} \quad (4\text{-}3)$$

Paired t-test (α= 0.05) was used to test differences between methods by using the means of all the samples; and one-way ANOVA and a Tukey's test (α= 0.05) by inputting data of each sample. Pearson's correlations were also used to compare the mean values from different treatments. All the statistical analyses were conducted by using either SPSS software (Version 13.0; SPSS, Chicago) or Sigmaplot software (Version 11, Systat Software Inc).

4.3 Results and discussion

4.3.1 Selected properties of biochars

Biochars used in the present study differed widely in their properties, as shown in Table 4-1. In short, pH ranged from 5.39 (BSe350) to 10.11 (EuL550A); electric conductivity (EC) from 59 μS cm^{-1} (EuW400) to 1063 μS cm^{-1} (PL400). The lowest total C content was observed in sample CM550A (15%) and the highest in sample EuW550A (82%). Sample CM550A also had the lowest H content (0.9%) whereas sample MAe250 contained the largest H concentration (5.2%). Nitrogen content varied from 0.2% (EuW400) to 5.4% (PL400). Results of proximate analysis illustrated that sample BSe550 had the lowest volatile matter (VM) fraction (14%); samples CM550A and BMC had the lowest fixed C (FC) fraction (both being 11%), and sample EuW400A had the lowest ash content (2%). The sample with the highest VM fraction was MAe250 (57%), the one with the highest FC was EuW550 (77%), and that with the highest ash content was CM550A (73%). X-ray diffractometry indicated that whewellite was the main crystalline mineral in biochars produced from eucalyptus materials at low pyrolysis temperature; yet calcite dominated in biochars produced from the same feedstock but with a high pyrolysis temperature (Singh et al. 2010). For manure

biochars (PL, CM and MAe), calcite and quartz were typical crystalline mineral forms (Singh et al. 2010; Wang et al. 2012a). For BSe biochars, no distinctive X-ray crystalline forms were identified. Calcium was one of the main cation species in almost all biochars except those produced from alum treated biosolids. Other cations, such as Al, K, Mg and Mn also existed in certain biochars depending on the type of feedstock.

4.3.2 Comparison of methods to determine carbonate-C in biochars

Values of carbonate-C were method-dependent (Table 4-2); however, no significant differences ($P > 0.05$) were detected between methods. Furthermore, significant ($r>0.92$, $P < 0.05$) correlations were found among the different methods studied (Table 4-3). Nevertheless, it should be noted that (i) the low mean values and relative high standard deviations (resulting in a high coefficient of variation) for some methods (e.g. values from acid wash treatment); and (ii) the extremely high carbonate-C value of sample 7, contributed to the lack of statistical significantly differences among methods (Table 4-3).

The titration method has been widely used in determination of carbonate-C in solid samples (Bundy and Bremner 1972; Yuan et al. 2011). A 5-d reaction time ensured a complete removal of carbonate-C in biochars. This was made evident by (i) the high recovery (90-109% with an average of 96%) of carbonate-C from the $CaCO_3$ standard (Figure 4-1); and (ii) the lack of detectable $CaCO_3$ in TG curves of samples treated with HCl solution (SI Figure S4-3). Walthert et al (2010) defines the limit of quantification (LoQ) of carbonate-C as the smallest value that can be measured with an error (difference between expected value and measured value) smaller than the expected value. The minimum weight of $CaCO_3$ used in this study was 13.22 mg (equivalent to 1.59 mg carbonate-C), its recovery rate was 90% and the experimental error 10%, indicating that the LoQ of the titration method should be even smaller (than 1.59 mg). If

1 g of biochar is used, as in the present study, at least 1.59 mg (equivalent to 0.16% of total weight) of carbonate-C could be detected. A larger sample size could ensure an even lower limit of quantification.

The acid wash treatment generally gave the highest carbonate-C values among methods (except samples 11, 15 and 16; Table 4-2). Total C recovery was calculated by adding carbonate-C content determined from the titration method to the TC content of acid-wash residue (based on the weight of original samples before acid treatment). An average TC recovery of 98.7% indicated that these procedures led to considerable loss of dissolved and fine particulate organic C (~1.3%). This is in accordance with previous findings (Harris et al. 2001). Furthermore, three additive errors (TC, OC and η, Equation (4-3) included into the calculation of IC, may partially explain the higher mean values and standard deviations. Therefore, this method was considered not suitable to be used in biochar carbonate-C determination.

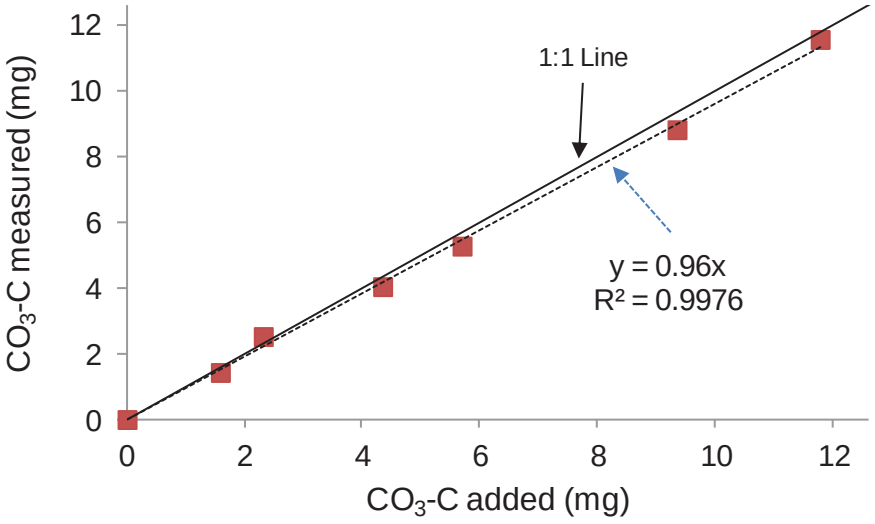

Figure 4-1. The calibration curve used for correcting concentration of carbonate-C in biochars determined by a titration method. Oven-dried $CaCO_3$ was used as a standard.

Table 4-1. Selected properties of biochars used in this study

No	biochars	pH	EC (us cm^{-1})	Total C	H	N	VM	FC	Ash	crystalline minerals [d]	main cations [d]
		1:100H_2O	1:100H_2O	%	%	%	%	%	%[a]		
1	EuW400A [b]	7.37	95	69.48±0.26 [e]	3.10±0.03	0.27±0.01	39	58	2	whewellite	Ca
2	EuW550A	9.13	86	82.27±0.02	2.53±0.08	0.41±0.00	20	74	5	calcite	Ca
3	EuW400	6.61	59	69.04±0.15	3.34±0.03	0.23±0.01	39	58	3	whewellite	Ca
4	EuW550	8.87	84	81.83±0.10	2.56±0.08	0.42±0.02	17	77	6	calcite	Ca
5	EuL400A	8.26	445	66.07±0.01	3.64±0.06	1.79±0.00	34	59	7	whewellite	Ca
6	EuL550A	10.11	477	71.01±0.13	2.88±0.10	1.86±0.02	27	63	9	calcite, sylvite	Ca
7	PS550A	8.95	182	30.45±0.07	1.36±0.02	0.30±0.02	36	18	47	calcite, kaolinite	Ca, Al
8	PL400	8.20	1063	41.32±0.16	3.11±0.01	5.37±0.01	32	35	33	sylvite, quartz, calcite	Ca, K
9	PL550A	9.87	1024	40.76±0.05	1.84±0.03	3.92±0.01	18	39	43	sylvite, quartz, calcite	Ca, K
10	CM400	8.62	1044	17.46±0.01	1.55±0.01	1.40±0.01	20	14	67	sylvite, quartz, calcite, kaolinite, albite	Al, K, Ca, Mg
11	CM550A	9.03	793	15.27±0.12	0.90±0.02	1.11±0.03	16	11	73	sylvite, quartz, calcite, kaolinite, albite	Al, K, Ca, Mg
12	Eu450	8.04	274	68.87±0.11	3.46±0.02	0.67±0.03	36	61	3	n.d. [f]	n.d.-
13	Eu550	9.79	258	74.73±0.00	2.98±0.07	0.69±0.01	24	69	7	n.d.	n.d.
14	BMC	6.14	690	25.49±0.26	2.52±0.00	1.15±0.02	35	15	50	n.d.	Ca, K, Al, Mn
15	BMC	6.80	433	20.55±0.33	2.24±0.02	1.07±0.04	31	11	58	n.d.	Ca, K, Al, Mn
16	BMC	6.24	747	26.97±0.16	2.26±0.07	1.24±0.03	34	17	49	n.d.	Ca, K, Al, Mn
17	BSe250 [c]	5.56	390	39.35	4.50	1.80	50	17	30	quartz	Al
18	BSe350	5.39	304	38.49	3.59	1.94	30	24	42	quartz	Al
19	BSe450	7.00	254	37.78	2.93	1.90	21	27	48	quartz	Al
20	BSe550	7.95	178	36.87	2.36	1.71	14	30	53	quartz	Al
21	MAe250	6.60	451	48.15	5.19	1.39	57	21	21	quartz, calcite	Ca, Mg
22	MAe350	7.39	498	54.50	3.96	1.81	36	38	30	quartz, calcite	Ca, Mg
23	MAe450	10.03	408	49.82	2.82	1.60	25	38	40	quartz, calcite	Ca, Mg
24	MAe550	10.53	393	55.46	2.24	1.63	17	43	40	quartz, calcite	Ca, Mg

a. Total C, H, N, volatile matter (VM), fixed C (FC) and ash contents are given on a dry weight basis.
b. Biochar abbreviations: Eu stands for Eucalyptus; W for wood; L for leaves; PS for paper sludge; PL for poultry litter; CM for cattle manure; BMC for biochar-mineral complex; BSe for biosolids-Eucalyptus wood mixture; MAe for cattle manure-Eucalyptus mixture; numbers indicate of pyrolysis temperature and A of activation treatment by steam.
c. Data of samples No 17-24 were adapted from Chapters 5-6.

d. Data on crystalline minerals and main cations of samples No 1-16 were from Singh et al.(2010), Keith et al. (2011) and Lin et al.(2012).
e. Mean ± standard deviation (n=2)
f. n.d., No data available

Table 4-2. Carbonate-C determined by different methods

		Titration	TGA-N_2	TGA-air	acid wash	acid fumigation
No	biochars	%	%	%	%	%
1	EuW400A	0.14±0.03 [a]	0.28±0.02	0.35	0.94±0.75	0.40±0.37
2	EuW550A	0.21±0.01	0.34±0.09	0.38	0.73±0.19	0.14±0.03
3	EuW400	0.07±0.09	0.28±0.04	0.31	1.72±1.03	0.32±0.21
4	EuW550	0.23±0.04	0.36±0.08	0.35	1.02±0.18	0.06±0.14
5	EuL400A	0.20±0.02	0.35±0.03	0.40	1.35±0.20	0.25±0.10
6	EuL550A	0.55±0.04	0.45±0.01	0.57	1.26±0.39	0.52±0.18
7	PS550A	5.54±0.19	5.16±0.02	5.18	6.27±0.49	5.46±0.15
8	PL400	0.31±0.05	0.12±0.05	0.31	1.04±0.17	0.52±0.23
9	PL550A	0.59±0.01	0.34±0.02	0.33	1.09±0.06	0.72±0.07
10	CM400	0.42±0.01	0.00±0.00	0.00	0.66±0.20	0.34±0.20
11	CM550A	0.33±0.04	0.00±0.00	0.00	-0.22±1.75	0.18±0.17
12	Eu450	0.06±0.07	0.33±0.00	0.26	0.98±0.13	0.66±0.41
13	Eu550	0.31±0.02	0.33±0.02	0.31	1.35±0.55	0.50±0.09
14	BMC1	0.73±0.09	0.43	0.65	1.86±1.88	1.10±0.37
15	BMC4	0.55±0.01	0.31	0.28	1.05±0.69	1.00±0.47
16	BMC5	0.67±0.00	0.51	0.56	0.55±1.94	0.91±0.22
17	BSe250	0.00±0.00	0.00	0.00	n.d. [b]	n.d.
18	BSe350	0.00±0.00	0.00	0.00	n.d.	n.d.
19	BSe450	0.00±0.00	0.00	0.00	n.d.	n.d.
20	BSe550	0.00±0.00	0.00	0.00	n.d.	n.d.
21	MAe250	0.05±0.01	0.10	0.13	n.d.	n.d.
22	MAe350	0.09±0.02	0.14	0.18	n.d.	n.d.
23	MAe450	0.24±0.01	0.25	0.23	n.d.	n.d.
24	MAe550	0.33±0.01	0.20	0.21	n.d.	n.d.

a. Mean ± standard deviation (n=2).
b. Not determined.

Table 4-3. Correlation matrix of carbonate-C in biochars determined by various methods.

with N° 7					
	acid wash	acid fumigation	titration	TGA-N_2	TGA-air
acid wash	1.00*				
acid fumigation	0.93*	1.00*			
titration	0.93*	0.98*	1.00*		
TGA-N_2	0.95*	0.96*	0.98*	1.00*	
TGA-air	0.94*	0.96*	0.99*	0.99*	1.00*
without N° 7					
	acid wash	acid fumigation	titration	TGA-N_2	TGA-air
acid wash	1.00*				
acid fumigation	0.28	1.00*			
titration	0.03	0.75*	1.00*		
TGA-N_2	0.45*	0.21	0.55*	1.00*	
TGA-air	0.27	0.28	0.68*	0.62*	1.00*

*Significant at α=0.05

The acid fumigation method represented a noticeable improvement in the determination of carbonate-C content in biochars (Table 4-2) compared with the acid wash approach, as it gave values closer to those obtained with the titrations. In soils containing more than 0.7% of carbonate-C, acid fumigation was proved to be an effective pre-treatment to obtain a reliable carbonate value (Walthert et al. 2010). However, as shown in Table 4-2, >90% of the biochars under study had a carbonate-C content lower than 0.7% (based on results from the titration method), which decreased the effectiveness of this method. The short-term precision (Walthert et al. 2010) of total C determined by the elemental analyser — calculated as the average standard deviations of duplicates from a dataset containing more than 50 biochar samples (data not shown) — was 0.2% (dry weight of sample). In other words, the lower limit of quantification of acid fumigation (generally $\sqrt{2}$ times than the short-term precision, Walthert et al. 2010) should be higher than 0.3% and is higher than the carbonate-C content of some of the samples under study here. In addition, this method for carbonate-C determination entails some risk for the equipment as halogenated compounds (chloride from HCl acid) are corrosive and harmful to the detectors (Fernandes and Krull 2008) of the elemental

analyser. Nevertheless, if the objective is the determination of the $\delta^{13}C$ the samples, the acid fumigation methodology should not be disregarded.

Data from the two TG methods (e.g., in the absence and in the presence of O_2) generally showed a good agreement (Table 4-2). Previous studies on the determination of carbonate-C in soils via a loss-on-ignition method estimated the carbonate-C content as either the weight loss from 375°C to 800 °C (Wang et al. 2012c) or that from 500 °C to 800 °C (Wang et al. 2011). However, this approach is considered incorrect if used in biochars because the weight loss during these temperature regimes is not only caused by the decomposition of carbonate, but also by the evolution of some elements, such as P and K, that volatilise ~ 700 °C (Chapter 6). Moreover, it should be noted that organic C in biochars is more resistant to oxidation than that in soils (as these contain a smaller fraction of charred material than biochar) and not all the C oxidised at temperatures < 600°C in this study (Figure S4-4). Consequently, the use of a deconvolution procedure at a specific temperature range (according to the visible peaks of the DTG curve) for the calculation of carbonate-C in biochars is proposed here. Nonetheless, as many carbonate-bearing compounds decomposed at a temperature < 600°C (Bush 1970) (also SI Table 4-1), it was not possible to include these compounds into these calculations as the decomposition of organic matter shielded the carbonate-related information; this explained the lower values of samples 14 to 16 when using the TGA than those obtained from the titration method. Carbonate in soils (Nelson 1982) and in most biochars (Table 4-1) occurs predominantly as calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$); however, whewellite (hydrated calcium oxalate, $CaC_2O_4 \cdot H_2O$) was also detected in Eu biochars (Table 4-1) produced at low pyrolysis temperatures. A reaction could therefore occur at ~ 500°C (Figure 4-2) as (associated water of crystallization releases below 200°C and thus is not shown in the reaction):

$$CaC_2O_4 \rightarrow CaCO_3 + CO\uparrow \quad (4\text{-}4)$$

$CaCO_3$ was thus formed during the TG analysis and decomposed thereafter at ~600-800°C. The HCl solution could dissolve CaC_2O_4 yet was not able to transform $C_2O_4^{2-}$ into CO_2, and therefore not trapped by the NaOH solution for carbonate-C determination. Therefore, the TGA method may have over-estimate carbonate-C content (Samples 1, 3, 5 and 12), whereas this does not occur when using the titration method. In biochars from eucalyptus materials produced at 550°C (Samples 2, 4, 6 and 13), no distinctive peaks of whewellite were found in their XRD spectra (Singh et al. 2010), which was further confirmed by our TGA data (Figure 4-2), and calcite was the main inorganic C form and thus TGA could estimate carbonate-C content correctly.

4.3.3 Simple tests for screening samples for accurate carbonate-C analysis

The distribution of carbonate-C contents of biochars from the literature (Calvelo Pereira et al. 2011; Yuan et al. 2011; Enders et al. 2012; Yuan and Xu 2012) and from the present study is shown in Figure 4-3. 42% of total samples contained carbonate-C less than 0.1%; 58% of samples less than 0.37%; 85% of samples less than 1%. Therefore, it is necessary to develop a screening methodology so that biochar samples with negligible amounts of carbonate-C are not analysed for such purpose thus making the characterisation of biochar more efficient and less costly. Here two methods are proposed for such purpose.

The first method derives from the field test used to identify carbonate-C in soils and rocks, which is based on the effervescence that occurs when adding acid to carbonate-bearing materials. However, because of the hydrophobic nature of most biochars, it is difficult to wet the sample with diluted HCl in a short time. Hence a 20% ethanol-1 M HCl water solution was tested. Higher liquid surface levels were found in samples 6, 7, 10, 14 and 7x+, indicating more CO_2 bubbles generated (as the same

amount of reaction solution was added into vials with same amount of biochar samples, Figure 4-4). The results obtained are thus consistent with data reported in Table 4-2.

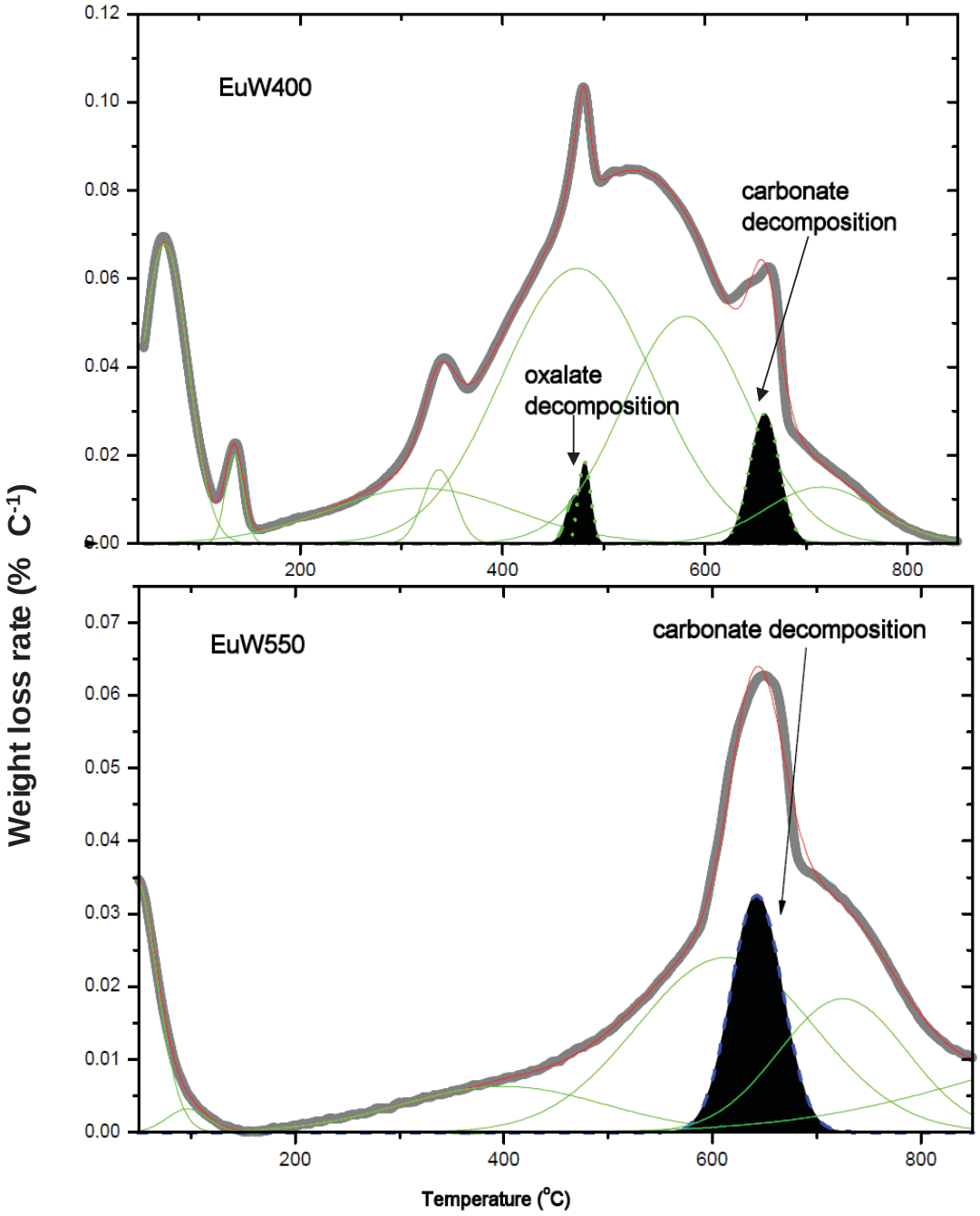

Figure 4-2. Examples of deconvolution of the derivative thermogravimetric (DTG) curves of biochars. The dark-filled peak of Sample EuW400 around 500°C represents the decomposition of whewellite (hydrated calcium oxalate).

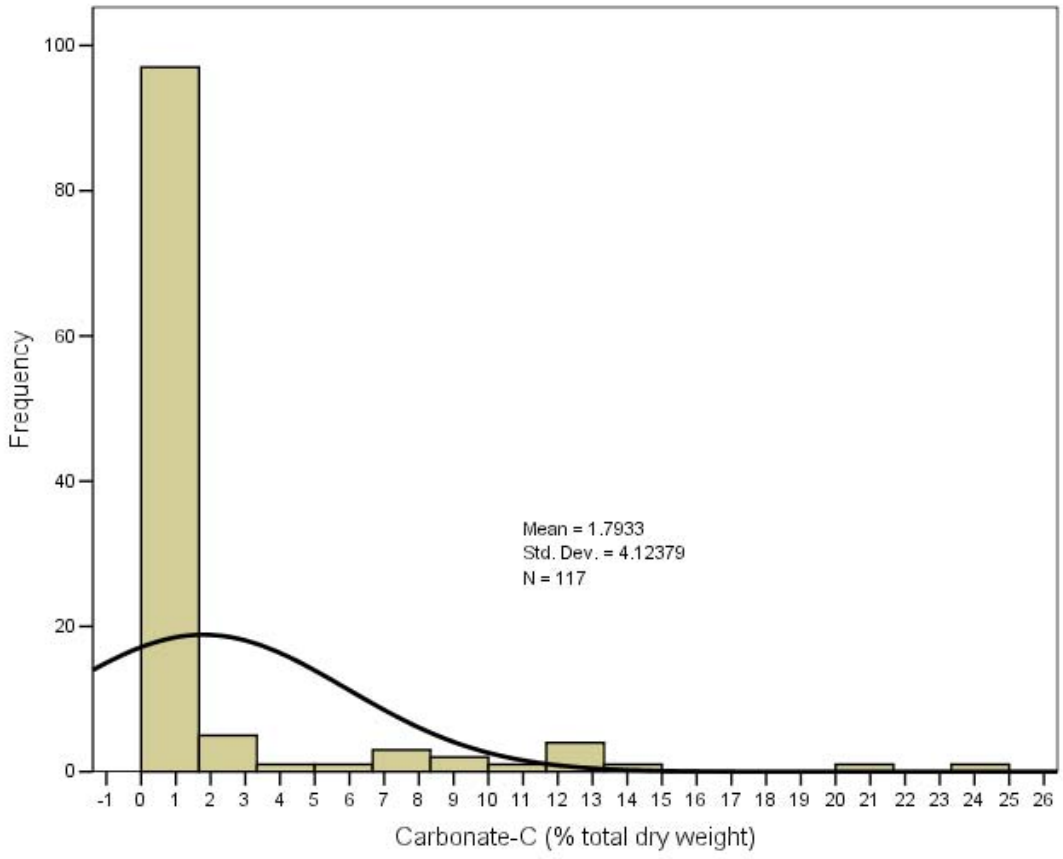

Figure 4-3. An overview of carbonate-C contents in biochars from literature and this study. The curve is the Normal curve representing the Normal distribution the data.

Figure 4-4. Effervescence tests for carbonate-C in biochars. Numbers are the samples numbers in Table 4-1. Sample "N^o 7x" is sample N^o 7 after acid treatment; "N^o 7x+" is "N^o 7x" plus 5mg of dry $CaCO_3$.

A second approach was as follows: fixed C to total C ratio (fixed C/total C) was plotted against H to total C ratio (H/total C) as shown in Figure 4-5. All the data were

fitted with a quadratic equation ($y=0.82+0.26x-0.35x^2$) with $r^2=0.51$ ($P<0.01$). Samples Nos 7, 11 and 14-16 were clearly separated by the fit curve. In fact, it was found that the % carbonate-C/total C of these samples was always greater than 2%. Therefore, we proposed the use of this graphic method to screen carbonate-rich biochars from the low-carbonate ones. However, the method will not work in the presence of inorganic H, as it was the case for sample 10, containing larger amount of Al minerals (kaolinite and amorphous Al hydroxides) and thus inorganic H from hydroxyl groups.

4.4 Conclusion

The results obtained in this study indicate that, among the methods compared for the determination of carbonate-C in biochars, the titration method was found to be the most adequate, whereas the acid wash approach was generally the least satisfactory. The acid fumigation method was suitable for biochars containing high amount of carbonate-C (>0.3% wt) and when the isotopic signature needs to be determined. The TGA procedures were good when $CaCO_3$ was the main carbonate form in biochars and carbonate-C could be a bonus when proximate analysis (measurements of volatiles, fixed C and ash content) was conducted. Considering that more than 58% of biochar samples containing carbonate-C less than 0.37%, it is convenient to screen for carbonate-C rich samples prior to its determination. Two methods, an effervescence test by adding a 20% ethanol-1 M HCl water solution to the samples and a graphic method by plotting fixed C/C_{org} vs. H/C_{org} are proposed for this purpose.

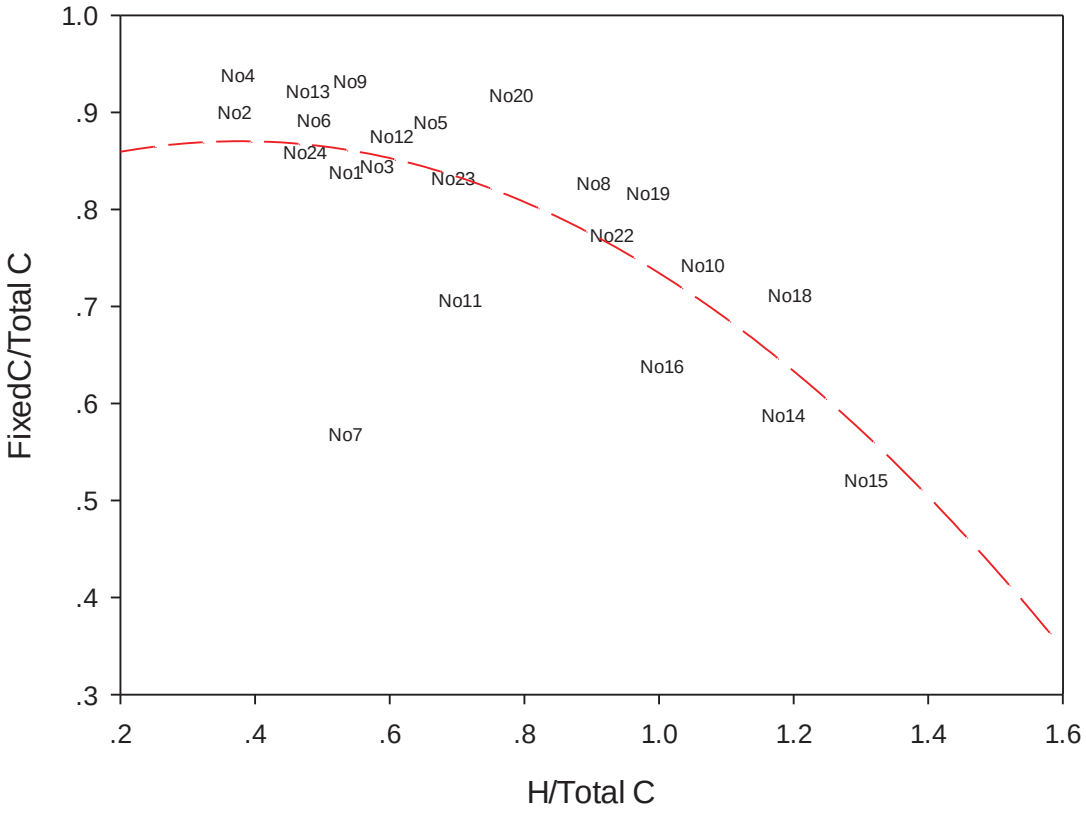

Figure 4-5. Relationship between atomic H/total C ratio and fixed C/total C ratio.

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CHAPTER 5. CHEMICAL AND BIOASSAY CHARACTERISATION OF NITROGEN AVAILABILITY IN BIOCHARS PRODUCED FROM DAIRY MANURE AND BIOSOLIDS

Biochar has been proposed to be used as a soil amendment not only because of its potential function in increasing C sequestration but also in benefiting soil fertility and other properties. Methodologies relevant to the characterisation of biochar C. either organic C or carbonate C, have been discussed in Chapters 3 and 4. In order to understand the potential agronomic benefits of biochar, its fertility value also needs to be characterised. As a nutrient element in largest demand by plants from soil, N in biochar, in terms of its forms and availability, is studied in this chapter.

A paper from this study has been published as:

Wang T, Camps Arbestain M, Hedley M and Bishop P 2012 Chemical and bioassay characterisation of nitrogen availability in biochar produced from dairy manure and biosolids. Organic Geochemistry 51, 45-54.

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_2. Nitrogen (N) forms in biochar can be complex and their lability likely to be influenced by pyrolysis temperature, which together with the nature of carbon (C), will influence N mineralisation or immobilisation. These complex relationships are poorly understood, yet impact strongly on the potential agronomic value of biochar. In this study, N in different biochar samples produced from human and animal waste streams (biosolids and cow manure; each mixed with eucalyptus wood chips in a 1:1 dry wt. ratio) at different pyrolysis conditions (highest heating temperature 250, 350, 450 and 550 °C) was extracted with 6 M HCl. The acid hydrolysable, extractable N (THN) was fractionated into ammonia N (AN), amino acid N (AAN), amino sugar N (ASN), and uncharacterisable hydrolysable N (UHN). Biochars were also treated with 0.167 M $K_2Cr_2O_7$ acid solution to determine potentially available N in the long term. An incubation study of the different biochar samples mixed with acid washed sand was conducted at 32 °C for 81 d to study both C and N turnover. During incubation, the CO_2 released was trapped in NaOH and quantified. Hydrolysable N decreased as pyrolysis temperature increased from 250 to 550 °C. Fractionation into AN, AAN, ASN and UHN revealed the progressive structural rearrangement of N with pyrolysis temperature. Based on HCl hydrolysis and dichromate oxidation results, C and N in biochar became more stable as pyrolysis temperature increased. The ratio of volatile C to THN was a useful indicator of whether net N mineralisation or immobilisation of N in biochar occurred. THN thus seems a sound estimate of the labile N fraction in biochars in the short term; however, dichromate-oxidisable N is probably more meaningful in a long run. Further studies

using different types of biochars need to be conducted under more realistic conditions to obtain more information of N availability in biochar once in soil.

Keywords

Manure biochar; biosolids biochar; N forms and availability; 6 M HCl acid hydrolysis; Dichromate oxidation

5.1 Introduction

The application of biochar to soil has been proposed as a novel approach to mitigate CO_2 emissions and improve soil properties (Lehmann et al., 2006). However, due to the large variability of biochar properties – which depend on the types of feedstock and pyrolysis conditions (Chan and Xu, 2009; De Luca et al., 2009) – there are still uncertainties about the effects of the application of biochar to soil ecosystems (McHenry, 2009), including its effect on the cycling of N (Clough and Condron, 2010).

N is the nutrient element in largest demand by plants from soil (Schulten et al., 1997). Biochar has the potential to manipulate the cycling of N in soil by (i) promoting the immobilisation of N that occurs along with the decomposition of the labile fraction of C in biochar (Bruun et al., 2011a), (ii) influencing the decomposition of native organic matter (OM) – with either a positive or negative priming effect (Wardle et al., 2008; Zimmerman et al., 2010) –, (iii) enhancing biological N_2 fixation (Rondon et al., 2007), (iv) promoting adsorption of NH_3 and NH_4^+ on biochar surfaces (Clough and Condron, 2010), (v) increasing soil pH due to its liming effect (Van Zwieten *et al.*, 2010; Calvelo Pereira *et al.*, 2011) and therefore (vi) affecting either directly or indirectly N ammonification, nitrification and denitrification reactions, N leaching, NH_3 volatilisation (De Luca et al., 2009; Clough and Condron, 2010; Bruun et al., 2011a,b; Taghizadeh-Toosi et al., 2011), and N_2O emissions (Singh et al., 2010). However, the mechanisms behind these interactions are still far from being understood.

The various C structures in charcoal are formed via heat-induced dehydration, decarboxylation, demethylation and cyclisation (Baldock and Smernik, 2002; Almendros et al., 2003). As a direct result of charring, aromatic and heterocyclic N-ring structures are formed (Almendros et al., 1990, 2003); these compounds are relatively recalcitrant to decomposition and limit the conversion of N to forms available for plant uptake (Almendros et al., 2003; Chan and Xu, 2009; Yao et al., 2010). Not all peptide structures in biomass are transformed simultaneously to aromatic C and heterocyclic N (Almendros et al., 2003; Knicker et al., 2005) but tend to increase with progressive heating (Knicker et al., 2005).

Acid hydrolysis using 6 M HCl is one of the methods more frequently used to characterise organic N (Kelley and Stevenson, 1995). It involves cleaving ester linkages, so it preferentially hydrolyses carbohydrates, proteinaceous material and ester-bound biopolymers (e.g. cutin and suberin), isolating OM-enriched with alkyl and aromatic structures (Kaal and Rumpel, 2009). Based on this procedure, the N is separated into (i) acid-hydrolysable N and (ii) insoluble, non-hydrolysable N. The hydrolysable N can be further fractionated into NH_3-N, amino acid-N, amino sugar-N, and uncharacterised hydrolysable-N (Kelley and Stevenson, 1995). Kaal and Rumpel (2009) used acid hydrolysis to investigate the degree of thermal alteration of new charcoal from a site of slash-and-burn agriculture in northern Laos and found 75-94% of N in charcoal could be removed by acid hydrolysis. Indeed, the hydrolysable N is generally deemed the more bioreactive N pool (Xu et al., 1997), while the non-hydrolysable N is considered chemically-stable N bound into heterocyclic N structures (Leinweber and Schulten, 2000; Rumpel et al., 2007). However, a fraction of the proteinaceous materials in charcoals could still survive this acid attack (Knicker, 2011); Moreover, recent studies have shown that heterocyclic N in charcoal is less recalcitrant

than generally assumed, since part of the heterocyclic N in grass charcoals was found to be bioavailable to both soil microorganisms and plants (Hilscher and Knicker, 2011a, b; de la Rosa and Knicker, 2011). Heterocyclic N fraction as an integral part of charcoal structure (Knicker, 2010), whose quality and quantity are very important factors controlling the biochemical resistance of charcoals in soils (de la Rosa and Knicker, 2011). Oxidation with 0.167 M $K_2Cr_2O_7$ acid solution appears be useful to study the lability of N (Knicker, 2010) in charcoal, since it attacks labile aromatic/heterocyclic ring structures (Knicker et al., 2007; Knicker, 2010).

Manure and biosolids are important sources of nutrients (e.g. N and P), but also are important contributors of greenhouse gas (GHG) emissions (Smith *et al.*, 2008). Conversion of these organic wastes into biochar by pyrolysis has been proposed as a new way to mitigate GHG emissions (Lehmann et al., 2006). So far, however, little information is available on changes in N availability of thermally treated manure and biosolids. Both pyrolysis temperature and type of feedstock certainly influence these (Knicker, 2010). The objective of this study was to investigate the influence of different type of feedstock and pyrolysis temperatures on N forms and lability in biochar. For this (i) N in different biochar samples – produced from human and animal waste streams at different pyrolysis conditions – was extracted via 6 M HCl acid hydrolysis and treated with 0.167 M $K_2Cr_2O_7$ acid solution, and (ii) the N mineralisation potential of these biochars was investigated in a 81-day incubation study.

5.2 Material and methods

5.2.1 Feedstock and biochar preparation

The detailed description of feedstock and biochar preparation is given in Chapter 6. In brief, two feedstock samples were used: one (BSe) was a mixture of biosolids (from anaerobic digestion of sewage) and eucalyptus wood chips; the other (MAe) was

a mixture of cattle manure (from a dairy farm) and eucalyptus wood chips. Both mixtures were made up to a 1:1 dry wt. basis ratio. Biochar was produced by slow pyrolysis in a 5 l gas fired rotating drum kiln (Calvelo Pereira et al. 2011) under four final heating temperatures (250, 350, 450 and 550 °C). The heating rate was controlled around 15~20 °C min^{-1} by controlling the combustion gas flow. When the desired temperature was reached, the heating source was switched off and the system was allowed to cool down to room temperature. During cooling, the outlet of the exhaust was blocked by a plastic bag with a rubber band to prevent O_2 going into the system. Feedstock for MAe and BSe was termed MAe-F and BSe-F, respectively. Biochar samples from different final temperature were referred to as MAe-250, MAe-350, MAe-450, MAe-550, BSe-250, BSe-350, BSe-450 and BSe-550.

Total C and N concentration in biochar and feedstock were determined using a CNS Analyser (LECO FP- 2000 CNS Analyser; Leco Corp., St Joseph, MI, USA). Total H was determined using a Tru-Spec CHNS analyser (LECO Corp. St. Joseph, MI, USA). The OH associated with reactive Al was determined by titrating biochar suspensions pre-treated with 1M NaF following following Bracewell et al. (1970) after Verde et al (2005). This was carried out to determine inorganic H in BSe biochar samples, rich in Al (unpublished results). The pH was determined on a solid to water ratio of 1:100 (Chapter 6). Inorganic C was determined from CO_2 evolution after treating char with acid. CO_2 was trapped in NaOH solution according to Bundy and Bremner (1972) and organic C (C_{org}) was obtained by subtracting inorganic C from total C. These data are summarised in Table 5-1.

5.2.2 Acid hydrolysis and N determination

Acid hydrolysis was conducted using a modification of the method of Pansu and Gautheyrou (2006). Briefly, ca. 0.5 g biochar was weighed into a 50 ml Pyrex® cation

digestion tube. Acid mixture (25 ml; 6 mol l^{-1} HCl and 0.1% phenol plus drops of octyl alcohol) was added, mixed with a vortex mixer and sonicated (5–10 min) to ensure the complete wetting of the biochar. The tubes were covered with a reflux funnel and placed on an Al digestion block for 24 h at 105 °C. The hydrolysate was passed through a pre-weighed dry Whatman® 542 filter paper and diluted to 100 ml. The filter paper and non-hydrolysable residues were weighed after being washed and oven dried at 60 °C. Total C content and N content of the non-hydrolysable residue were determined using the above LECO equipment. The hydrolysate was neutralized with 5 M NaOH. Total hydrolysable-N (THN) was determined (i) from the difference between TN in biochar and residue and (ii) from oxidation of the hydrolysate with alkaline potassium peroxodisulfate and autoclave heating (Maher et al., 2002). NH_3 N (AN) was determined using a Technicon autoanalyser. NH_4^+ + amino sugar-N were determined after adding phosphate–borate buffer (pH 11.2) in a tightly sealed centrifuge tube as described by Pansu and Gautheyrou (2006). Amino sugar-N (ASN) was determined by subtracting NH_4^+-N. The α-amino acid N (AAN) was determined via colorimetry after reacting the hydrolysate with a ninhydrin/KCN mixture following to the removal of the (NH_4^+ + amino sugar)-N from the system by adding excess 5 M NaOH (Kögel-Knaber, 1995). The amount of uncharacterisable hydrolysable N (UHN) was obtained by subtracting the sum of other known N forms (NH_4^+-N+amino sugar-N + amino acid-N) from THN. Standard solutions for AN, ASN and AAN were prepared by dissolving NH_4NO_3, glucosamine HCl and alanine in water, respectively. Recovery for AN, ASN and AAN was 102.5 ± 3.0%, 115.7 ± 16.3% and 89.0 ± 8.0% respectively.

5.2.3 Thermogravimetric and derivative thermogravimetric (TG/DTG) analysis

TG/DTG scanning of biochars and the non-hydrolysable residues were conducted on a thermogravimetric analyser (SDT Q600, TA Instruments, Melbourne,

Australia) according to Calvelo Pereira et al. (2011). The samples (~20 mg) were placed in a small Al_2O_3 crucible and heated from room temperature to 900 °C (at 5 °C min^{-1}) under a N_2 atmosphere; then air was provided and the sample was burnt for 30 min (when weight changes stopped). The weight loss and weight loss rate (recorded as wt.%) were recorded. Moisture, volatile matter (VM), fixed C (FC) and ash content (wt. %) were calculated according to Donahue and Rais (2009).

5.2.4 Chemical oxidation

Chemical recalcitrance of biochars was estimated by a potassium dichromate ($K_2Cr_2O_7$) acid oxidation method following Knicker (2007; 2010). Briefly, 0.2 g biochar samples were oxidized with 30 ml of 0.167 M $K_2Cr_2O_7$/2 M H_2SO_4 solutions at 70 °C in a digestion block. Samples were every hour vortexed for 20 s and sonicated for 2 min. A previous study showed no premature saturation (Knicker, 2007) of the acid solution. For all samples, a total 6 h oxidation was performed. After oxidation, samples were cooled down to 4 °C, filtered with a pre-weighed glass fibre filter, and the filtrate collected. After rinsing the residues with DI water for several times, they were dried at 50 °C oven and then weighed. C and N concentrations in the residues were determined using an elemental analyser (Elementar, Vario MACRO, Germany). C and N solubilised by the $Cr_2O_7^{2-}$ oxidation were quantified by calculating the difference in soluble C and N between treated and untreated samples. The $Cr_2O_7^{2-}$ left after oxidation was titrated with a standardized $FeSO_4$ solution using diphenylamine as an indicator (Pansu and Gautheyrou, 2006). Then the C oxidized was estimated according to Pansu and Gautheyrou (2006) assuming an e^-/C ratio of 0.25.

5.2.5 Incubation study for C and N turnover

To minimise sample disturbance, a non-leaching procedure was used to study N transformation kinetics. Biochar (0.1 g) was mixed with 10 g analytical grade acid

washed sand (Unilab, Australia) in a 30 ml plastic vial by vigorous vortexing. For each biochar type, 18 vials were prepared (3 replicates for 6 destructive sampling). Acid washed sand without biochar was used as a control. Each vial was supplied with 1.5 ml of a N-free nutrient solution and 0.5 ml soil inoculum, taken from the supernatant obtained after mixing 50 g fresh soil (Tokomaru silt loam; Typic Fragiaqualf; Soil Survey Staff, 2006) with 500 ml water and left to stand overnight. The vials were vortexed again and pre-incubated (4 °C, 24 h; Christensen and Olesen, 1998) to avoid a CO_2 flush immediately after re-wetting dried sand and biochar mixture. The N-free nutrient solution (adjusted to pH 6.4) contained 0.0025 M K_2SO_4, 0.002 M $CaSO_4 \cdot 2H_2O$, 0.002 M $MgSO_4 \cdot 7H_2O$ and 0.0005 M $CaHPO_4 \cdot 2H_2O$ (per l, 208 mg S, 195 mg K, 100 mg Ca, and 49 mg Mg; Christensen and Olesen, 1998), micronutrient elements (per l) [$ZnCl_2$ (0.131 mg), $CoCl_2 \cdot 6H_2O$ (0.099 mg), $Na_2MoO_4 \cdot 2H_2O$ (0.078 mg), H_2BO_3 (0.076 mg), $MnCl_2 \cdot 4H_2O$ (0.074 mg), $CuSO_4 \cdot 5H_2O$ (0.049 mg), $NiCl_2 \cdot 6H_2O$ (0.048 mg) and $CuCl_2$ (0.028 mg)] according to Rentz et al. (2004), and 6 g l^{-1} of KH_2PO_4 as P source and pH buffering reagent.

A total of 198 experimental units (8 biochars+2 feedstocks+1 control; ×3 replicates; ×6 sampling times) were used. Five vials from each treatment were randomly selected and placed into a 1 l sealable preserving jar. Each jar contained a CO_2 trap (30 ml of 0.25 M NaOH in a 100 ml plastic vial). All jars were sealed and incubated at 32 °C for 81 days in dark. At days 7, 21, 35, 56, and 81 the CO_2 trap was replaced and one sample randomly removed and replaced with a similar sized vial containing ca. 7.5 ml water. The jar was vented (2–3 h) for fresh air exchange and resealed. From the 35th sampling day onwards, a vial with 5 ml 0.5 M H_2SO_4, instead of DI water was placed in the jar to trap any volatilised NH_3. On removal from the preserving jar, the biochar-sand mixture in each vial was extracted with 20 ml 2 M KCl (Mohanty et al., 2011). The

mixture was sonicated (10 min) and rested overnight to ensure adsorbed NH_4^+-N could be released into solution. Nitrate and NH_4^+ in the extract were determined with a Technicon autoanalyser. Concentration of NO_3^- and NH_4^+ in the biochar-sand mixture at time 0 was determined in the KCl extracts obtained immediately after the addition of the nutrient solution and inoculum to the samples. The CO_2 evolved during incubation was determined by titrating (TIM 865 Titration Manager, Radiometer Analytical) the NaOH trap solution against 0.2 M HCl to pH 6.8, following precipitation of $BaCO_3$ with $BaCl_2$.

5.2.6 Data analysis

Results are expressed as an average of three replicates with standard deviation, if not stated otherwise. One-Way ANOVA post hoc tests were carried out using for mean comparisons between treatments SPSS software (Version 13, SPSS Inc., Chicago). Significant differences were determined according to a Turkey HSD test at a probability level of 0.05. A Pearson's correlation coefficient was used to determine the relationship between different variables in this study.

C mineralization data were fitted by a two component model (Voroney et al., 1989; Hilscher and Knicker, 2011b):

$$y = a \times e^{(-k1 \times t1)} + b \times e^{(-k2 \times t1)} \quad (5\text{-}1)$$

Where a and b refer to fast- and slowly-decomposable C pools, and k1 and k2 are the fast and slow turnover rate constants, respectively. Sigmaplot (version 10, Scientific Graphing Software, SPSS Inc.) was employed to perform nonlinear regression analysis. Then the half-lives of the C in biochars were calculated according to the following equation:

$$t_{1/2} = \ln 2 / k \quad (5\text{-}2)$$

5.3 Results

5.3.1 Biochar characterisation

The main physical and chemical characteristics of the biochar samples have been described in detail in Chapter 6 and are presented in Table 5-1. Yield decreased but fixed C concentration and ash content increased with increasing pyrolysis temperature, as expected. Biochar samples from pyrolysis of BSe tended to show lower C concentration, pH, VM, and FC than those from MAe at the same pyrolysis temperature. In contrast, BSe biochar had higher atomic H/C_{org} ratio and ash content than MAe biochar produced at the same temperature. Inorganic C was present in much lower concentration than C_{org} (<0.11% in BSe biochar and <0.84% in MAe biochar; Chapter 6).

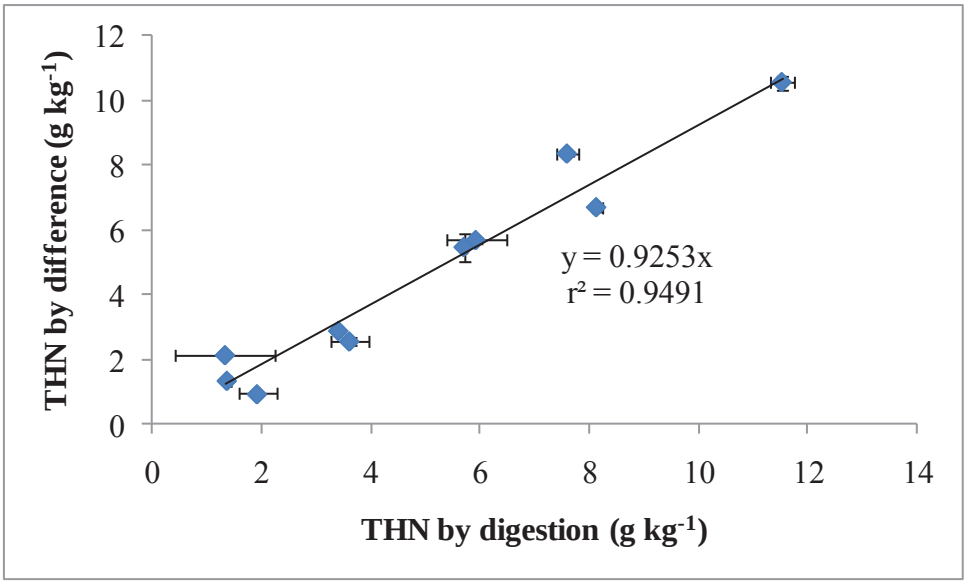

Figure 5-1. Correlation between hydrolysable N determined by difference between original biochar N content and residual N content and by alkaline potassium peroxodisulfate digestion.

5.3.2 N forms in biochar solubilised by acid hydrolysis

Through 6 M HCl acid hydrolysis, N in biochars was partitioned into THN and non-hydrolysable N (NHN). THN was further fractionated into AN, ASN, AAN and

UHN (Table 5-2). For quality control, a N mass balance was carried out. As shown in Figure 5-1, THN values estimated from the difference between total N in biochar and total N in non-hydrolysable residues determined via LECO were of similar magnitude to the THN values obtained after digesting the hydrolysates with alkaline potassium peroxodisulfate. A significant relationship (r^2 0.95) and a slope (0.925) were found between these two variables, indicating hydrolysable N can be estimated in either way. THN values obtained by digestion were slightly higher than those obtained using elemental analysis, probably due to experimental error.

As pyrolysis temperature increased, the fraction of non-hydrolysable biochar increased for both types of biochars, being greater for MAe biochars (Table 5-2). Biochar C concentration in the residue increased as the temperature of pyrolysis increased (Table 5-2). Compared with the original samples, C:N ratio of the residues increased, indicating preferential extraction of N via hydrolysis, which is consistent with results from Kaal and Rumpel (2009). Hydrolysable C and N concentrations and the hydrolysable fraction of biochar (Table 5-2) decreased with increasing pyrolysis temperature. The C:N ratio of the biochar hydrolysable fraction (7–26) was lower than the values for the whole samples (20–39) and the non-hydrolysable residues (23–82).

The absolute amount of the different forms of N in the THN extracts is reported in Figure 5-2. THN and AAN decreased with increasing pyrolysis temperature. The absolute concentration of AN and ASN decreased up to 350 °C and then levelled off (Figure 5-2). Interestingly, UHN displayed a totally different tendency, with values increasing up to 350 °C and then levelling off.

In terms of the relative contribution of each fraction to THN (Table 5-2) for both types of biochar the following trends were observed: AN decreased from feedstock (28.6% of THN for MAe and 39.7% for BSe) to biochar made at 350 °C (19.7% of

THN for MAe-350 and 22.4% for BSe-350) and then increased to ca. 60% of THN for MAe-450, BSe-450 and BSe-550. ASN in MAe samples ranged from 2.9 to 14.4% and showed a similar trend to AN, with the lowest value for MAe-450 (2.9% of THN). In contrast, ASN values of the BSe samples increased from 9.3% to 20.0% as pyrolysis temperature increased. AA decreased with pyrolysis temperature in both types of biochar. MAe-350 and BSe-350 biochar had an UHN fraction >50% of THN, whereas in the rest of the biochar samples values were much smaller (ca.21.1 – 33.1% for MAe biochar and 9.6 – 17.8% for BSe biochar).

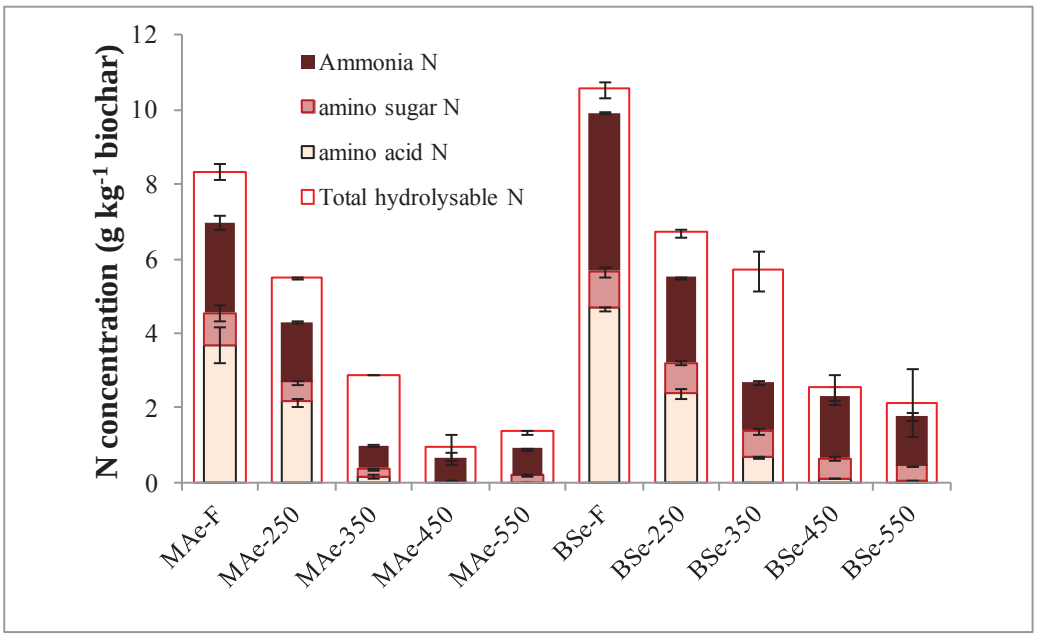

Figure 5-2. Concentrations of different hydrolysable N forms by 6 M HCl hydrolysis. AN, ammonia-N; ASN, amino sugar-N; AAN, α-Amino acid N and; UHN, unknown hydrolysable N.

Table 5-1. Selected properties of biochar samples [a]

Feedstock/ biochars	Yield %	Corg g kg^{-1}	Inorganic C g kg-1	C Recovery %	N g kg^{-1}	N Recovery %	H %	O[b] %	pH	Atomic H/C_{org}	Modified Atomic H/C_{org} [c]
MAe-F	-	425.6	-	-	10.8	-	-	-	7.56	-	-
MAe-250	82	467.4	0.5	90.6	13.5	103.0	5.0	28.0	6.60	1.4	-
MAe-350	55	527.4	0.9	68.0	17.5	88.8	3.8	15.3	7.39	0.9	0.9
MAe-450	44	481.3	2.4	50.5	15.5	63.8	2.7	10.4	10.03	0.7	0.7
MAe-550	43	547.1	3.3	54.1	15.9	63.0	2.2	5.7	10.53	0.5	-
BSe-F	-	342.7	-	-	13.8	-	-	-	7.42	-	-
BSe-250	70	382.0	-	78.4	17.5	89.1	4.4	27.6	5.56	1.5	1.3
BSe-350	54	373.5	-	58.8	18.8	73.5	3.5	18.0	5.39	1.2	1.0
BSe-450	51	367.5	0.2	54.7	18.5	68.4	2.9	12.8	7.00	1.0	0.7
BSe-550	47	357.4	1.1	48.9	16.6	56.2	2.3	9.8	7.95	0.8	0.5

[a] Some data adopted from Chapter 6; yield =mass of biochar/mass feedstock;
[b] calculated from weight difference (O%=100-ash%-moisture%-C%-N%-H%);
[c] Modified atomic H/Corg ratio was calculated as atomic (total H- inorganic H from OH associated with reactive Al displaced by F^-)/C_{org} (Inorganic C content was very low and IS not shown).

Table 5-2. C, N and organic N forms in whole samples of feedstock (F) and biochar (pyrolysed at different temperatures) and in fractions produced from 6 M HCl hydrolysis (n.d., not detected), ±standard deviation (n=3).

Feedstock /biochar	Whole	Non-hydrolysable fraction				Hydrolysable fraction						
	C:N	%[a]	C g kg^{-1}	N g kg^{-1}	C:N ratio	H-C [b] %	H-N [b] %	C:N ratio	AN [c] %	ASN [c] %	AAN [c] %	UHN [c] %
MAe-F	39	48.3±0.2[d]A	539.1	6.6	82	38.8	69.8	22	28.6±1.3B	10.4±2.5BC	44.1±5.8B	16.4±10.3A
MAe-250	35	58.1±4.3B	551.0	13.4	41	31.6	40.1	26	28.4±1.1B	9.9±0.9BC	39.4±2.2B	21.1±4.7A
MAe-350	30	83.3±1.7C	593.8	16.9	35	6.4	16.1	10	19.7±1.1A	7.3±1.0AB	5.6±1.7A	65.7±4.5B
MAe-450	31	87.2±0.9D	564.6	16.2	35	n.d.	6.8	n.d.	66.5±6.2D	2.9±4.3A	n.d.	28.3±37.3AB
MAe-550	34	87.3±0.3D	598.1	16.0	37	3.4	9.3	9	51.9±1.2C	14.4±2.4C	n.d.	33.1±8.0AB
BSe-F	25	33.6±0.7A[d]	553.3	7.0	79	45.7	82.6	14	39.7±1.1C	9.3±1.1A	44.4±1.0D	5.9±4.1A
BSe-250	22	45.4±0.7B	584.0	20.6	28	30.6	44.4	14	32.4±1.1B	12.3±0.8A	35.8±2.2C	17.8±4.6B
BSe-350	20	53.2±0.7C	582.6	24.2	24	17.1	28.5	11	22.4±1.4A	12.3±1.6A	12.1±1.2B	52.7±6.4C
BSe-450	20	56.6±2.0C	602.0	26.3	23	7.4	16.6	7	61.4±2.2D	20.7±3.2C	4.8±0.7A	9.6±15.4AB
BSe-550	22	56.3±1.0C	619.7	27.1	23	2.7	4.6	7	60.4±5.8D	19.3±8.2C	1.7±2.5A	16.4±43.3ABC

[a] non-hydrolysable residue wt. vs .original sample wt;
[b] hydrolysable C or N proportion;
[c] AN: ammonia N; ASN: amino sugar N; AAN: α amino acid N; UHN: unknown hydrolysable N vs total hydrolysable N;
[d] The same letter indicated no significant difference ($p<0.05$) between samples from same feedstock by a Turkey HSD test.

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5.3.3 DTG curve

The DTG curves of biochar samples and residues after hydrolysis were shown in Figure 5-3. The peak observed in the 200–400 °C range for the original feedstock disappeared or shifted to a higher temperature region by either an increase in pyrolysis temperature or after hydrolysis.

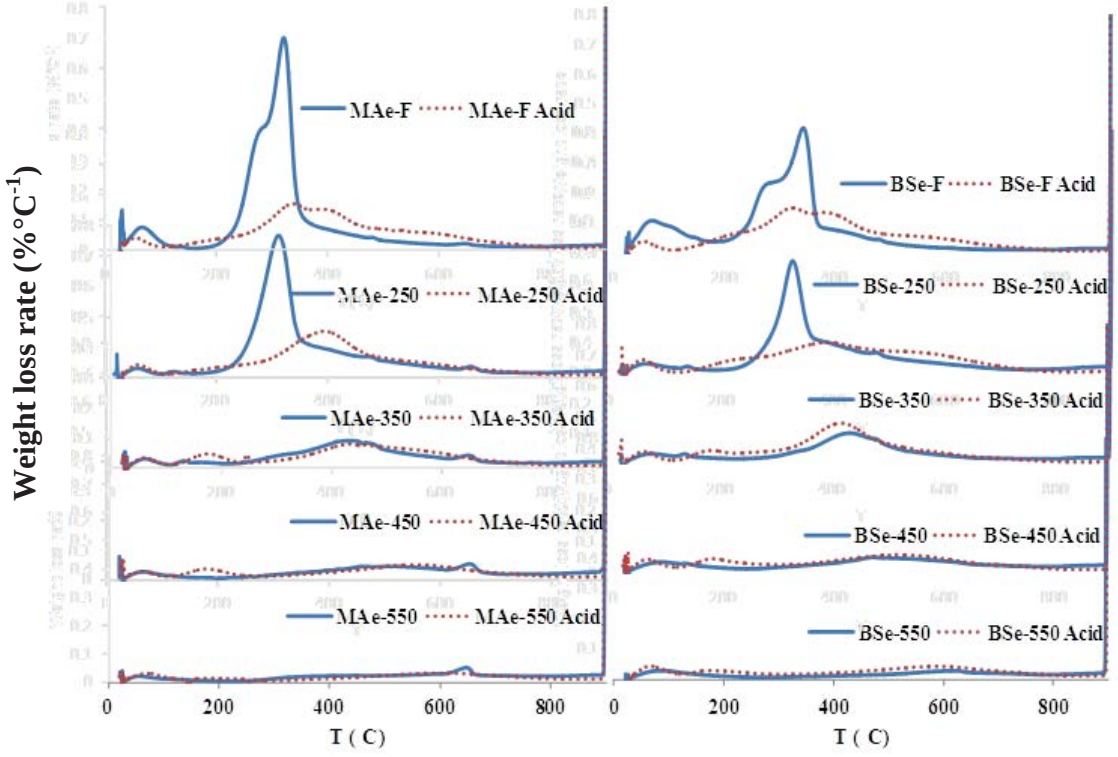

Figure 5-3. DTG curves of feedstocks and biochars and their residues after acid hydrolysis.

5.3.4 Chemical oxidation by $K_2Cr_2O_7$ acid solution

Data concerning C and N in biochars treated with 0.167 M $K_2Cr_2O_7$ acid solution are reported in Table 5-4. For biochars produced from the same feedstock, $K_2Cr_2O_7$-oxidisable C in biochars decreased in both absolute values and relative values

as pyrolysis temperature increased, whereas, elemental C and N composition in the residues followed the opposite pattern, as expected. The percentage of chemical oxidation resistant elemental (CORE) C and N were higher in MAe biochars (29~93% for C and 17~88% for N) than those of BSe biochars (14~60% for C and 6.7~46% for N) produced at the same temperature (biochars produced at 250 °C were an exception).

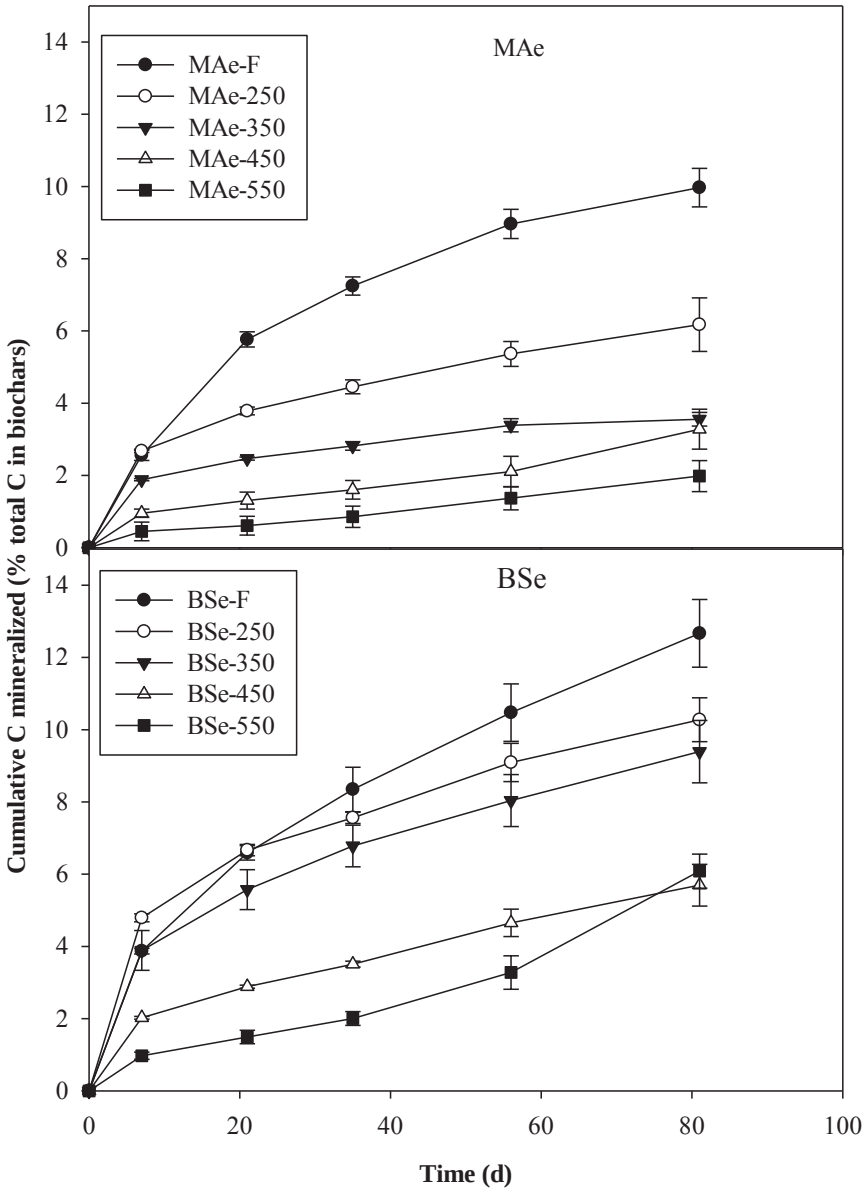

Figure 5-4. Cumulative C mineralised on the basis of per unit of initial C.

Table 5-3. TG analysis of biochars and their non-hydrolysable residues

	Moisture		Volatile matter			Fixed carbon			Ash		
	biochar (%)	residue (%)	biochar (%)	residue (%)	recovery (%)	biochar (%)	residue (%)	recovery (%)	biochar (%)	residue (%)	recovery (%)
MAe-F	6.5	3.8	62.5	42.2	32.6	16.6	35.2	102.6	14.4	18.9	63.2
MAe-250	2.8	4.1	55.6	38.4	40.1	20.9	36.8	102.4	20.7	20.7	58.2
MAe-350	3.1	3.7	34.5	31.3	75.5	36.8	44.0	99.6	28.7	21.0	61.0
MAe-450	2.9	3.4	24.7	21.3	75.4	37.0	45.4	107.1	38.4	29.9	67.8
MAe-550	2.6	3.4	16.7	15.8	82.7	42.3	50.4	104.0	38.5	30.4	68.9
BSe-F	9.4	4.1	52.9	45.1	28.7	11.8	34.7	99.0	16.5	16.1	32.8
BSe-250	2.9	4.6	48.4	41.2	38.7	16.2	38.2	107.3	29.6	16.0	24.5
BSe-350	3.0	4.5	29.5	35.8	64.5	23.6	41.5	93.4	40.9	18.1	23.5
BSe-450	2.7	4.3	20.9	25.6	69.2	26.8	50.0	105.8	47.0	20.1	24.2
BSe-550	2.8	4.9	13.8	20.7	84.1	29.6	53.3	101.6	51.1	21.1	23.2

Table 5-4. Changes in C and N in biochars after $K_2Cr_2O_7$ oxidation

Charcoals	Recovery	$K_2Cr_2O_7$ oxidisable C		Residual C		Residual N		C loss	N loss	C:N Ratio in loss
		mg kg^{-1}	% total C	mg kg^{-1}	C recovery	mg kg^{-1}	N recovery	%	%	
MAe-250	18	303.9±3.8D[a]	68.6	135.9±0.3A	5.6	3.5±0.1A	4.5	94.4	95.5	31.5
MAe-350	42	210.6±2.8C	42.4	339.1±1.0B	29.0	6.8±0.0B	17.1	71.0	82.9	25.1
MAe-450	66	131.4±3.2B	28.7	408.3±0.9C	58.9	9.6±0.1C	40.4	41.1	59.6	20.2
MAe-550	90	46.6±8.2A	9.1	526.3±4.1D	93.1	15.5±.2D	87.5	6.9	12.5	17.5
BSe-250	11	235.6±10.2D	65.6	216.7±8.8A	6.7	5.9±0.1A	3.9	93.3	96.1	21.0
BSe-350	19	182.2±3.1C	52.7	248.2±1.6B	13.9	6.3±0.0B	6.7	86.1	93.3	17.5
BSe-450	31	145.1±1.5B	42.4	413.7±0.9C	37.1	14.2±0.1C	23.9	62.9	76.1	15.6
BSe-550	42	109.6±3.7A	32.6	480.7±1.9D	59.5	18.9±0.1D	45.7	40.5	54.3	14.6

[a] The same letter indicated no significant difference ($p<0.05$) between samples from same feedstock by a Turkey HSD test.

5.3.5 C and N turnover in feedstock and biochar

Cumulative C mineralisation as per unit of total C_{org} for the different treatments is represented in Figure 5-4. Data reveal a decrease in evolved CO_2 C as pyrolysis temperature increased (Figure 5-4). Cumulative C mineralised accounted for 10.3% and 13.0% of total C_{org} in MAe feedstock and BSe feedstock respectively, decreasing to 2.2% of total C in MAe-550 and 6.3% of total C in BSe-550. As shown in Table 5-5, the two-component decay model fitted well to the C turnover data, with a p value <0.01 except for BSe-550 and MAe-550 biochars. The estimated fast decomposable C pool decreased while the slowly decomposable C pool increased as pyrolysis temperature increased. Correspondingly, the half-lives of decomposable pools increased as pyrolysis temperature increased.

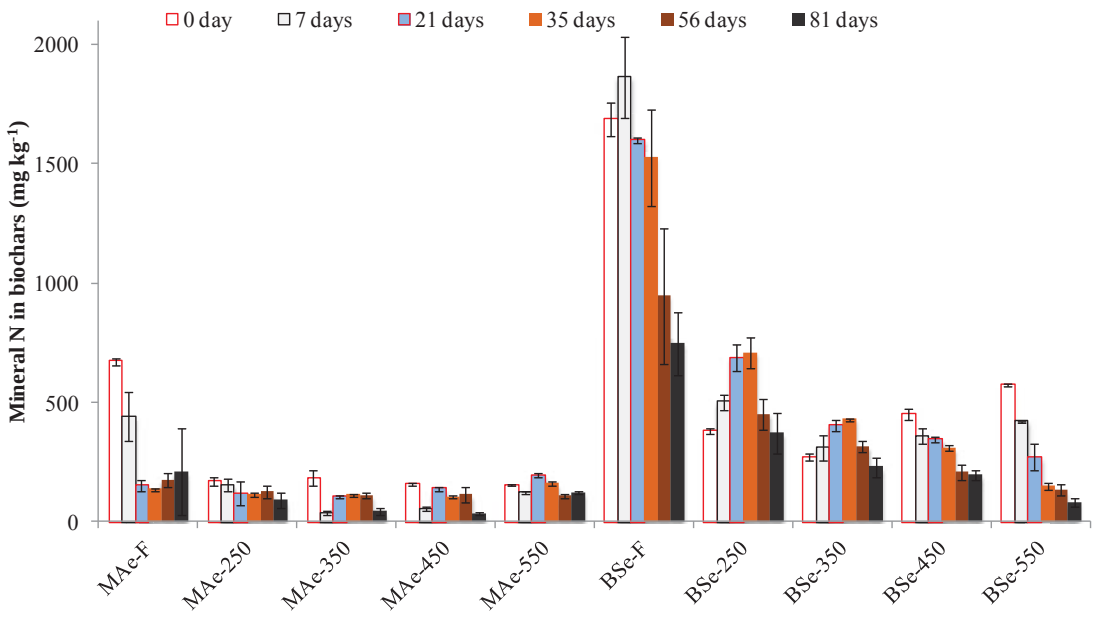

Figure 5-5. Extractable mineral N [$\Sigma(NH_4^+ + NO_3^-)$] change in a biochar-sand mixture system. All data were obtained by subtracting the values from the blank control.

Table 5-5. Estimation of C turnover dynamics of the decomposable fraction of C in biochars (the recalcitrant fraction is thus not included) fitted to a two-component decay model.

Sample	Fast decomposable pool		Slowly decomposable pool			r^2	p-value
	Percentage (%)	$t_{1/2}$ (d)	Percentage (%)	$t_{1/2}$ (d)	$t_{1/2}$ (yr)		
MAe-F	7	12	93	1733	5	1.00	0.0008
MAe-250	3	3	97	1733	5	1.00	0.0012
MAe-350	2	3	98	3466	9	0.99	0.0090
MAe-450	1	1	99	3466	9	0.98	0.0274
MAe-550	0	0	100	3466	9	0.99	0.0148
BSe-F	5	5	95	630	2	1.00	0.0006
BSe-250	5	3	95	990	3	1.00	0.0013
BSe-350	4	3	96	990	3	1.00	0.0014
BSe-450	2	2	98	1386	4	1.00	0.0010
BSe-550	1	0	99	1386	4	0.99	0.1261

N mineralisation (estimated from extraction of NH_4^+ and NO_3^- with 2 M KCl) during the incubation of the different treatments is shown in Figure 5-5. All samples, except BSe-F, BSe-250 and BSe-350, showed a progressive net N immobilisation from the beginning of the incubation. No significant amount of NO_3^- was produced during incubation (data not shown).

5.4 Discussion

5.4.1 C and N change during pyrolysis, acid hydrolysis and chemical oxidation

It is well known that as the temperature of pyrolysis increases, C and N concentration in biochars tends to increase, as these elements become incorporated into aromatic or heterocyclic rings – formed via the preferential lost of H and O from the system (Table 5-1; Almendros et al., 2003). However, these trends are less obvious when pyrolysing ash-rich feedstocks, such as manure or biosolids, as biochar also tends to become enriched in the mineral ash component at increasing pyrolysis temperatures (here up to values of 38 and 47% ash for MAe biochar and BSe biochar, respectively),

thus diluting the enrichment of C and N in the carbonised material (Table 5-1). C and N recovery in biochar produced at different pyrolysis conditions was in the range of those reported by other authors (Chan and Xu, 2009). These tended to decrease with increasing temperatures of pyrolysis, as expected, except for one odd value in the C recovery of MAe-550, which was unexpectedly higher than that of MAe-450. This could have been caused by a recapture of C containing compounds during secondary reactions. Recovery of N followed the expected trend (Table 5-1) and was always higher than that of C.

Biochars clearly contain less hydrolysable N than feedstock and this diminished as the carbonisation process became more intense (Figures 5-2 and 5-3). This was caused by progressive rearrangement of the C and N structures, which resulted from either (i) labile structures that became degraded, e.g. peaks located from 250 to 400 °C decreased or disappeared (Figure 5-3) or (ii) newly synthesised structures of high stability formed during pyrolysis (Almendros et al., 2003), which could be partially related to the shift of peaks on DTG curves to higher temperatures. The amount of N released during hydrolysis was much higher than that of C, which contrasts with the higher recovery of N in biochar than C during pyrolysis. N in feedstock exists mainly as carbohydrate, protein and other biopolymers (Kaal and Rumpel, 2009) that could be hydrolysed with 6 M HCl but had a higher resistance to thermal degradation than carbonyl and O-alkyl structures; the latter, in contrast, would be turned into acid-resistant unsaturated rings via dehydration and decarboxylation (Baldock and Smernik, 2002; Almendros et al., 2003).

Biochar produced from MAe left a higher amount of non-hydrolysable residue than the biochar from BSe, and this was mainly attributed to (i) the presence of an important mineral fraction that was less affected by hydrolysis – and thus tended to

accumulate in the residue (Table 5-3), and (ii) MAe feedstock and biochar having more stable C than BSe feedstock and biochar, which can be also evidenced from the chemical oxidation data (Table 5-4). Elemental composition of the hydrolysates was determined (data not shown): 44.3-105.0 g kg^{-1} Al and 21.-50.8 g kg^{-1} P in the hydolysates of BSe feedstock and biochar, but only 12.1-31.2 g kg^{-1} Al, Ca, Mg, Fe and P in the MAe feedstock and biochar hydrolysates.

The absolute amount of fixed C recovered in the acid-insoluble biochar residue was equivalent to that of the fixed C fraction in the non-treated biochar sampled (Table 5-3), so it was inferred that both the hydrolysable C and N derive from the VM fraction. Furthermore, except for MAe-550 and BSe-550, the hydrolysis residues of MAe feedstock and biochar samples showed a higher VM recovery than those of BSe produced at same pyrolysis temperature (Table 5-3), consistent with the C mineralisation data, where a greater C decomposition in the latter was observed (Figure 5-4 and Table 5-5), as discussed below, suggesting that labile C should relate to the VM fraction.

In the two feedstocks, AAN accounted for the main fraction of hydrolysable N, followed by AN, UHN and ASN (Table 5-2 and Figure 5-3). This result was coincident with the general relative N distribution among soil hydrolysated fractions (Pansu and Gautheyrou, 2006). AAN can be derived from either the hydrolysis of proteins or free amino acids in the feedstock. Values of AAN were below negligible levels for MAe-450 and MAe-550 biochar, consistent with the results from Douda and Basiuk (2000) and Thipkhunthod et al. (2007). The former authors reported that most amino acids are destroyed after heating above 400 °C (although the different amino acids differed in thermal stability) and the latter stated that protein decomposition occurs in the range 300-400°C (Thipkhunthod et al., 2007). AN consisted mostly of mineral NH_4^+-N and

that generated from amine and amide hydrolysis, e.g. total or partial destruction of certain amino acids, and partial destruction of hexosamines (Pansu and Gautheyrou, 2006). As shown in Figure 5-5, extractable NH_4^+-N with 2 M KCl represented 10.8%-44.1% of AN from the acid hydrolysis (Figure 5-2). Therefore, AN may originate mostly from (i) amino acids in feedstock and low temperature biochar, and (ii) amides in high temperature biochars, which is consistent with the results of Russell et al.(1974). Furthermore, amide and sugar fractions can be thermally stable in melanoidin-like structures (Almendros et al., 2003; Knicker et al., 2005), and these would be hydrolysed, explaining the considerable fraction of AN in high temperature biochars. AS-N seemed more stable with regard to other fractions since its concentration in BSe biochar tended to increase up to 350 °C. This could be attributed to its possible association with amorphous Al hydroxides (Stevenson, 1982; Buurman et al., 2002) of which large amounts were present in BSe. In contrast, in MAe biochar – with relatively low ash content vs. BS biochar – ASN concentration (Table 5-2 and Figure 5-2) decreased as pyrolysis temperature increased.

The difference between THN and the sum of AN, ASN and AAN was referred to as uncharacterisable N (UHN). Heterocyclic N compounds have been suggested to be the major components of the "unknown" soil-N (Schulten et al., 1997); this may also be true for biochar N. Heat treatment results in an enrichment in heterocyclic N forms (Almendros et al., 2003; Knicker et al., 2005), such as pyrrole type-N, pyridine type N and indole-N, with a corresponding decrease in amide N (Almendros et al., 2003), and therefore of AAN and AN (Table 5-2 and Figure 5-3). This could explain the fact that the highest absolute and relative values of UHN were found in BSe-350 biochar and MAe-350 biochar, as most amino acids and proteins decompose <400 °C. At pyrolysis temperatures above this range, low molecular heterocyclic N compounds are

transformed to high aromatic or heterocyclic forms by cross-linking reactions (Almendros et al., 2003), which are acid resistant (Leinweber and Schulten, 2000; Rumpel et al., 2007), resulting in a decrease in UHN.

Chemical oxidation with 0.167 M $K_2Cr_2O_7$ acid solution was used to estimate the black carbon (BC) content (Rumpel *et al.*, 2006; Calvelo Pereira *et al.*, 2011).Results indicated that the sum of oxidisable C and total C in the residue was not 100% of the initial C in biochar samples, indicating that part of the biochar C (~30 % of C loss, data not shown) was not fully oxidised to CO_2, but to intermediate organic molecules— e.g., benzoic/carboxylic acids— remaining in solution (Wolbach and Anders, 1989) and not quantified with the titration with Fe^{2+}. Chemical oxidation was able to extract a greater fraction of N in biochars than acid hydrolysis, especially in high temperature biochars (12-96% for MAe biochars and 54-96% for BSe biochars). Biochars from N-rich feedstock (BSe) appeared to be less stable with dichromate acid compared with those from MAe (seen from the C/N ratio, Tables 5-2 and 5-4), which is accordance with previous results from Knicker (2010). Moreover, pyrolysis temperature played an important role decreasing N lability in biochars despite the type of feedstock (Table 5-4), as expected (Brewer, 2009).

5.4.2 C turnover

The C mineralised during the incubation of the different organic materials mixed with OM-free sand decreased as pyrolysis temperature increased (Figure 5-4), except for the last sampling. The greater initial C mineralisation of BSe-250 and MAe-250 biochar compared with the original feedstocks, BSe-F and MAe-F, respectively, was a priori unexpected. However, this may be explained by the fact that the particle size of fresh feedstock was coarser than that of biochar, and thus had a smaller surface area, which has been shown to affect biochar degradation rate negatively (Zimmerman,

2010).There were odd values for MAe-450 and BSe-550 at day 81 (Figures 5-4 and S5-1), which were attributed to experimental error. That is why only 5 points were used for these biochars in the two component decay modelling (supplementary materials Figure S5-2).

Both abiotic and biotic factors (Zimmerman, 2010) contribute to biochar decomposition and the relative importance of these factors depends on the soil environment (i.e. moisture) and biochar properties (Bruun et al., 2011c). As shown in Tables 5-1 and 5-3, VM and [VM/(VM+FC)], atomic H/C_{org} and/or atomic H_{org}/C_{org} decreased as pyrolysis temperature increased, leaving a biochar richer in aromatic C (unpublished results) and thus in recalcitrant C. The atomic H_{org}/C_{org} ratio was calculated as atomic (total H – inorganic hydroxyl-H)/C_{org} ratio. The H in the inorganic fraction of biochar tends to be negligible as temperature of pyrolysis increases, as it was the case of MAe biochars (unpublished results). However, biochars made from biosolids had a considerable amount of Al (10.0% in BSe-550 biochar) bound to –OH to form Al oxyhydroxides (unpublished results). According to current IBI Guidelines for Specifications of Biochars (IBI, 2012), the upper H/C_{org} limit of 0.7 is used to distinguish biochar samples from other carbonaceous biomass. Therefore, MAe-450 and MAe-550 comply with this specific requirement of the guideline; this is also the case when the H values of BSe-450 and BSe-550 were corrected to eliminate the contribution of inorganic H from Al oxy-hydroxides.

The [VM/(VM+FC)] ratio and the atomic H_{org}/C_{org} ratio significantly correlated with the degraded C/total C ratio after 81 days incubation (r 0.826, $p<0.01$ and r 0.765, $p<0.05$, respectively, which accords with the results of Calvelo Pereira et al. (2011). THC (Table 5-2) was found to have a strong positive relationship with degraded C/total C (r 0.774, $p<0.05$), atomic H_{org}/C_{org} ratio (r 0.946, $p<0.01$) and VM/(VM+FC) (r 0.966,

p<0.01). Hydrolysable C is thus a highly reactive fraction of biochar. For biochar produced at 350-550 °C, however, the values of THC were lower than the corresponding mineralised C values (i.e. for MAe-550 with THC 5 g kg^{-1} but 12 g kg^{-1} of C mineralised), suggesting that hydrolysis by 6 M HCl only estimates a portion of the degradable organic C_{org} in biochar. Dichromate-oxidisable C also correlated with degraded C/total C_{org} ratio (r 0.77, p<0.05), but showed larger values than the amount of decomposed C, indicating the presence of a less labile C in this fraction compared with HCl-hydrolysable C.

From the two-component decay modelling, the half-lives of C in MAe and BSe biochars were calculated (Table 5-5) and were comparable with the data of Hilscher and Knicker (2011b). The very small half-lives (<9 yrs) obtained for the two components in the decay model, are contrary to the well-known finding that black C could be thousands of years old (1160–5040 carbon-14 years, from Schmidt *et al.*, 2002). This suggests that a three-compartment model is required for high temperature biochars with the third pool having a half life appropriate for black C. Considering the very slow decomposition rate of black C, the Equation (5-3) can be re-written as:

$$y = a \times e^{(-k1 \times t1)} + b \times e^{(-k2 \times t1)} + blackC\% \times e^{(-k3 \times t1)} \quad (5\text{-}3)$$

We propose that the black C is the fraction of recalcitrant C in biochars, whilst the dichromate oxidation indicated that the percentage of recalcitrant pool increased markedly with pyrolysis temperature. Further research is required to establish the half life the decomposition of this fraction.

5.4.3 N lability in biochar

N availability has a strong influence on the decomposition of labile C (Neff et al., 2002). Because of this the degree of correlation between labile C and THN fractions deserves special attention. The results indicate that THN and total evolved CO_2 C

showed a strong positive relationship (r 0.958, $p<0.01$), suggesting that (i) the THN fraction represents the available N in biochars and (ii) available N in biochars was probably limiting C decomposition.

N immobilisation in soils treated with MAe feedstock and its corresponding biochars concurs with the findings of Novak et al. (2010) in that biochar induced significant N immobilisation in the short-term incubation. BSe-F, BSe-250 and BSe-350 showed net N mineralisation until 35 days (although only minor for BSe-F) while BSe-450 and BSe-550 showed net N immobilisation to the end of the experiment. As CO_2 was trapped in NaOH, the lack of NO_3^- detected during the incubation was consistent with low CO_2 availability limiting autotrophic nitrifiers (Azam et al., 2004). During incubation, concentrations of mineral N fluctuated strongly, suggesting a very complex N turnover. The fact that a trap for NH_3 was included in the incubation vessels from day 35 onwards further complicates the interpretation of the results.

It was not possible to determine the absolute values of available N in biochar [e.g., following the classic leaching procedure of Stanford and Smith (1972)], as N immobilisation was taking place. The C/N ratio of a substrate is often used to assess the N mineralisation or immobilisation in soil. Generally, a critical C/N value < 25 is considered to indicate the probability of net N mineralisation (Chapin III et al., 2002). As a fraction of C and N in biochar is not readily available to microbes (Paré et al., 1998), the use of the C/N for charcoal considering total amount of these elements is not a suitable indicator for this purpose. The labile C to labile N ratio (C_{labile}/N_{labile}) is thus considered more appropriate. Brewer et al. (2011) found a direct correlation between aromaticity and proximate analysis of the FC fraction in 17 different charcoal samples and concluded that FC was a chemically stable fraction. Volatile matter in biochar has been proved to influence soil C and N turnover (Deenik et al., 2010, 2011; Brewer et al.,

2011; Bruun et al., 2011b); however, in addition to C, it contains S, N, H, O, and other volatile elements or compounds. For this reason, to estimate labile C, we first calculated C in volatile matter (VC) as:

$$VC=TC-FC \quad (5\text{-}4)$$

where TC is the total C in feedstock/biochar; FC is fixed C content.

THN was then used as an estimate of labile N. The ratio was then calculated as:

$$C_{labile}/N_{labile} = VC/THN \quad (5\text{-}5)$$

C_{labile}/N_{labile} from feedstock and biochar was thus calculated following Equation (5-4) and Equation (5-5) and plotted in Figure 5-6. The corresponding values for BSe-F and BSe-350 were <25; that of BSe-250 was only slightly > 25. However, for the rest of BSe biochar samples and all MAe biochar samples, values were > 25. These values agree with the patterns of N immobilisation/mineralisation observed in the incubation. Therefore, the index can be a suitable indicator of potential N immobilisation/mineralisation and further supports the idea that acid hydrolysis could be used to estimate the labile fraction of N in biochar. Further studies using different types of biochar are necessary to confirm the usefulness of the new index before its large scale use for biochar classification test purposes.

As the incubation experiment only lasted 81 d, THN could represent the labile N fraction in the short time. Based on the results from de la Rosa and Knicker (2011), Hilscher and Knicker (2011a; 2011b) and Knicker (2011), heterocyclic N could be potentially available in the longer term. However, since heterocyclic N is an integral part of the biochar structure, the availability of this N also depends on the lability of biochar C, as shown in Table 5-4. As biochars are produced primarily with the intention to increase soil C stock, a compromise needs to be reached if the production of a biochar with stable C and available N is targeted.

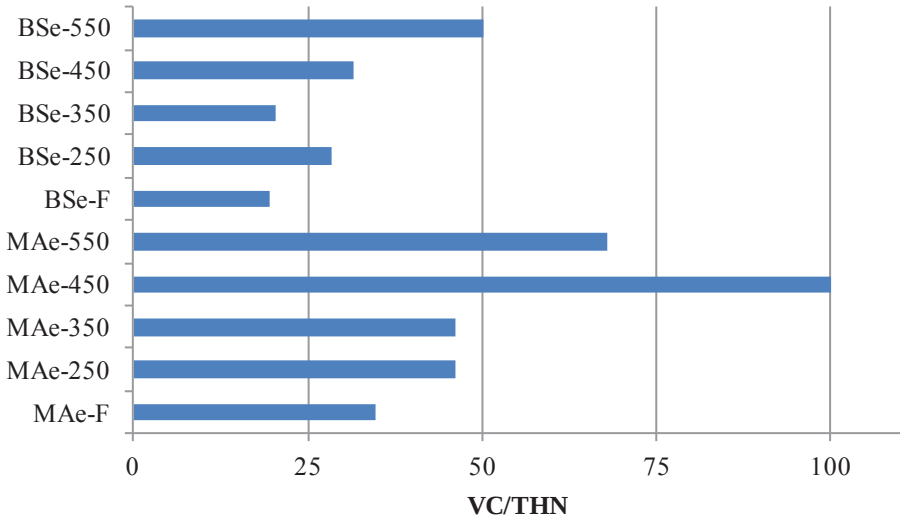

Figure 5-6. A modified C:N ratio for assessing net N mineralization or immobilization. VC, C fraction in volatile matter fraction; THN, total hydrolysable N by 6 M HCl hydrolysis.

5.5 Conclusion

The fractionation of acid hydrolysates of N in biochar into NH_3-N, amino acid-N, amino sugar-N and hydrolysable unknown-N (UHN) provides a method that reveals the progressive structural rearrangement of N as pyrolysis temperature increases. Total hydrolysable N was shown to represent the labile N pool in biochars. Dichromate oxidisable N, which may include some heterocyclic N, may represent available N pools in a long run. Pyrolysis induces (i) loss of N in the oil and gas streams and (ii) decrease in N availability as the temperature of pyrolysis increases. A modified C:N ratio, derived from volatile C:THN ratio, was shown to be an adequate predictor for assessing the net N mineralisation or immobilisation in biochars in a short-term incubation study. Further studies with more types of biochars need to be conducted to evaluate the index.

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CHAPTER 6. PREDICTING PHOSPHORUS BIOAVAILABILITY FROM HIGH-ASH BIOCHARS

In Chapter 5, N forms and availability have been investigated. Phosphorus is also an essential element for plant growth. Considering that organic wastes are important sources/sinks of P, biochar produced from these wastes can have considerable amount of P and thus can be used as a potential P fertiliser. In this chapter, bioavailability of P is examined by chemical extraction methods and bioassay test. 2% formic acid extractable P is proposed as an indicator of available P in biochar.

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Abstract

Background and Aims Biochars are highly variable in nutrient composition and availability, which are determined by types of feedstock and pyrolysis conditions. The aim of this research was to (i) study the bioavailability of phosphorus (P) in biochars using different feedstocks and pyrolysis conditions; (ii) develop a robust chemical method for biochar P availability measurements.

Methods In the present study, (i) chemical analysis – including total P and extractable P (2% citric acid, 2% formic acid, and neutral ammonium citrate extraction), and (ii) a bioassay test using rye-grass grown in a P deficient sandy soil were used to compare the P bioavailability of different biochars. Biochars were produced from two different feedstocks (dairy manure-wood mixture, MAe; biosolid-wood mixture, BSe) at four different pyrolysis temperatures (250, 350, 450, and 550 °C).

Results Results showed that P in feedstock was fully recovered in the biochars. After 6 harvests, the biochars were as effective as the P fertilisers tested [Sechura phosphate rocks (SPR) and calcium dihydrogen phosphate (CaP)] in increasing the shoot yield. However, P uptake followed the order of CaP> MAe biochars> BSe biochars >SPR, on a same TP basis. Based on the Mitscherlich equation, 2% formic acid was the most sensitive indicator of P bioavailability in biochars.

Conclusions The results suggest that high-ash biochars with high P concentrations are potential P sources with high-agronomic efficiency. We propose the use of 2% formic acid extraction to predict the availability of P in ash-rich biochars.

Keywords

Dairy manure biochar; biosolids biochar; P bioavailability; 2% formic acid extractability; P fertiliser

6.1 Introduction

It is estimated that ~ 5.7 billion ha of arable soils worldwide are low in available phosphorus (P) (Hinsinger 2001) – due to the low concentration and/or low solubility of soil P compounds (Hedley and McLaughlin 2005) – and unable to sustain optimal crop production. Approximately 15 million tonnes of P as fertilisers and an unknown quantity of P in organic wastes (manure, biosolids) are therefore applied each year to agricultural soils to increase the supply of P to plants (Hedley and McLaughlin 2005). Phosphorus is mainly derived from mined rock phosphate, which is a non-renewable resource. It has been proposed that agricultural demand for P will outstrip mineable resources in 50–100 years (termed "peak phosphorus") (Cordell et al. 2009), and economically mineable resources will be depleted before the end of this century. Approximately 50% of the mined P rock passes through the fibre and food chain (Cordell et al. 2009) to end up in biosolid and other organic wastes. The use of low cost and readily available animal wastes and high-quality biosolids as a source of P is generally encouraged as this is not only an effective way to recover nutrients and manage waste but also contributes to the improvement of soil chemical and physical properties (Kleinman et al. 2002; Azeez and Van Averbeke 2010). Total P contents in manures are ~ 0.7 – 4.7% (DW basis), and in biosolids ~ 0.1 – 14% (mainly 1–5%; DW basis) (Hedley and McLaughlin 2005). Although manure P has been reported to have a generally lower efficiency in the first application season compared with inorganic fertiliser, it has an equivalent effect in the longer term (Smith et al. 1998). Compared with manure, biosolids have a much more complex chemical composition and reactivity (Hedley and McLaughlin 2005); however, some P compounds present in biosolids, such as struvite (magnesium ammonium phosphate hexahydrate) recovered from the

anaerobic digester supernatant, have comparable agronomic effectiveness as readily available P sources such as single superphosphate (Plaza et al. 2007).

The conversion of manure and biosolids into biochars through pyrolysis has more advantages than business-as-usual methods of disposal such as landfilling and direct-land application (Hossain et al. 2011). Pyrolysis (i) greatly reduces the waste volume (Inguanzo et al. 2002), (ii) decreases the risk of pathogens, organic pollutants (Cantrell et al. 2007) and heavy metal availability (Inguanzo et al. 2002), and, most important, (iii) increases C stability, thus decreasing the greenhouse gas emissions associated with these wastes (Lehmann et al. 2006). Nutrient composition and availability in biochar varies widely, depending on the nature of the feedstocks and pyrolysis conditions (Chan and Xu 2009; Hossain et al. 2011). However, little information on P transformations during pyrolysis (Chan and Xu 2009) and the effect of this thermal treatment on P bioavailability is available at present.

Knowledge of the amount of available P in biochar is essential to determining the rate to be applied to meet crop P requirement, while ensuring a low risk of water eutrophication (Plaza et al. 2007). The bioavailability of added P in soils is influenced by the nature of P sources (López-Martínez et al. 2004; Güngör et al. 2007; Hunger et al. 2008), a range of soil properties (e.g., pH, variable charge surfaces – particularly metal hydrous oxides –, the presence of complexing compounds, and water-filled pore space), and plant root development (Hinsinger 2001; Hedley and McLaughlin 2005). Phosphorus availability in fertilisers can be determined using either (i) bioassay tests or (ii) chemical methods. The bioassay tests are based on the plant yield increase or P uptake under controlled greenhouse conditions or in field trials. Chemical methods are based on either (i) the study of the fertiliser mineralogy or (ii) the use of selective chemical extraction. Bioassays are the most reliable methods to predict P availability

(Rajan et al. 1992); however, these methods are soil specific, plant specific, and time and cost consuming. In the P fertiliser industry, chemical methods are widely employed as an important alternative to bioassay tests to measure the agronomic effectiveness of P fertilisers. Methods are generally country specific; for example, to extract certain forms of P associated with available P in phosphate rocks, 2% citric acid is used in New Zealand, 2% formic acid in the EU, and 1 M ammonium citrate at pH 7 in the USA and Australia (Hedley and McLaughlin 2005). These methods emphasized the influence of soil pH and organic ligands on P complexation, dissolution and precipitation, with special focus on inorganic fertiliser P. Phosphorus in both biosolids and manure is predominantly in inorganic form (Hedley and McLaughlin 2005), and so it will be in biochars. This is why it is further hypothesized that the above-mentioned chemical methods can be useful for P bioavailability testing of biochars.

The objectives of the present study were to (i) study the bioavailability of P in biochars using different feedstocks and pyrolysis conditions, and (ii) develop a robust chemical method for biochar P availability measurements. A bioassay and selective chemical analysis, including total P, extractable P (2% citric acid, 2% formic acid, and neutral ammonium citrate extraction) and X-ray diffraction, were conducted to investigate the availability and forms of P in biochars.

6.2 Materials and methods

6.2.1 Feedstocks and biochar preparation

Two different organic wastes were used in this study: (i) biosolids (BS) produced during the anaerobic digestion of wastewater from Palmerston North City Council wastewater treatment plant (Manawatu, New Zealand) and treated with Al to precipitate P from wastewater, and (ii) cattle manure (MA) from Massey University No. 4 Dairy Farm. The BS sample was from a non-industrial area and classified with a

contaminant grade A (Zn 750 mg kg^{-1}; Cu 210 mg kg^{-1}; Cd 1.6 mg kg^{-1}; Cr 47 mg kg^{-1}; Pb 66 mg kg^{-1}; and Ni 21 mg kg^{-1}), according to New Zealand Water and Wastes Association (2003). Separated fresh BS and MA wastes were thoroughly mixed with eucalyptus (e) wood chips (previously sieved through a 5-mm mesh) at a 1:1 ratio (dry-weight basis) to increase the calorific value of the former and thus facilitate carbonization (Hossain et al. 2009). The corresponding mixtures were identified as BSe and MAe and used as feedstocks. The mixtures were then oven-dried at 60°C.

Biochars were produced by slow pyrolysis in a 5 l gas-fired rotating drum kiln, as described by Calvelo Pereira et al (2011), using four different highest heating temperatures, 250°C, 350°C, 450°C, and 550°C. The heating rate was controlled around 15~20 °C min^{-1} by controlling the combustion gas flow. When the desired temperature was reached, the heating source was switched off and the system was allowed to cool down to room temperature. During cooling the outlet of the exhaust was blocked by a plastic bag with a rubber band to prevent oxygen going into the system. The biochars produced from BSe and MAe feedstocks (termed BSe-F and MAe-F, respectively) at these four different temperatures were referred to as BSe-250, BSe-350, BSe-450, BSe-550, MAe-250, MAe-350, MAe-450, and MAe-550. After cooling, subsamples of biochars were ground using a ring mill (Ring grinder, Rocklabs, Auckland, New Zealand) for 30 s to a particle size less than 100 μm and used in bioassays and subsequent analyses.

6.2.2 Biochar characterisation

Carbon and N concentrations in biochars and feedstocks were determined by CNS Analyser (LECO FP- 2000 CNS Analyser; Leco Corp., St Joseph, MI, USA). Inorganic C was determined by titration method following CO_2 evolution on treating with acid and trapped with NaOH solution according to Bundy and Bremner (1972), and

organic C (Corg) was obtained by subtracting inorganic C from total C. The moisture, volatile matter, fixed C, and ash contents were determined following Donahue and Rais (2009) and Calvelo Pereira et al (2011) using a thermogravimetric analyser (SDT Q600, TA Instruments, Melbourne, Australia); pH and EC were measured in a suspension of biochar in deionised water (ratio of 1:100; w/w) according to Ahmedna et al (1997); $CaCO_3$ equivalence (liming equivalence) was determined according to AOAC standard method (AOAC 1999) using an auto titrator (TIM 865 Titration Manager, Radiometer Analytical).

6.2.3 Phosphorus extraction and analysis

Total P (TP), 2% formic acid extractable P (FA-P), 2% citric acid extractable P (CA-P), and 1 M neutral ammonium citrate extractable P (NA-P) were investigated to compare P reactivity in biochars and Sechura phosphate rock (SPR) following the methodology from Rajan et al. (1992) and AOAC (2005). For the biochar samples, a sonication step in the FA and CA extractions was included to disperse the biochar materials and compared with the official method without sonication. Briefly, for FA-P and CA-P, ~ 0.35 g of biochars were shaken with 35 ml extractant on an end-over-end shaker at 32 rpm for 30 min at room temperature after dispersing with ultrasonication for 10 min. For TP, ~ 0.35 g of biochars were digested with 20 ml 10% HCl:10% HNO_3 (v/v). For NA-P, ~ 0.35 g of biochars were shaken with 35 ml 1 M neutral ammonium citrate-EDTA solution (AOAC 2005) for 24 h at room temperature, as it was proved to have an extractability comparable to that obtained after shaking the samples at 65°C for 1 h (Mackay et al. 1990). Each extraction was conducted in triplicate. Finally, extractants and biochars were separated by centrifugation (Sorval Centrifuge , with S34 head at 15,000 rpm for 10 min and the supernatant was filtered through a Whatman No. 41 filter paper. Filtrate P concentrations were determined by using the vanado-

molybdate colorimetric method at 420 nm (AOAC 2005). Background colour interference was compensated for by subtracting the absorbance of filtrates in the absence of P analysis reagents.

6.2.4 Metal analysis and X-ray diffraction (XRD) analysis

In order to investigate the chemical composition of P in biochars, Al, Fe, Ca, and Mg in the above-mentioned extractants were analyzed by Flame Atomic Absorption Spectrometer (AAS, GBC 904AA, Australia).

Phosphate mineral forms in biochars crystalline to X-ray were identified using a GBC EMMA diffractometer (GBC, Australia). This was operated at 35 kV and 20 mA using monochromatic Co Kα radiation and data were collected over the 2Θ range from 5 to 60° with a scan speed of 2° per minute and a scan step of 0.1°. Observed XRD patterns were compared with standards compiled by Traces Software (Version 6.7.13, GBC Scientific). BSe-F was also analyzed after getting rid of the organic matter with H_2O_2.

6.2.5 Bioassay test

A greenhouse study was conducted to compare the availability of P in biochars. Moata' tetraploid Italian ryegrass (*Lolium multiflorum Lam.*) was chosen as the test crop. Ryegrass was chosen because it has been widely used in previous studies on P availability using phosphate rock and other P fertilisers (Plaza et al. 2007; Rajan et al. 1992). Moreover, it is the dominant grass in temperate pastures. A Waitarere sandy soil, classified as Typic Udipsamment (Soil Survey Staff 2006), was the test soil (selective properties are shown in Table 6-1). The top 15 cm of soil was collected from the surroundings of Foxton beach, Manawatu, New Zealand. The soil had a bulk density of 1.49 g cm^{-1}, a pH of 5.8, a low CEC (2.04 cmol kg^{-1}), and a low organic C (5 g kg^{-1}), organic N (0.5 g kg^{-1}), and Olsen P (7 mg kg^{-1}) contents (Table 6-1). These soils are

also characterised by having high water repellence (Wallis et al. 1993) and a low P retention capacity (Sparling et al. 2006). BSe feedstock and biochars were applied at equivalent to 2.5 t ha^{-1} and 5 t ha^{-1}, and biochars made from MAe were applied at equivalent to 5 t ha^{-1} and 7.5 t ha^{-1},while for MAe feedstock only one dose was used (5 t ha^{-1}). Three application rates (100, 200, 800 kg ha^{-1}) of calcium dihydrogen phosphate [$Ca(H_2PO_4)_2 \cdot H_2O$] (CaP) and four application rates (0.25, 0.5, 1 and 2 t ha^{-1}) of SPR powder (ground and passed through 100 μm sieve) were used as routine P fertilisers comparisons, which corresponded to a total P content ranging from 40 to 240 kg P ha^{-1}. A control treatment without P addition was included. One kg soil was mixed thoroughly with each of the amendments under study, and was then divided into 4 parts by a Riffle divider. A 150-ml pot with nylon mesh at the bottom was then filled with 250 g soil. The total number of treatments was 27 and all the treatments were prepared in triplicate and arranged on a glasshouse table in a randomized block design. Each pot was watered to field capacity (–0.1 bar) with distilled water. Field capacity had been previously determined for each mixture using a pressure plate apparatus (data not shown). The soil was incubated for 3 weeks before seeding 15 seeds per pot to avoid any negative impact of the liming properties of biochars on seed germination (Free et al. 2010). After germination and growth of the seedlings to 5 cm height, the grass was thinned to 7 plants per pot. A P-free nutrient solution (Middleton and Toxopeus 1973) containing N, K, Ca, Mg, Fe, S and other micronutrients was used to water the plants once a week and DI water was used the rest of the week. The grass was cut to 5 cm height every 3 weeks for the first five harvests and 4 weeks for the 6th harvest. The grass was collected in a paper bag and dried at 70 °C for 48–72 hours in an oven. The grass was then weighed and ground to <1 mm particle size using a Cyclotech mill. Total P in the plants of the

first three harvests and fourth to sixth harvests was analysed on a Technicon autoanalyser after Kjeldahl digestion (McKenzie and Wallace 1954).

6.2.6 Model and data analysis

Yield responses to P fertiliser application and P uptake by ryegrass can be described by a Mitscherlich equation (Harmsen et al. 2001). This equation, based on Liebig's law of the minimum, describes the yield response of a crop to an increase in the main factor that is limiting growth (Harmsen 2000). It can be written as:

$$Y = Y_0 + {}_{\Delta}Y - {}_{\Delta}Ye^{-\varepsilon N_f} \quad (6\text{-}1)$$

where

Y = The total dry matter yield or P uptake of the ryegrass (g pot^{-1} or mg pot^{-1} for P uptake),

Y_0 = The yield or P uptake (g pot^{-1} or mg pot^{-1} for P uptake) without biochar or fertiliser application,

${}_{\Delta}Y$ = The difference (g pot^{-1} or mg pot^{-1} for P uptake) between the maximum yield or P uptake Y_{max} and Y_0, that is, $Y_{max} = Y_0 + {}_{\Delta}Y$,

ε = an activity coefficient (mg^{-1} pot), which is a measure of plant available P in biochars or fertilisers,

N_f = the rate of P applied to the crop (mg pot^{-1}).

Results are expressed as an average of three replicates with standard deviation if not stated. Sigmaplot (version 10, Scientific Graphing Software, SPSS Inc.) and Microsoft Excel were employed to perform linear and nonlinear regression analysis and figure drawing. A coefficient of determination (r^2) was used to measure of goodness of fit of least square fitted regression models. One-way ANOVA and Student-Newman-Keuls (SNK) analysis were used to evaluate statistical differences in plant yield and P

uptake between different treatments by SPSS software (Version 13, SPSS Inc., Chicago, IL, USA).

6.3 Results

6.3.1 Biochar characterisation

Selective properties of biochars produced from MAe and BSe at different temperatures are shown in Table 6-2. For both MAe and BSe feedstocks and biochars, P concentration, fixed C content, and ash content increased with pyrolysis temperatures. Volatile matter and volatile matter/(volatile matter+ fixed C) decreased with an increasing pyrolysis temperature. At the same forming temperature, MAe biochars showed higher C, volatile matter, and fixed C contents but lower ash content and N and P concentrations than BSe biochars. However, other properties showed no consistent trends. Interestingly, for both feedstocks, the pH shifted from values > 7 in the fresh feedstock to acidic values for low temperature biochars (MAe-250, BSe-250, and BSe-350) and to values > 7 for high temperature biochars. This result is consistent with the finding of Hossain et al. (2011). Electrical conductivity (EC), an indicator for total dissolved salts, increased at low pyrolysis temperature (e.g., 250, 350°C) compared with the fresh feedstock, but decreased at higher pyrolysis temperature. The $CaCO_3$ equivalence ranged from 83.0 to 178.5 g kg^{-1} for MAe biochars, and from 75.5 to 164.8 g kg^{-1} for BSe biochars. Except for MAe-350 and BSe-350, MAe biochars showed higher $CaCO_3$ equivalence values than BSe biochars. From 250 to 450°C, $CaCO_3$ equivalence of both classes of biochars increased but it decreased from 450 to 550°C, which differs from results obtained by other researchers (Singh et al. 2010).

Feedstock P was fully recovered in the biochars produced. As shown in Table 6-2, 98–119% of the initial P was recovered in MAe biochars, and 93–108% in BSe biochars. This result is consistent with those of Bridle and Pritchard (2004), in which

full recovery of P from sewage sludge after pyrolysis at 450°C was achieved. More interestingly, high temperature biochars showed higher total P recovery than low temperature biochars.

The XRD spectra of the biochars under study are depicted in Figure 6-1. None showed clear evidences of the presence of crystalline P to X-ray, except for the small peaks at 17.44, 35.43, 53.71 2θº in MAe and BSe biochars attributed to struvite ($MgNH_4PO_4 \cdot 6H_2O$). The XRD spectrum of BSe-250 biochars had strong background noise in the region of 10–30 2θº, which was attributed to the high proportion of non-carbonised organic matter (Mandile and Hutton 1995). The distinct peaks at 24.35, 31.04, 42.93, and 49.91 2θº were attributed to the presence of quartz.

6.3.2 Phosphorus and cation extractability in feedstocks and biochars

As the temperature of pyrolysis increased, so did the thermal degradation of the feedstock, resulting in increased concentrations of total P in the biochars. Phosphorus content ranged from 4 to 9 g kg^{-1} in the MAe biochars and from 30 to 51 g kg^{-1} in the BSe biochars (Table 6-2).

The results of P extractability in feedstocks and biochars using FA, CA and NAC methods are reported in Table 6-3. As the effect of the sonication step on CA-P extractability was small, only the effect on FA-P extractability is discussed here, and the modified method is referred to as FAs-P. Sonication resulted in a 6–9.5% and 10–50% increase of FA-P in MAe and BSe, respectively (Table 6-3). In the MAe biochars, the percentage of extractable P was the highest with FAs-P (ranging from 79 to 99%), followed by FA-P (ranging from 72 to 93%) and NAC-P (ranging from 70 to 83%), and the lowest being CA-P (ranging from 67 to 90%). In the BSe biochars, the percentage of extractable P was lowest with the CA-P (ranging from 7 to 19%). The NAC reagent extracted a high percentage of P from BSe biochars, especially at low and high

temperatures of pyrolysis (with values around 90%). At 350 °C, extractability with NAC dropped <48%. Extractability of P in BSe biochars using the FAs and FA methods showed a more consistent pattern with values ranging from 36 to 47% and 27 to 38% respectively. In all biochars except BSe-350, BSe-550 and MAe-550, P extractable with FA, FAs, and NAC increased in absolute value as pyrolysis temperature increased.

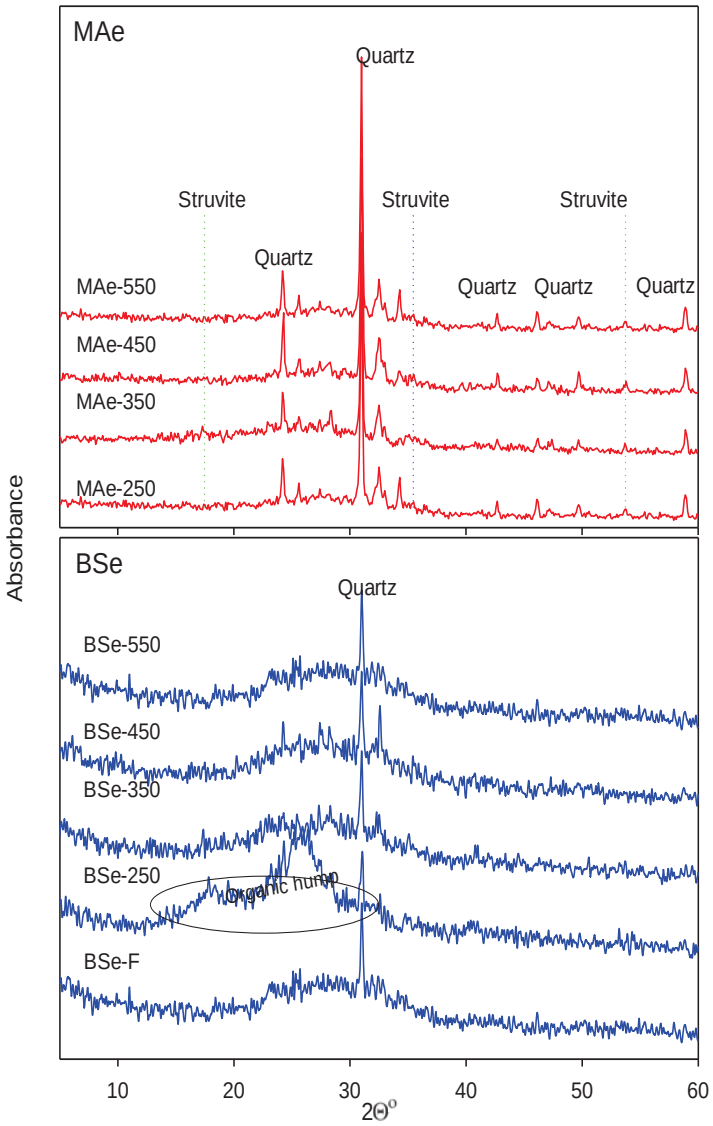

Figure 6-1. XRD spectra of biochars and biosolid feedstock (BSe-F). Possible struvite peaks in MAe were lined out by dotted lines; the region in the ellipse in BSe was attributed to"organic hump".

Table 6-1. Selected properties of Waitarere sandy soil

pH	bulk density ($g\ cm^{-3}$)	CEC ($cmol\ kg^{-1}$)	Total C ($g\ kg^{-1}$)	Total N ($g\ kg^{-1}$)	C/N Ratio	Olsen P ($mg\ kg^{-1}$)	Total S ($mg\ kg^{-1}$)	Exchangeable Cations ($cmol\ kg^{-1}$)			
								K	Ca	Na	Mg
5.8	1.49	2.04	5	0.5	9.4	7	45	0.13	1.1	0.15	0.66

Table 6-2. Selected properties of biochars used in this study

Feedstocks/ biochars	Corg ($g\ kg^{-1}$)	C ($g\ kg^{-1}$)	N ($g\ kg^{-1}$)	P ($g\ kg^{-1}$)	P recovery (%)	Moisture (%)	VM[a] (%)	FC[b] (%)	Ash (%)	VM/ (VM+FC)[c]	pH	$CaCO_3$ equivalence ($g\ kg^{-1}$)	EC ($\mu s\ cm^{-1}$)
MAe-F	425.6	425.6	10.8	2.86	-	6.52	62.49	16.57	14.42	0.79	7.56	-	351
MAe-250	467.4	467.9	13.5	3.55	98	2.83	55.62	20.87	20.68	0.73	6.60	82.95	451
MAe-350	527.4	528.3	17.5	6.16	114	3.07	34.54	36.82	28.65	0.48	7.39	110.66	498
MAe-450	481.3	483.7	15.5	7.97	119	2.91	24.65	36.98	38.37	0.40	10.03	178.52	408
MAe-550	537.1	540.4	15.9	8.31	119	2.56	16.65	42.30	38.49	0.28	10.53	161.83	393
BSe-F	342.7	342.7	13.8	20.95	-	9.42	52.87	11.80	16.48	0.82	7.42	-	256
BSe-250	382.0	382.0	17.5	29.71	93	2.92	48.41	16.16	29.59	0.75	5.56	75.52	390
BSe-350	373.5	373.5	18.8	41.56	101	2.97	29.51	23.63	40.92	0.56	5.39	123.18	304
BSe-450	367.7	367.7	18.5	47.76	108	2.68	20.90	26.75	46.98	0.44	7.00	164.76	254
BSe-550	358.5	358.5	16.6	50.64	105	2.77	13.84	29.55	51.08	0.32	7.95	151.02	178

a: VM, volatile matter
b: FC, fixed C
c: VM/(VM+FC), Volatile matter/(volatile matter+ fixed C) ratio

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Table 6-3. Phosphorus extractability of biochars in 2% formic acid (FA-P), 2% citric acid (CA-P) and 1M neutral ammonium citrate (NAC-P). Fraction is the % of TP extracted. Standard deviation (n = 3) in parentheses. For FA-P, data from official method (FA-P, 30 min shaking only) and modified method (FAs-P, official method+10min sonication) are presented.

	2% formic acid				2% citric acid		1 M neutral ammonium citrate	
	official method		modified method					
	Mean (g kg^{-1})	Fraction (%)	Mean (g kg^{-1})	Fraction (%)	Mean (g kg^{-1})	Fraction (%)	Mean (g kg^{-1})	Fraction (%)
MAe-250	3.28 (0.01)	92.60	3.48 (0.14)	98.15	3.17 (0.03)	89.18	2.88 (0.08)	81.11
MAe-350	4.56 (0.03)	74.00	4.84 (0.09)	78.54	4.10 (0.01)	66.54	4.59 (0.01)	74.54
MAe-450	6.62 (0.03)	83.03	7.09 (0.18)	88.99	6.07 (0.02)	76.22	6.60 (0.04)	82.85
MAe-550	5.98 (0.03)	71.95	6.55 (0.28)	78.78	5.81 (0.06)	69.90	5.81 (0.03)	69.88
BSe-250	11.09 (0.29)	37.34	14.20 (0.44)	47.81	4.55 (0.05)	15.30	26.89 (0.70)	90.50
BSe-350	11.01 (0.51)	26.48	16.46 (0.16)	39.61	2.82 (0.41)	6.78	19.79 (0.82)	47.63
BSe-450	17.34 (0.35)	36.31	20.14 (1.42)	42.16	8.73 (0.58)	18.28	29.46 (0.67)	61.68
BSe-550	16.71 (0.03)	33.00	18.37 (1.00)	36.27	7.99 (0.07)	15.78	45.51 (1.37)	89.86

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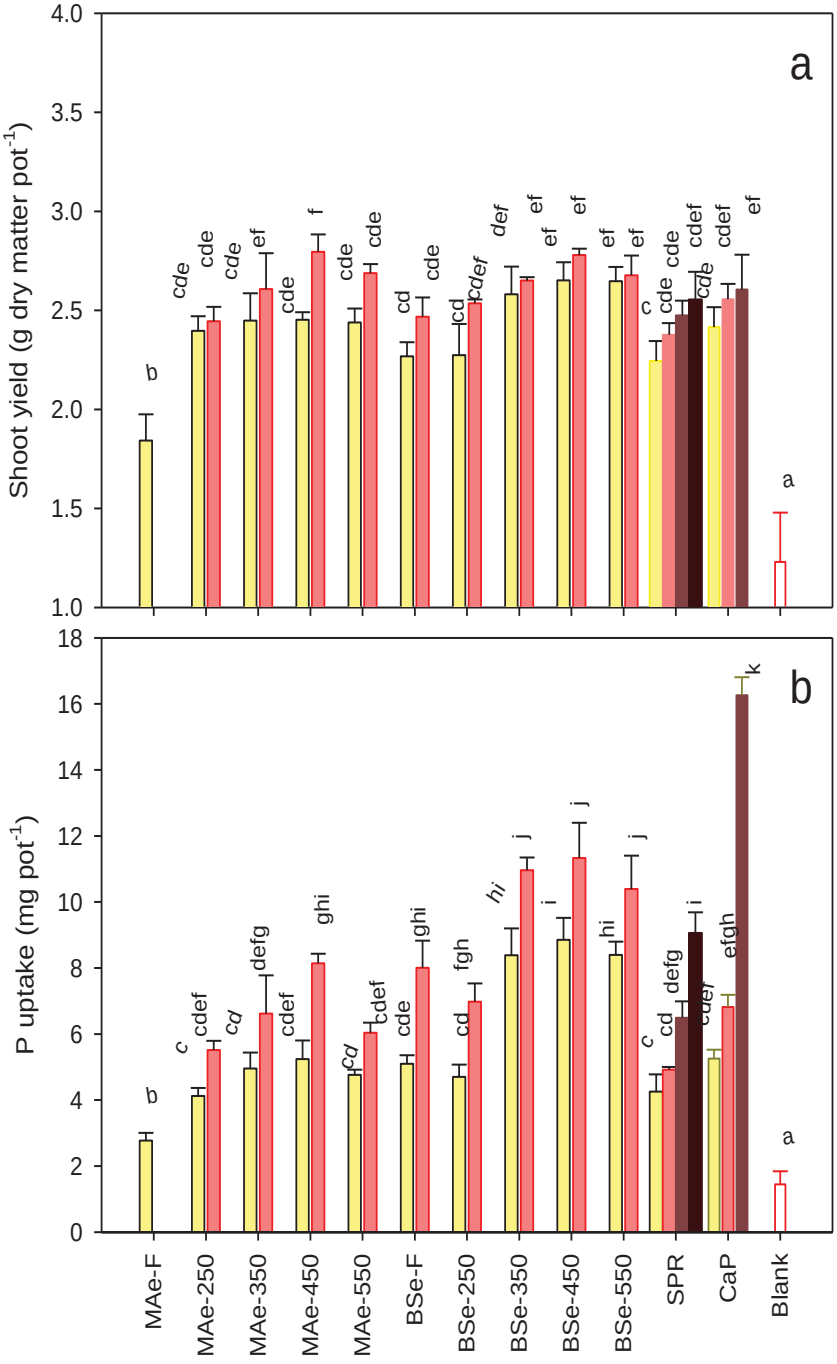

Figure 6-2. Shoot dry matter yield (a) and P uptake (b) from 6 harvests of ryegrass grown in pots of Waitarere sandy soil fertilised with feedstocks, biochars, and P fertilisers. In the same treatment, deeper colour indicated higher dose amendment. Doses for biosolid biochars (BSe) are 2.5t ha^{-1} and 5t t ha^{-1}; for manure biochars (MAe), 5 t ha^{-1} and 7.5 t ha^{-1}; for phosphate rocks (SPR), 0.25, 0.5, 1 and 2 t ha^{-1}; for calcium dihydrogen phosphate (CaP) , 100, 200, 800 kg ha^{-1}. Error bars indicate standard deviations of experimental replicates (n=3). Different letters indicate statistically significant according to the S-N-K test at the 0.05 level.

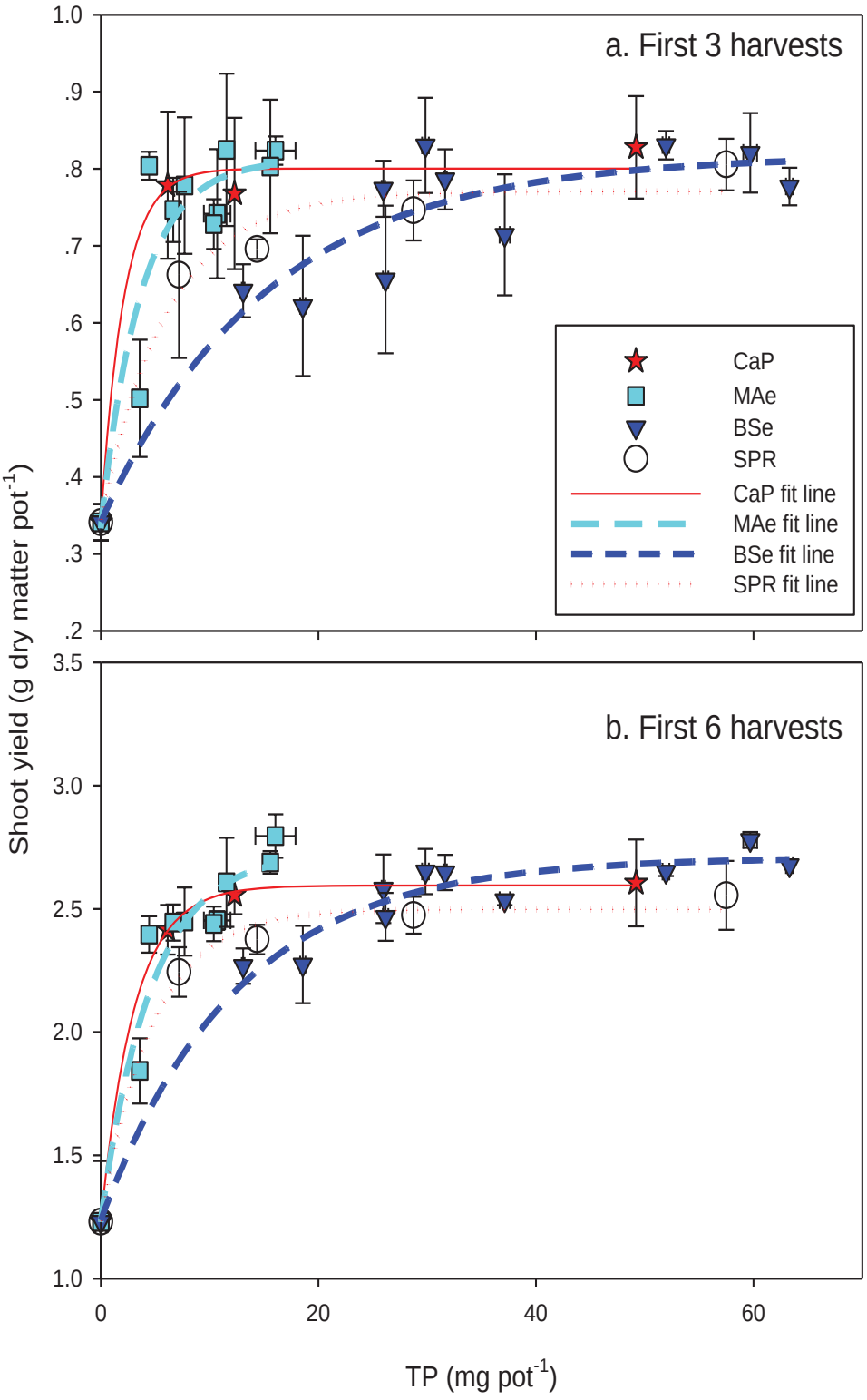

Figure 6-3. Shoot dry matter yield of ryegrass grown in pots of Waitarere sandy soil fertilised with feedstocks, biochars, and P fertilisers at first 3 harvests (a) and first 6 harvests (b). Data were fitted by a Mitscherlich equation. Error bars indicate standard deviations of experimental replicates (n=3).

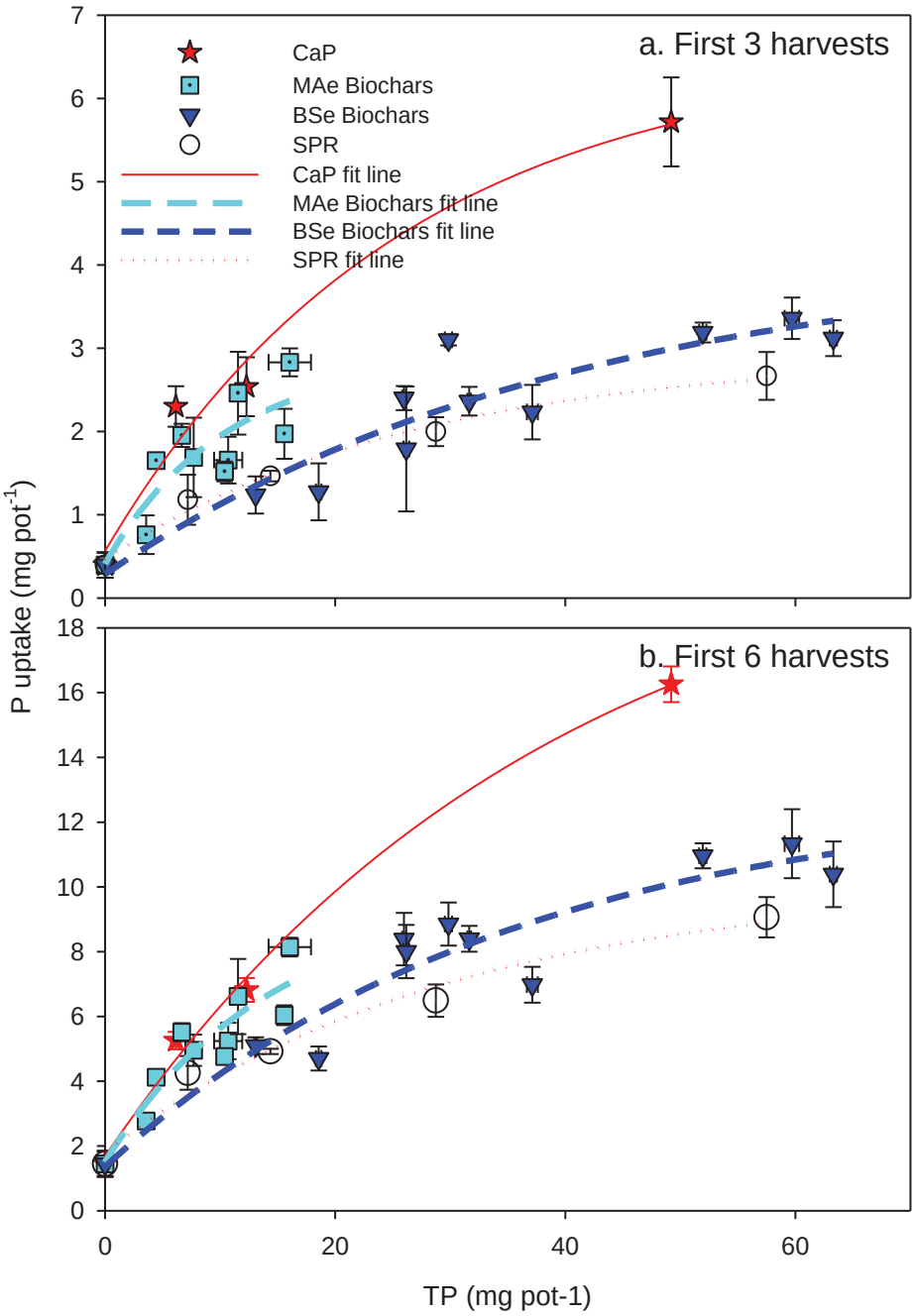

Figure 6-4. P uptake by ryegrass grown in pots of Waitarere sandy soil fertilised with feedstocks, biochars, and P fertilisers at first 3 harvests (a) and first 6 harvests (b). Data were fitted by a Mitscherlich equation. Error bars indicate standard deviations of experimental replicates (n=3).

Calcium, Mg, Al, and Fe present in the TP digestion solution and in the FAs- and CA-extraction solutions were determined (data not shown). In the MAe biochars, the extractable-Ca to extractable-P atomic ratio ranged from 1.3 to 1.8, and the extractable-Mg to extractable-P atomic ratio ranged from 0.6 to 1.1; those of

extractable-Al and -Fe to extractable-P ratios were below 0.5 and 0.2, respectively. In BSe the biochars, the atomic ratio of extractable-Al and -Ca to extractable-P ranged from 1.9 to 3.2 and 0.4 to 1.4, respectively; whereas, those of extractable-Mg and -Fe to extractable-P were negligible.

Table 6-4. Selected parameters of dry matter yields and P uptake by ryegrass fitted by the Mitscherlich equation

		r^2	Y_{max}	Y_{max}-SE*	ε	ε-SE
Yields			(g pot^{-1})	(g pot^{-1})	(mg^{-1} pot)	(mg^{-1} pot)
3 harvests	CaP	0.989	0.800	0.094	0.473	0.342
	MAe	0.817	0.812	0.163	0.274	0.115
	BSe	0.883	0.817	0.116	0.065	0.019
	SPR	0.974	0.771	0.091	0.163	0.049
6 harvests	CaP	0.997	2.595	0.041	0.326	0.020
	MAe	0.923	2.726	0.311	0.217	0.058
	BSe	0.966	2.709	0.166	0.081	0.010
	SPR	0.993	2.498	0.138	0.209	0.036
Uptakes			(mg^{-1} pot)	(mg^{-1} pot)	(mg^{-1} pot)	(mg^{-1} pot)
3 harvests	CaP	0.977	6.572	2.031	0.039	0.025
	MAe	0.729	2.905	1.541	0.096	0.095
	BSe	0.865	4.147	1.352	0.025	0.013
	SPR	0.989	2.914	0.383	0.038	0.010
6 harvests	CaP	0.995	21.815	5.092	0.026	0.011
	MAe	0.843	9.652	4.908	0.071	0.065
	BSe	0.899	12.955	3.065	0.028	0.011
	SPR	0.974	10.120	2.186	0.033	0.015

*: SE, standard error from model fitting

6.3.3 Ryegrass yield and P uptake

Both ryegrass yield and P uptake increased significantly (p<0.05) with the addition of biochars and fertilisers compared with (i) the control (un-amended soil), and (ii) the pots amended with feedstocks in terms of similar biochar application rates (Figure 6-2). All the biochar treatments showed plant yields comparable to P fertilisers (95% confidence interval) (Figure 6-2 a). However, increasing the dose of biochar – and thus of available P – had no significant effect on plant yield (except MAe-450), although the treatments with the high dose always showed higher mean values (Figure 6-2a). In contrast, P uptake was more sensitive to the dose and type of P source (Figure

6-2b) than plant yield (Figure 6-2a); the greatest P uptake was at the highest P dose, this uptake being greater from BSe biochars than from MAe biochars. Furthermore, both dry matter yield and P uptake for both MAe-550 and BSe-550 decreased, even not significantly, compared with those of MAe-450 and BSe-450, respectively (Figure 6-2).

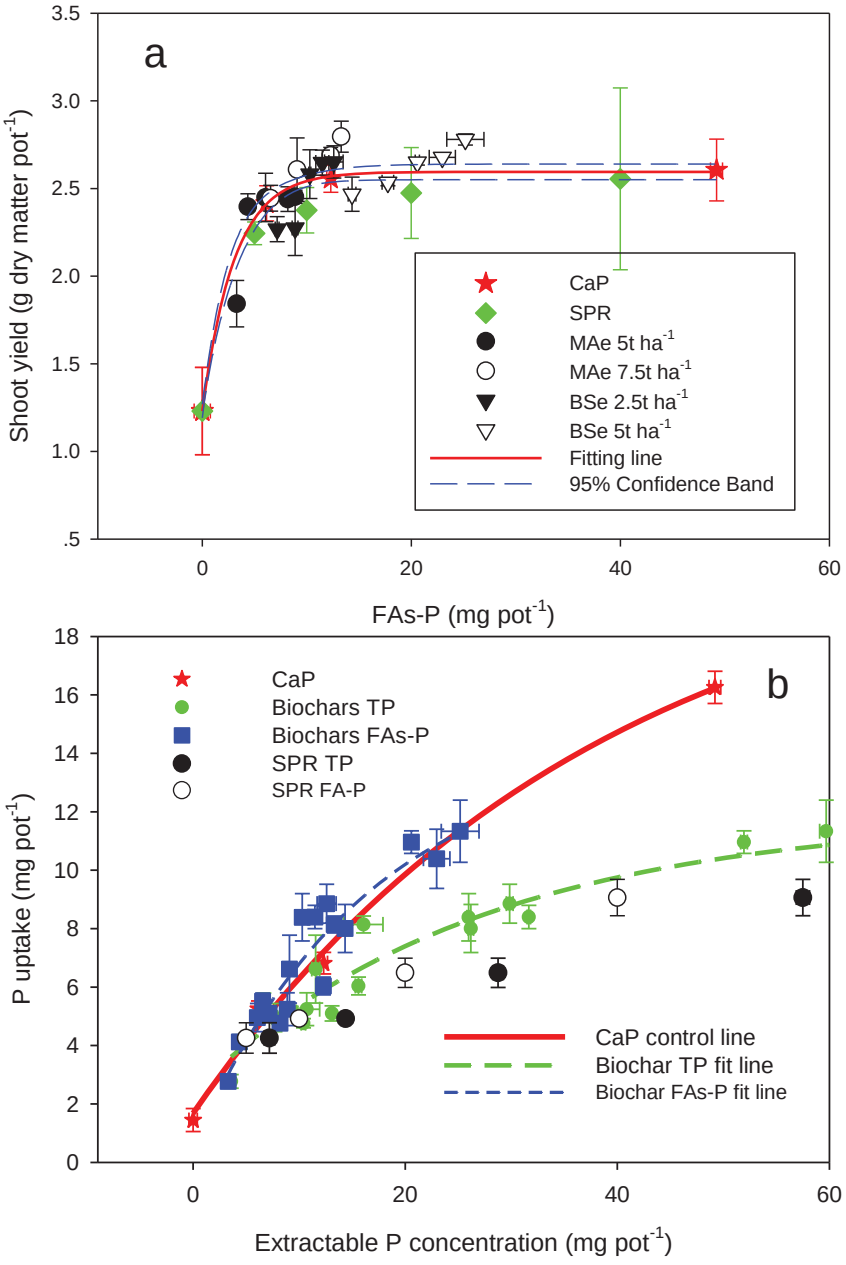

Figure 6-5. Relationship between dry matter yields and formic acid extractable P after sonication (FAs-P) (a), plant P uptake and extractable P concentration (b). Data were fitted by a Mitscherlich equation. Error bars indicate standard deviations of three experimental replicates (n=3).

Both yields and P uptake data vs TP were fitted to a Mitscherlich equation (Figures 6- 3 and 6-4, and Table 6-4). Coefficients of determination (r^2) increased as the number of harvests increased from three to six (Table 6-4) (except for P uptake of SPR). From the dry matter yield modelling, all the groups shared a maximum dry matter yield (Y_{max}), and the activity coefficient (ε) followed a descending order as CaP>MAe>SPR>BSe (Table 6-4). For P uptake modelling, the maximum P uptake followed an order CaP>BSe>SPR>MAe (Table 6-4).

Both yields and P uptake from all the six harvests vs different extractable P (FA-P, FAs-P, CA-P, NAC-P) from all the P sources were also fitted to the Mitscherlich equation (data not shown). When the Mitscherlich equation was used to model ryegrass yield vs the amount of extractable P applied, coefficients of determination (r^2) for FAs-P and FA-P were 0.86 and 0.85 respectively; while CA-P and NA-P failed to be incorporated into the model. The modelled curve of plant yield plotted against FAs-P, is presented as the solid line in Figure 6-5a. All the CaP and biochar data fell around this line, while SPR data were a little lower than line (not significant). High temperature biochars (MAe-350, MAe-450, MAe-550, BSe-350, BSe-450, and BSe-550) exhibited higher biomass yield per unit of FAs-P than conventional fertilisers, whereas the opposite effect was observed for feedstocks and BSe-250 biochar. Phosphorus uptake was regressed against extractable P (TP and FAs-P) and data from CaP treatment were used to represent the standard data for plant available P (solid line, Figure 6-5b), assuming CaP was added in a form readily available to plants. The biochar treatment data were then modelled using the Mitscherlich equation. Good fits were found between P uptake and FAs-P (r^2=0.89) and TP (r^2=0.77) (Figure 6-5b); Data from FAs-P of biochars fell around the same curve as CaP (this curve is referred to CaP model hereafter), which contrasts with that of SPR. In order to examine the predictive ability

of FAs-P further, P uptake predicted with the CaP model was compared with measured P uptake (Figure 6-6), as carried out by Hedley et al. (1985) when studying available P in superphosphate fertilisers. Both FA-P and FAs-P methods showed a good prediction of available P in biochars. However, FA-P (with a slope of 1.07, r^2=0.70) underestimated available P, while FAs-P (with a slope of 0.98, r^2=0.79) slightly overestimated available P. Furthermore, FAs-P showed a lower sum of residual squared (19.23) than that of FA-P (30.97).

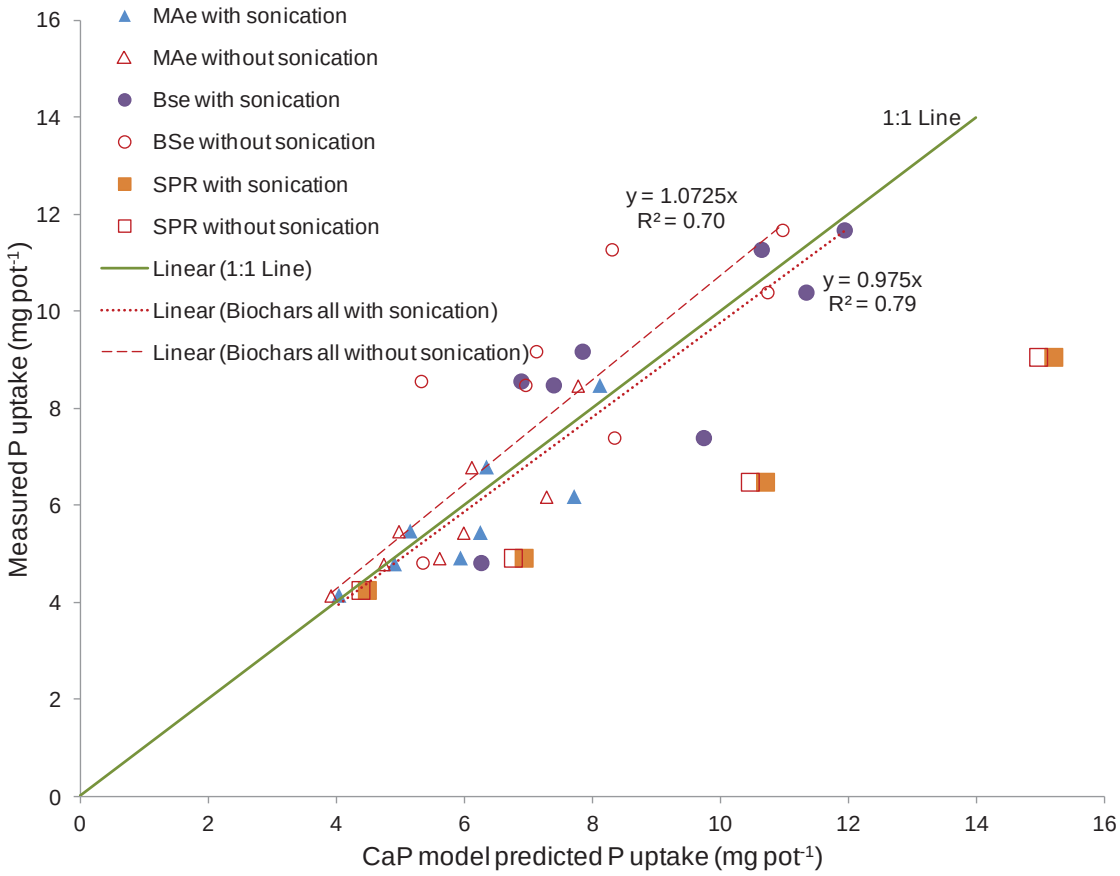

Figure 6-6. Relationship between P uptake predicted by the CaP model and measured P uptake using either FA-P (official method; shake for 30 min only) or FAs-P (modified method; 30 min shaking plus 10 min sonication) as the available P content.

6.4 Discussion

In the present study, both volatile matter and the ratio of volatile matter/(volatile matter+ fixed C) decreased with increasing pyrolysis temperature, indicating an increase

in C stability (Zimmerman et al. 2011), in agreement with previous studies (Calvelo Pereira et al. 2011; Zimmerman et al. 2011). Carbon sequestration via conversion of biomass into more durable forms has been proposed as a strategy to combat global climate change (Macías and Camps Arbestain 2010). Due to the relative recalcitrance of C in biochar (Lehmann et al. 2006), biochar production is one of the most attractive methods to manage waste while decreasing the greenhouse gas emissions footprint (Lehmann J and Joseph S 2009). In biochars produced from wastes with a high nutrient content, a compromise should be achieved between C stability and the added value of the biochar as fertiliser, as it will be discussed below.

The highest pyrolysis temperature used in this study was 550 °C, which was much below the threshold temperature of 700 °C for P volatilization (De Luca et al. 2009). At the pyrolysis temperatures used here, P will tend to accumulate in the biochar, resulting in P enrichment and a full recovery of this element in the solid fraction. Higher recovery of high temperature biochars compared with low temperature ones, could be due to the incomplete total digestion of organic P in the feedstocks (Hedley and McLaughlin 2005), although small errors caused by sub-sampling the variable feedstocks cannot be discarced. As pyrolysis cleaves the organic P bonds present in the feedstocks, which results in an increase of acid soluble P salts (De Luca et al. 2009), recovery of P improved with final pyrolysis temperatures above 250°C.

The atomic ratios between specific extractable cations and extractable P and the similar XRD spectra pattern among biochars from the same feedstock suggest a strong influence of feedstock composition on the type of cation-phosphate complexes existing in biochars. The nature of these complexes determines their reactivity/bioavailability (Güngör et al. 2007; Hunger et al. 2008). Data obtained here suggest that Ca/Mg-P complexes dominated in MAe feedstock and biochars and that Al and possibly Ca

phosphates dominated in BSe feedstock and biochars. However, further studies are required to clarify the P forms existing in these materials.

In order to compare the availability of P in biochars, the recovery of P in ryegrass expressed as the % of TP added in each pot was calculated (data not shown). A higher recovery of P in plants was found in the MAe treatments (39–93%) compared with in the BSe treatments (16–35%). Furthermore, the biochars and fertilisers treatments shared similar maximum dry matter yields, which made the Mitscherlich equation valid to compare the relative agronomic effectiveness (RAE) of P sources (Palmer et al. 1979; Chien et al. 1990). The fact that the activity coefficient (ε) followed a descending order as CaP>MAe>SPR>BSe (Table 6-4) suggests that CaP was most available (as expected, given the high solubility of CaP in water), followed by MAe, SPR, and BSe. Considering the chemical stability constants and findings from previous studies (Hinsinger 2001; Plaza et al. 2007), it is clear that Ca/Mg-P precipitates are more soluble than those of Al/Ca-P. This mostly explains the higher availability of P in MAe feedstock/biochars, which are richer in Ca/Mg-P compounds, compared with BSe biochars, which are dominated by Al/Ca-P compounds. Sechura phosphate rock is a very reactive carbonate-substituted fluoroappatite (Gregg et al. 1988), containing 34% Ca, 0.28% Al, and 0.28% Fe (Rajan et al. 1992); this explains its higher P bioavailability compared with BSe, but its lower availability compared with MAe. These results suggest that (i) the chemical composition and, especially, the coordinated cations, play a key role in controlling P availability in biochars; and (ii) this is mainly determined by the type of feedstock used. However, further studies are needed to identify P forms in biochars.

Numerous bioassay studies (Rajan et al. 1992; Smith et al. 1998; Plaza et al. 2007) used both crop yield and P uptake as indicators for P availability. Yield is much

easier to measure than P uptake because the latter requires chemical analyses. However, yield is not as sensitive as P uptake (Plaza et al. 2007). In this study, where small pots (150 ml) were used, it is possible that the space for grass root development was constrained, limiting shoot development and plant yield. Phosphorus uptake was thus considered a more valid indicator of available P and was compared with the chemical extractants used. Phosphorus extractable with FA has been widely proved to be a reliable indicator of available P in phosphate rocks (SPR) (Rajan et al. 1992; Hedley and McLaughlin 2005), and was shown to be a good extractant to test P availability in biochars since data from FAs-P of biochars and CaP fitted in a similar asymptotic relationship (Figure 6-5b). Phosphorus uptake predicted using the CaP model and employing FA-P as the measure of available P content showed good correlation with measured P uptake (Figure 6-6). In this study, a 10-min sonication step was added to the official formic acid extraction method to extract P in biochars to favour the dispersion of the hydrophobic biochar particles. The results obtained proved that this modification improved the predictive capability of the FA-P test (Figure 6-6) especially for BSe biochars but not for the MAs biochars. These results suggest that the sonication step might only be useful for biochar samples with hydrophobic properties and/or sparingly soluble P compounds richer in Al and Fe.

A good linear relationship was found between FAs-P and TP (r^2=0.98, p<0.1) for both feedstocks and all the biochars made below 450 °C. It suggested that pyrolysis temperature played a minor role in influencing the P availability of biochars produced below this temperature compared to the types of feedstock. However, as seen from data of (i) FAs-P (Table 6-3), (ii) dry matter yield, and (iii) P uptake (Figure 6-2), both MAe-550 and BSe-550 showed decreases in P availability compared to MAe-450 and BSe-450, respectively. This was attributed to a structural change in biochars (Chan and Xu

2009) produced at high pyrolysis temperatures (above 450°C in this study), which may stabilize the P within the amorphous C matrix (Kercher and Nagle 2003). When P fertiliser value of biochar is important, then more attention should therefore be paid to the pyrolysis temperature region of 450–550 °C to achieve a compromise between P availability and C stability.

High temperature biochars (MAe-350, MAe-450, MAe-550, BSe-350, BSe-450, and BSe-550) exhibited higher biomass yield per unit of FA-P than conventional fertilisers. The reason behind this pattern is unknown and more work is needed to understand this. The opposite effect was observed for the BSe-250 biochar; we hypothesize that the latter could be due either to the low liming ability of this biochar (Table 6-2), and/or to the higher levels of tar compounds present in low temperature biochars (Gell et al. 2011).

6.5 Conclusion

Pyrolysis successfully reduced the volume of organic wastes, producing ash-rich biochars. Phosphorus was fully recovered in the biochars after pyrolysis. Both the extractability and bioavailability of P primarily depended on P composition in the feedstocks and to a less extent on final pyrolysis temperature. In this study, Ca/Mg-P may influence P availability in the dairy manure-eucalyptus wood mixture (MAe) biochars, whereas amorphous Al/Ca-P was probably the main P species in biochars made from biosolids-eucalyptus wood mixture (BSe). This may explain the higher extractability and bioavailability of P in MAe biochars. Plant growth response modelling based on a Mitscherlich equation indicates 2% formic acid extractable P (FA-P) is the recommended measure of P availability in biochars. In addition, the inclusion of a sonication step is suggested for biochars samples with large amount of sparingly soluble P compounds. Biochars – especially those made at 350 and 450°C – had

comparable agronomic efficiency on a FA-P basis to commercial fertilisers. Their suitability as P fertilisers should be assessed using standard chemical extraction methods already used to characterise manufactured P fertilisers and also with consideration of the environmental and health aspects of biochar production, such as the emission of organic pollutants and the load of heavy metals in biochars.

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CHAPTER 7. THE FATE OF PHOSPHORUS OF ASH-RICH BIOCHARS IN A SOIL-PLANT SYSTEM

In Chapter 6, P availability in biochar has been studied. However, the transformation of biochar P after its incorporation into soils is still unclear. Therefore, in this Chapter, P forms and their transformations in soil amended with biochar are investigated using soluble P extractions, a sequential P fractionation and a successive P extraction via resin strips.

A paper from this study has been submitted for publication:

Wang T, Camps-Arbestain M, Hedley M and Bishop P 2013 The fate of phosphorus of ash-rich biochars in a soil-plant system. Plant and Soil (in revision)

Abstract

Aims The objectives were to investigate (i) the forms and release pattern of P from a biochar-amended sandy soil; (ii) the transformation of biochar P in a soil-plant system.

Methods Several methodologies (a bioassay test, soluble P extractions, a sequential P fractionation and a successive P extraction via resin strips) were used to study the bioavailability and transformation of P in a sandy soil fertilised with either conventional P fertilisers [$Ca(H_2PO_4)_2$ (CaP) and Sechura phosphate rock (SPR)] or biochars produced from cattle manure (MAe) and Alum-treated biosolids (BSe) at four temperatures (250, 350, 450, and 550°C).

Results Biochar P mainly contributed to resin-extractable P- and inorganic NaOH-extractable P-fractions, and thus to plant available P. The decrease in P concentration of those fractions was caused by the uptake of P by plants rather than their transformations into more stable forms. P release rates diminished following the order: CaP>MAe>BSe>SPR, which indicates a decline in P availability from these P sources.

Conclusions Phosphorus-rich biochar can be used as a slow-release fertiliser. It is necessary to determine available P (either soil or fertiliser tests) in biochars prior to its application to soil, so that dose, frequency and timing of application are correctly established.

Keywords

P fractionation; biochar; bioavailability; transformation

7.1 Introduction

Biosolids and manure are ubiquitous organic wastes and important agricultural resources (Shafqat and Pierzynski 2011), for increasing soil fertility, improving the physical and chemical /biochemical properties of soils to enhance crop growth and soil carbon storage (Brown et al. 2011). Risks associated with the direct application of municipal biosolids from unwanted contamination of heavy metals (Sloan et al. 1998), organic pollutants (Poulsen and Bester 2010), pathogens (Gerba and Smith 2005) and greenhouse gases (e.g. N_2O and CH_4) emissions (Smith et al. 2008) require active management to avoid threats to environmental quality. Conversion of these wastes into biochar through slow-pyrolysis before land application provides a promising approach to manage some of these associated risks (Inguanzo et al. 2002; Cantrell et al. 2007). Biochar with highly recalcitrant condensed aromatic C (Atkinson et al. 2010; Keiluweit et al. 2010; Schimmelpfennig and Glaser 2011), also has potential for long-term soil C sequestration. In addition, nutrient-rich ash, highly porous C structure and large surface area facilitate biochar have potential for soil quality improvement (Lehmann 2007; Atkinson et al. 2010; Woolf et al. 2010).

Application of biosolids and animal wastes in excess of agronomic nutrient requirements, particularly P, can induce serious surface water eutrophication problem (Sharpley et al. 2001; Shober and Sims 2003). P enrichment through application of wastes or biochars made from those wastes can be avoided if the bioavailability of P in such materials is known. Understanding the environmental fate of biochar P requires information on its chemical form and solubility (Turner and Leytem 2004). Sequential chemical fractionation of P in soil, aiming to separate Al, Fe and Ca phosphates successively, provides an empirical approach to quantifying and characterising the

forms and transformations of this nutrient in soil (Hedley and McLaughlin 2005). Hedley and colleagues developed a series of methods (Hedley et al. 1982; Tambunan et al. 1993; Hedley et al. 1994) to sequentially fractionate P in soils, which were proved to be effective to separate labile and recalcitrant organic and inorganic P pools in soils (Johnson et al. 2003), with or without fertiliser and organic material amendments (Cross and Schlesinger 1995; Hedley and McLaughlin 2005; Toor et al. 2006). These methods have also been adopted for studying the forms of P in manure (Turner and Leytem 2004) and biosolids (Huang et al. 2008). As P in biochars mainly exists in inorganic forms associated with Al, Ca, Fe and Mg (Chapter 6) (Wang et al. 2012a), the above-mentioned fractionation scheme could be suitable to study the P forms and transformation in soils amended with P-rich biochars. However, the information obtained from sequential fractionation of biochar P , will need to be supported by concurrent studies of relative availability of P from similar P form (e.g. different Ca-P salts)(Saavedra and Delgado 2005). In order to evaluate temporal aspects of P release, P sinks (Lookman et al. 1995; Saavedra and Delgado 2005) are employed to provide supplementary information to the sequential fractionation method.

The transformation of P in soils can be influenced by soil properties, rhizosphere processes (e.g. root and microbial activities), plant growth and other land management practices (Hedley et al. 1994; Schmidt et al. 1997; Negassa and Leinweber 2009). Evidences have shown that biochar is able to influence plant growth (Asai et al. 2009) and soil biota (e.g. microbial biodiversity) (Anderson et al. 2011; Lehmann et al. 2011), which in turn affected the transformation of P in soils. Up to now, however, little is known about how P transforms in a soil-biochar-plant system.

The objectives of this study were to investigate (i) the forms and release pattern of P in a sandy soil treated with biochar by employing a sequential fractionation

scheme and successive resin extractions; (ii) the transformation of biochar P in the soil-plant system, and (iii) the influence of pyrolysis temperature and type of feedstock on the availability of biochar-P .

7.2 Materials and methods

7.2.1 Feedstocks and biochar preparation and characterisation

Information concerning feedstock and biochar preparation and characterisation has been described Chapters 5-6 (Wang et al. 2012a; Wang et al. 2012b). In brief, two types of feedstock were used: (i) a mixture of alum-treated biosolids (from anaerobic digestion of sewage, ~5% dry wt. of Al) and eucalyptus wood chips (BSe-F), and (ii) a mixture of cattle manure (from a dairy farm) and eucalyptus wood chips (MAe-F). Both mixtures were made up to a 1:1 dry wt. basis ratio. Biochar was made via slow pyrolysis (in the absence of O_2) in a gas-fired rotating drum kiln (Calvelo Pereira et al. 2011) under four temperature regimes (highest heating temperature: 250, 350, 450, and 550°C). Biochar samples from different temperature regimes were referred to as MAe-250, MAe-350, MAe-450, MAe-550, BSe-250, BSe-350, BSe-450, and BSe-550. All biochars were ground <100 μm (feedstocks <300 μm) for chemical analysis and bioassay test. Selected characteristics of biochars are provided in Table 7-1. The characterisation methods can be found in Chapters 5-6.

7.2.2 Greenhouse experiment

A bioassay test was conducted to investigate the availability of biochar-P in a Waitarere sandy soil (Typic Udipsamment)(Soil Survey Staff 2006). Moata' tetraploid Italian ryegrass (*Lolium multiflorum Lam.*) was chosen as the test crop. Details about the soil properties (Chapter 6, Table 6-1, sandy soil; pH5.8; CEC 2.04 cmol kg^{-1}; organic C 5 g kg^{-1}; organic N 0.5 g kg^{-1}; and Olsen P 7 mg kg^{-1}) and experimental setup

can be found in Chapter 6. In brief, BSe feedstock and biochars were applied at equivalent doses of 2.5 and 5 t ha^{-1}; MAe-F at 5 t ha^{-1} and MAe biochars at 5 and 7.5 t ha^{-1}. Three application rates (100, 200, 800 kg ha^{-1}) of calcium dihydrogen phosphate [$Ca(H_2PO_4)_2 \cdot H_2O$] (soluble CaP) and four application rates (0.25, 0.5, 1 and 2 t ha^{-1}) of Sechura phosphate rock (SPR) powder (ground and passed through 300 μm sieve) were used as routine P fertiliser comparisons. These corresponded to a total P content ranging from 40 to 240 kg P ha^{-1}. A total of 27 treatments (in triplicate) were arranged on a bench in a randomized block design. Soil was mixed thoroughly with each of the amendments and a 150-ml pot with nylon mesh at the bottom was then filled with 250 g soil. Soil water was checked once a day and adjusted to a field capacity (–0.1 bar) with DI water during the experiment. A P-free nutrient solution (Middleton and Toxopeus 1973) containing N, K, Ca, Mg, Fe, S and other micronutrients was used to water the plants once a week. After pre-equilibrating for 3 weeks (set as T_0), 15 seeds were sown in every pot and then thinned to 7 plants after seed germination. The grass was cut to 5 cm height every 3 weeks for the first five harvests, 4 weeks for the 6th harvest and every 5 weeks for the 7th to 9th harvests. The grass was collected in a paper bag and dried at 70 °C for 48 hours in an oven. The grass was then weighed to get dry yield. Plant shoot samples of the first three harvests were pooled together, so being the fourth to sixth harvests and the seventh to ninth harvests, and ground to <1 mm particle size using a Cyclotech mill. After the last harvest, soil and plant root samples were separated; soil was mixed homogenously (this time was referred to as T_h) and root samples were ground and stored in a same way as plant shoots. Total P in the soil samples, plant roots and plant shoots was analysed on a Technicon autoanalyser after Kjeldahl digestion (McKenzie and Wallace 1954).

7.2.3 Olsen and acid ammonium oxalate extraction

Sodium bicarbonate extractable P (Olsen P) of soils at T_0 was determined based on Olsen et al (1954). Acid ammonium oxalate solution (0.2 mol L^{-1}, pH3) was used to extracted soils sampled at T_0 with a soil/liquid ratio of 1:15 following Maguire et al (2000). Oxalate extractable P was determined according to He et al (1998).

7.2.4 Soil P fractionation

Soil samples at T_0 (after pre-equilibrating for 3 weeks but before sowing the seeds) and T_h (after the separation of the root and soil) were used for fractionation following Hedley et al (1994). Briefly, ~0.5 g soil was shaken overnight with 30 ml deionised water (suspension 1) containing one anion (HCO_3^- saturated) and one cation (Na^+ saturated) exchange resin strip. After shaking the resin strips were removed and eluted using 0.5 M NaCl solution (resin-P); then 3.3 ml of 1 M NaOH solution was added to the above soil suspension (1), which was re-shaken overnight (suspension 2). Then suspension 2 was centrifuged at 15000 rpm (Sorvall Centrifuge, with an S34 rotor) for 10 min and the supernatant was filtered through a Whatman No 41 filter paper for NaOH-Pi (inorganic P) and NaOH-Pt (total P after digesting with concentrated H_2SO_4) analysis [NaOH-Po (organic P) was the difference between NaOH-Pt and NaOH-Pi]. The remaining soil was then extracted by 30 ml 0.5 M H_2SO_4 overnight (suspension 3) and suspension 3 was centrifuged and the supernatant was analyzed for H_2SO_4-P. Finally, the soil residue was digested by 5 ml concentrated H_2SO_4 on a digestion block for 4 hours to obtain the residual P. Phosphorus concentrations in this study were manually determined colorimetrically or using a Technicon autoanalyser after adjusting solution pH to ca. 4.

7.2.5 Release of P via successive resin extractions

One HCO_3^- saturated anion resin strip and one Na^+ saturated cation resin strip were added to a suspension of 0.5 g of soil in 30 ml DI water in a 50 ml centrifuge tubes and then shaken for 16 h. Then resin strips were removed and eluted with 0.5 mol L^{-1} NaCl solution and P was determined on a Technicon autoanalyser. A total of 7 successive extractions were conducted for soils samples at T_0 and 5 for those at T_h. Resin membranes were regenerated with $NaHCO_3$ or NaCl solution (Saggar et al. 1990). All extractions were conducted in duplicates. After the extraction steps, all the soil suspension were subjected to a sequential fractionation scheme as described above.

7.2.6 Data analysis

One way ANOVA was conducted by SPSS software (Version 13, SPSS Inc., Chicago, IL, USA) to compare the means of different treatments. Significant differences were determined according to a Turkey HSD test at a level of 0.05. Student's t test was used to test the significant change in P fraction between soil samples at T_0 and T_h.

Release kinetics of P by a successive resin extraction were fitted with a pseudo-second-order kinetic (PSO) model (Ho and McKay 1999) and a 2-component model (Lookman et al. 1995) using Sigmaplot software (version 11, Scientific Graphing Software, SPSS Inc.).

The pseudo-second-order kinetic model is written as (Ho and McKay 1999):

$$\frac{dQ}{dt} = k(Q_{\max} - Q)^2 \qquad (7\text{-}1)$$

where Q is the amount of released P at a time t; Q_{max} is the maximum releasable P; and k is the PSO rate constant. Applying the initial conditions, Equation (7-1) can be integrated as:

$$\frac{t}{Q} = \frac{1}{kQ_{\max}{}^2} + \frac{1}{Q_{\max}} t \quad (7\text{-}2)$$

The 2-component model can be written as (Lookman et al. 1995):

$$Q = Q_{fast}(1 - e^{-k_1 t}) + Q_{slow}(1 - e^{-k_2 t}) \quad (7\text{-}3)$$

$$Q_{fast} + Q_{slow} = Q_{\max} \quad (7\text{-}4)$$

where Q_{fast} and Q_{slow} are the fast- and slow- releasable P pool respectively. Q_{max} is same as the one from the Equation (7-2); k_1 and k_2 are P release rate constants for the two pools separately.

7.3 Results

7.3.1 Biochar characterisation and soil available P test

Table 7-1. Selected characteristics of feedstocks and biochars [a]

Feedstocks/ biochars	C_{org} (g kg^{-1})	N (g kg^{-1})	P (g kg^{-1})	pH	Ash (%)	$CaCO_3$ equivalence (g kg^{-1})	EC (μs cm^{-1})
MAe-F	425.6	10.8	2.9	7.6	14	-	351
MAe-250	467.4	13.5	3.6	6.6	21	83	451
MAe-350	527.4	17.5	6.2	7.4	29	111	498
MAe-450	481.3	15.5	8.0	10.0	38	179	408
MAe-550	537.1	15.9	8.3	10.5	38	162	393
BSe-F	342.7	13.8	21.0	7.4	16	-	256
BSe-250	382.0	17.5	29.7	5.6	30	76	390
BSe-350	373.5	18.8	41.6	5.4	41	123	304
BSe-450	367.7	18.5	47.8	7.0	47	165	254
BSe-550	358.5	16.6	50.6	8.0	51	151	178

a. Data were adopted from Chapter 6.

The biochar properties have been reported in previous studies (Chapters 5-6) (Wang et al. 2012a; Wang et al. 2012b) and the most relevant information to the present

study is reported in Table 7-1. Biochars had higher organic C concentration (C_{org}, 467 - 537 g kg^{-1} for MAe biochars and 382 – 359 g kg^{-1} for BSe biochars) and higher N content (1.4% - 1.8% for MAe biochars and 1.7% -1.9% for BSe biochars) than those of the corresponding feedstocks. Pyrolysis temperature had no consistent effect on biochar C and N contents. Both P concentration (3 – 8 g kg^{-1} for MAe biochars and 29 - 51 g kg^{-1} for BSe biochars) and ash content (21% -38% and 30% -51% for MAe and BSe biochars respectively) increased as pyrolysis temperature increased. Biochars produced at ≥450 °C had high $CaCO_3$ equivalence (>151 g kg^{-1} $CaCO_3$ equivalence), making them potential liming materials.

Both resin-P and Olsen P reflected the increment in available P from increasing doses of different P sources (Figure 7-1). Strong correlations were found between resin or Olsen P and total P for each type of P sources. Extractable resin or Olsen P vs. total P added clearly distinguished between the different P sources (Kashem et al. 2004). Resin-P was more sensitive than Olsen P due to the greater difference in slope between the different sources of P. P extractability followed a descending order as: CaP > MAe > BSe > SPR, in both resin-P and Olsen P figures, indicating a decreasing availability of P in these P sources. In contrast, oxalate-extractable P (P_{ox}) extracted most of the total P added (slope of 0.97) and was unable to distinguish the difference in P bioavailability between CaP and biochar treated soil (Figure 7-1). Similar to the other two extractions, oxalate extracted little P from SPR treated soil; however, like the other extracts a gentle slope (0.04 – 0.07) indicated dissolution controlled release of P in the SPR treated soils.

7.3.2 Plant yields and P uptake

Plant shoot yields from the 9 harvests and root weights are shown in Figure 7-2. Phosphorus uptake by ryegrass is shown in Figure 7-3. Almost all fertilised pots had

significantly ($p<0.05$) higher yields of plant shoots and total biomass than the control (except shoots of 1-3 harvests and 7-9 harvests for MAe-F). However, there were no major differences in biomass among treatments amended with different P sources. In contrast, plant P uptake responded well to different P treatments (Figure 7-3). For CaP and SPR treatments, plant P uptake increased with the fertiliser dose. Generally, BSe treatments showed higher P uptake compared with those in MAe treatments and this was due to the higher total P concentrations in the former (Figure 7-1). Furthermore, as harvest number increased, the extent of difference among treatments decreased.

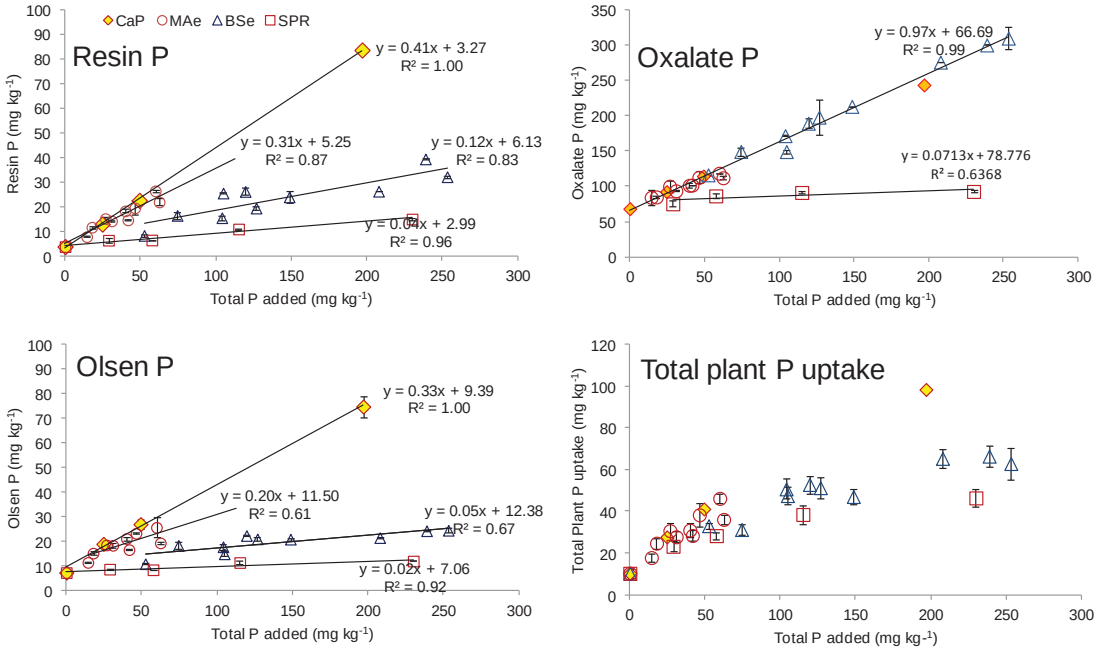

Figure 7-1. Soil available P as tested by resin-P, Olsen P, oxalate P and total plant P uptake in soil amended with different P sources at T_0 (after 21 days of equilibration with moist soil).

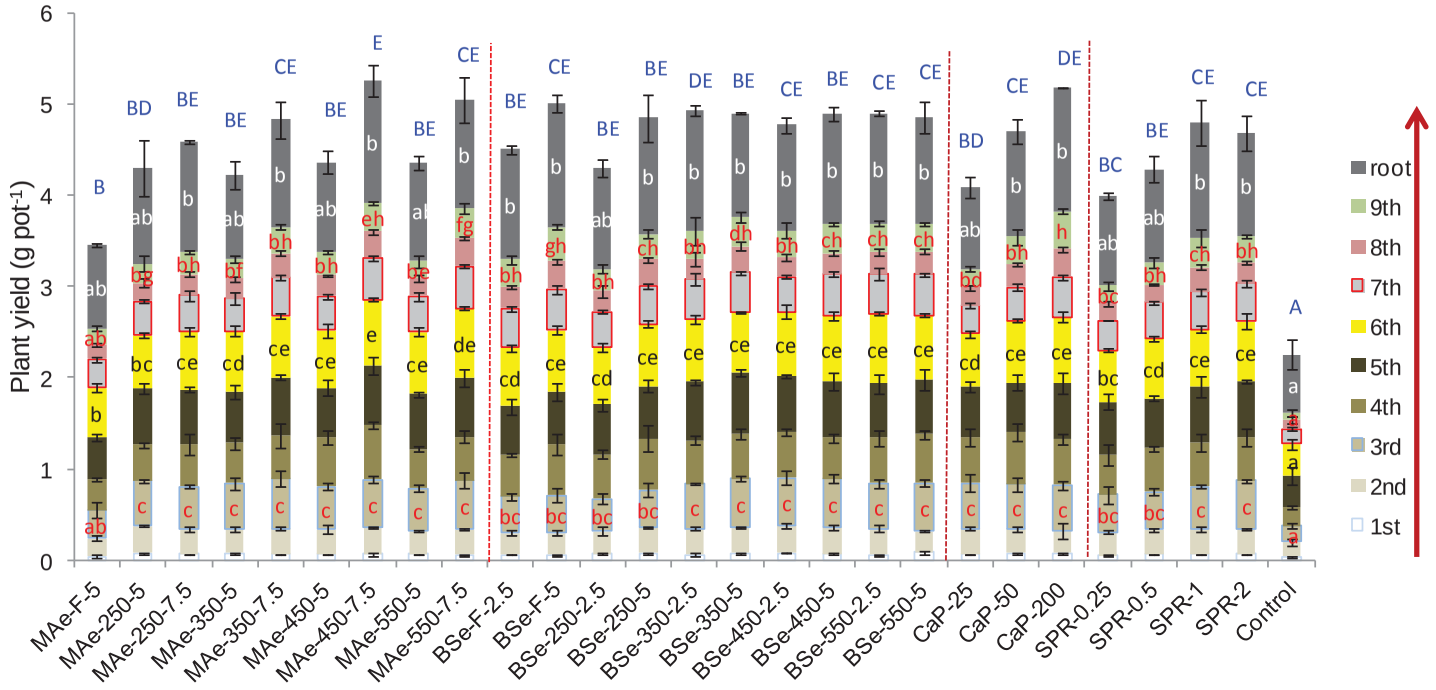

Figure 7-2. Shoot dry matter yields and root dry weight of ryegrass grown in pots of Waitarere sandy soil fertilised with feedstocks, biochars, and conventional P fertilisers (mean ± std., n=3). Shoots (5 cm above soil surface) were harvested for 9 times successively. Means of shoot yields from 1-3 harvests, 4-6 harvests and 7-9 harvests, root weights and total biomass (shoot + root) were compared using one way ANOVA method. Values not sharing the same letter indicate a significant difference (Turkey HSD at a level of 0.05). Lower case was used for shoot yields of every 3 harvests and root weights; capital letters for total biomass.

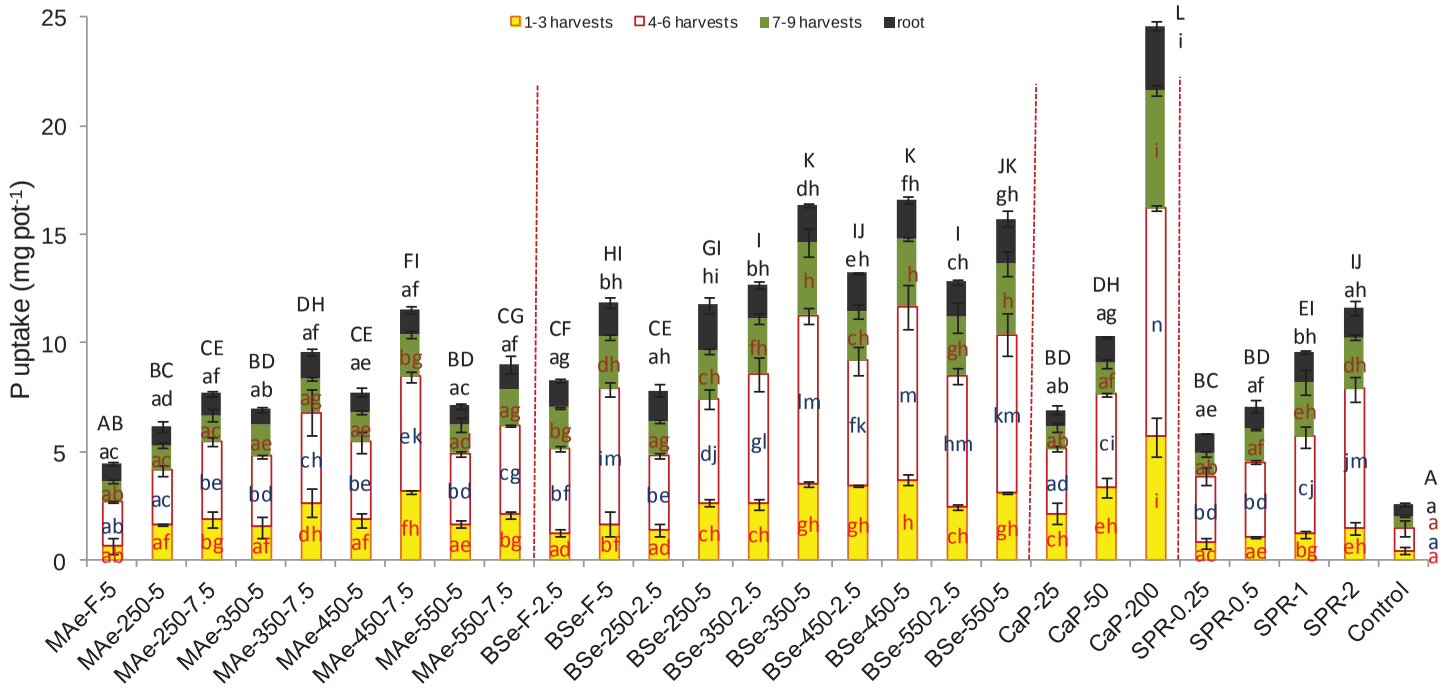

Figure 7-3. P uptake of ryegrass grown in pots of Waitarere sandy soil fertilised with feedstocks, biochars, and conventional P fertilisers (mean ± std., n=3). Shoots (5 cm above soil surface) were harvested for 9 times successively. Means of shoot P contents from 1-3 harvests, 4-6 harvests and 7-9 harvests, root P content and total P uptake (shoot + root) were compared using one way ANOVA method. Values not sharing the same letter indicate a significant difference (Turkey HSD at a level of 0.05). Lower case was used for shoot P content of every 3 harvests and root P content; capital letters for total P uptake.

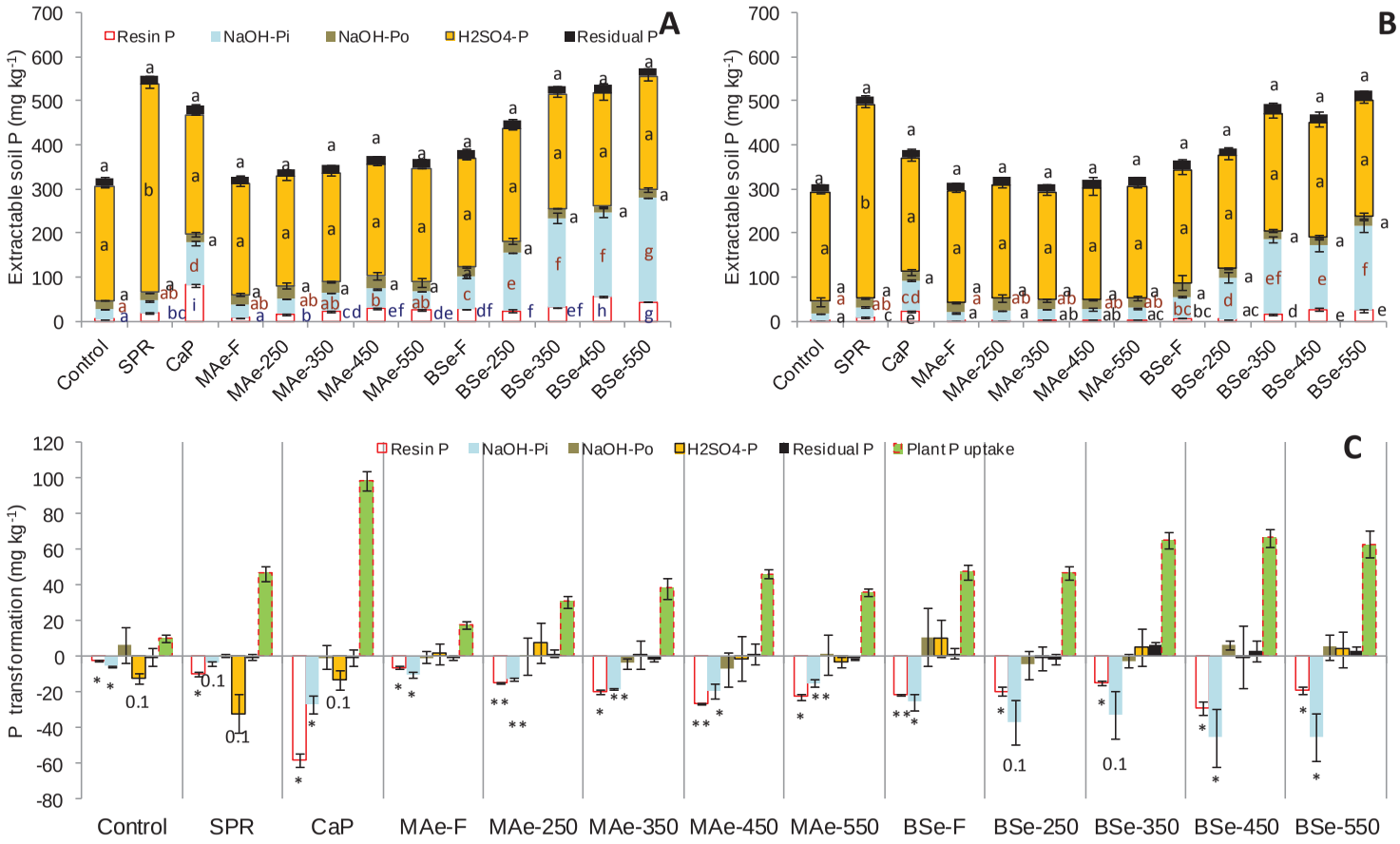

Figure 7-4. Extractable soil P in soils A) at T_0 (after pre-equilibrating for 3 weeks but before sowing the seeds); B) at T_h (after the separation of the root and soil) and; C) plant P uptake and difference in extractable P before and after plant growth. Values not sharing the same letter indicate a significant difference (Turkey HSD at a level of 0.05) (Figure 2A and 2B); (0.1), (*) and (**) denote a statistically significant difference with 0 at the *P*<0.1, *P*< 0.05 and P<0.01 according to Student's t test (one-tailed).

7.3.3 P fractionation

Preliminary study showed that the rate of application of P source in this study did not influence the % distribution of P amongst fractions (data not shown). Here the P fractionation was only conducted in treatments with the higher dose of each P source (i.e. MAe: 7.5 t ha^{-1}; BSe: 5 t ha^{-1}; CaP: 200 kg ha^{-1} and SPR: 2t ha^{-1}). At T_0, as shown in Figure 7-4 (A), four groups of P sources differed in terms of P fractionation. Specifically, i) CaP amendment increased soil resin-P and NaOH-Pi to a large extent, and H_2SO_4-P to a less extent but not significantly; ii) MAe feedstock and biochar application increased soil resin-P and NaOH-Pi almost equally; iii) BSe feedstock and biochars resulted in a major significant increase of NaOH-Pi, and to a less extent of resin-P; iv) SPR-P was mainly in H_2SO_4-P form and a minor fraction of resin-P. A sum of the increments of resin-P and NaOH-Pi [Δ(resin-P + NaOH-Pi)] of biochar treatments compared with the control treatment was almost equal to the amount of P added [Δ(resin-P + NaOH-Pi)=0.94*total P added, R^2=0.98, SI Figure S7-1], indicating a nearly full recovery of biochar P by resin and NaOH extraction. Figure 7-4 (B) shows P forms of soils at T_h. A path analysis (Zheng et al. 2002) of P transformation was carried out by calculating the differences in P forms of the same treatment at T_0 and T_h, as shown in Figure 7-4(C). Corresponding to the P fraction pattern, > 50% of plant P was derived from i) resin-P for CaP and MAe treatments; ii) NaOH-Pi for BSe treatment, and iii) H_2SO_4-P for Control and SPR treatment.

7.3.4 P release kinetics via successive resin extractions

The release pattern of resin extractable P (Figure 7-5) from CaP and MAe treated soil at T_0 was markedly curvilinear, whereas the control and BSe treated showed slight curvature and the SPR treated soil showed a linear pattern. Both the PSO and the 2-component model worked well for the data from Control, CaP, MAe and BSe

treatments (high r^2 value in Table 7-2 and SI Figure S7-2). Based on the PSO model, the maximum release capacities of all the treatments except for SPR were calculated (SI Figure S7-2) and summarised in Table 7-2. Lack of asymptotic trend made it impossible to estimate the maximum P release capacity of soils amended with SPRs. After exploring the maximum releasable P (Q_{max}), the 2-component model was used to divide soil P into 2 pools, as shown in Table 7-2.

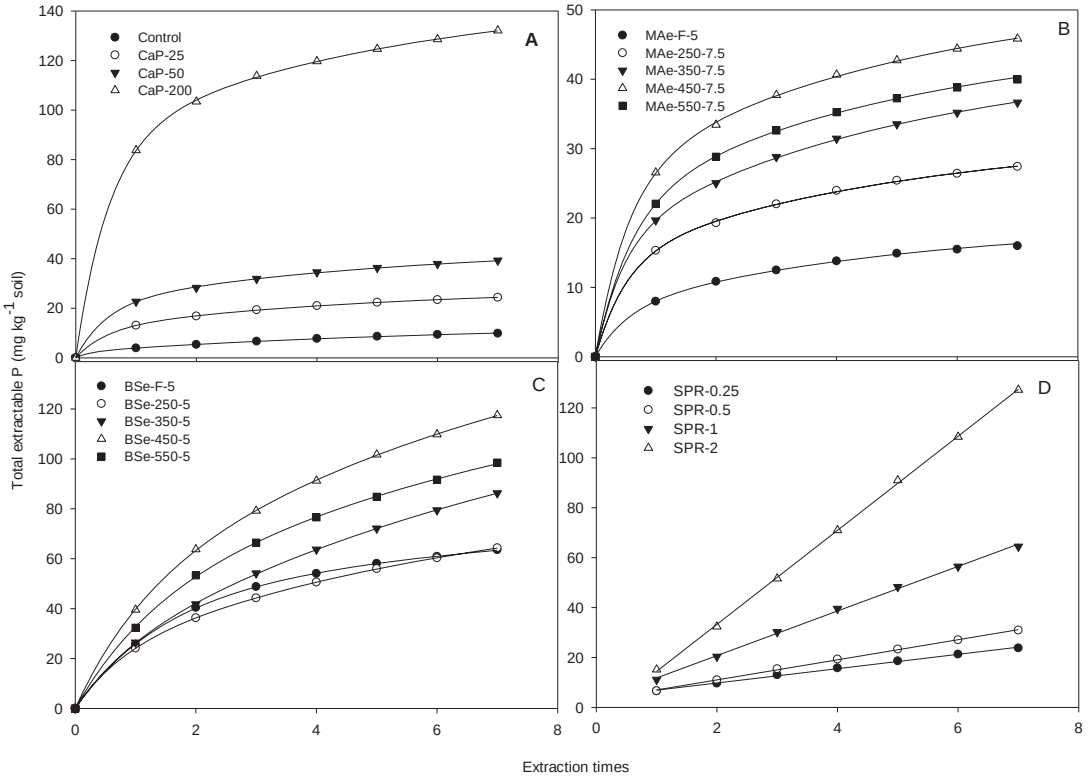

Figure 7-5. Release pattern of P in soils fertilised with different P sources (at T_0): A) Control and CaP; B) MAe; C): BSe and; D) SPR. For Control, CaP, MAe and BSe treatments, data were fitted via a 2-component model (Equations (7-3) and (7-4)) after exploring the maximum release capacity according to Equation (7-2); data of SPR treatments were fitted by a linear model. Parameters are shown in Table 7-2.

Generally, $Q_{max\text{-}T0}$ (Q_{max} at T_0) increased with total P added, with exception of treatments amended with biochars produced at 550°C. CaP treatments showed slightly higher ratio of ($Q_{max\text{-}T0}$ /total P added) than those of MAe and BSe treatments (Table 7-2), but the difference was not significant (P>0.05, data not shown). The rate constants

for the two P pools changed only slightly for CaP and MAe treatments; while those of BSe were relatively variable (Table 7-2). At T_h, the soil P release pattern (e.g. curve shape) resembled that of the same treatment at T_0 (data not shown). However, the relative error increased due to the significant decrease in soil P concentration caused by plant uptake. The Q_{max} of these soils ($Q_{max\text{-}Th}$) were also estimated according to the PSO model. All the $Q_{max\text{-}Th}$ decreased significantly ($p<0.05$) compared to $Q_{max\text{-}T0}$. Furthermore, there was a 1:1 relationship between $Q_{max\text{-}T0}$ and ($Q_{max\text{-}Th}$ + total plant P) (Figure 7-6).

Table 7-2. Estimated maximum release capacity (Q_{max}) of soil fertilised with different P sources (at T_0) and estimated fast and slowly releasable P pools via a 2-component model. For Q_{fast}, k_1, Q_{slow} and k_2, left column are mean values and right standard errors.

Treatment	Q_{max} /P added	Q_{max}	Q_{fast}		k_1		Q_{slow}		k_2		r^2
	%	mg kg^{-1}	mg kg^{-1}		mg $kg^{-1}t^{-1}$		mg kg^{-1}		mg $kg^{-1}t^{-1}$		
Control	-	12.2	1.9	0.4	4.4	7.3	10.3	0.8	0.2	0.0	1.0
CaP-25	67.7	28.7	11.6	1.0	2.0	0.2	17.0	0.5	0.2	0.0	1.0
CaP-50	67.2	45.1	20.1	1.4	2.2	0.3	24.9	0.7	0.2	0.0	1.0
CaP-200	68.6	147.1	86.0	4.0	1.9	0.1	61.0	1.9	0.2	0.0	1.0
MAe-F-5	65.1	19.5	6.7	1.8	1.9	0.7	12.7	0.9	0.2	0.1	1.0
MAe-250-5	67.9	26.3	10.5	1.5	1.9	0.4	15.8	0.8	0.2	0.1	1.0
MAe-250-7.5	64.3	32.0	13.8	1.5	2.0	0.3	18.2	0.8	0.2	0.1	1.0
MAe-350-5	58.8	30.1	12.7	0.8	2.1	0.2	17.4	0.4	0.2	0.0	1.0
MAe-350-7.5	67.7	43.3	16.7	1.1	2.2	0.3	26.6	0.7	0.2	0.0	1.0
MAe-450-5	64.2	37.6	17.7	1.6	1.8	0.2	19.9	0.7	0.2	0.0	1.0
MAe-450-7.5	68.0	52.6	25.4	2.3	1.9	0.2	27.2	1.1	0.2	0.1	1.0
MAe-550-5	51.6	33.4	13.2	1.7	1.8	0.3	20.3	0.8	0.2	0.1	1.0
MAe-550-7.5	55.3	46.5	21.2	1.8	1.7	0.2	25.3	0.8	0.2	0.0	1.0
BSe-F-2.5	59.8	43.3	5.5	0.8	2.9	1.3	37.8	2.3	0.1	0.0	1.0
BSe-F-5	68.1	83.3	24.9	30.5	1.3	1.4	58.4	26.0	0.2	0.4	1.0
BSe-250-2.5	60.4	51.3	13.0	1.4	1.8	0.3	38.3	1.5	0.2	0.0	1.0
BSe-250-5	59.5	89.3	20.6	1.0	1.3	0.1	68.7	1.2	0.1	0.0	1.0
BSe-350-2.5	55.0	63.7	9.9	1.8	2.0	0.6	53.8	3.9	0.1	0.0	1.0
BSe-350-5	62.0	140.9	19.0	3.8	1.2	0.2	121.9	9.5	0.1	0.0	1.0
BSe-450-2.5	61.5	85.5	23.3	2.5	1.4	0.2	62.1	2.6	0.2	0.0	1.0
BSe-450-5	68.4	175.4	42.8	9.9	0.9	0.1	132.6	13.7	0.1	0.0	1.0
BSe-550-2.5	46.5	70.9	18.5	2.9	1.2	0.2	52.4	3.1	0.1	0.0	1.0
BSe-550-5	53.3	147.1	39.1	19.8	0.8	0.2	107.9	25.4	0.1	0.1	1.0

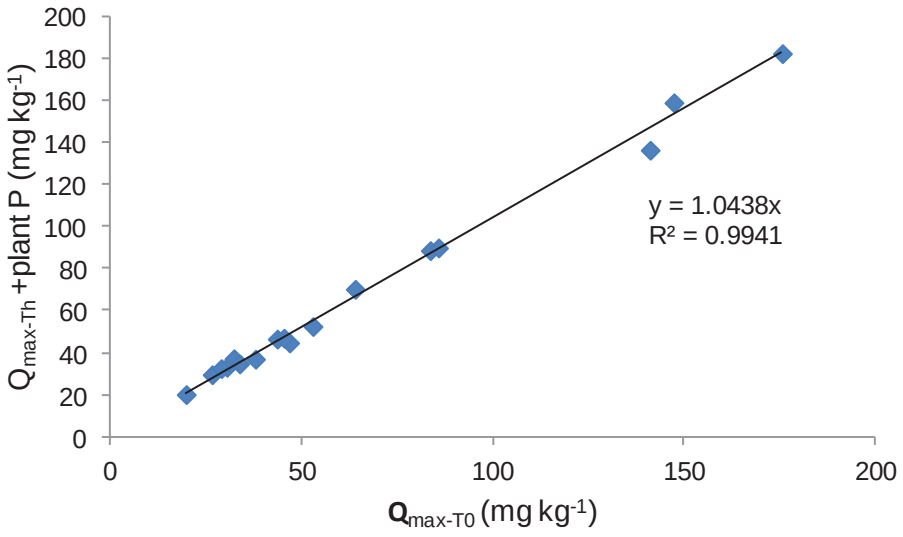

Figure 7-6. Relationship between estimated Q_{max}-T_0 and (Q_{max}-T_h + total plant P uptake).

7.4 Discussion

7.4.1 Soil P tests for soils amended with biochars

Both fertiliser P tests and soil P tests can be useful for evaluating P status of soils amended with fertilisers and deriving fertiliser recommendation to meet crop P requirement, while ensuring a low risk of water eutrophication (Saggar et al. 1992a; Sharpley et al. 2001; Horta and Torrent 2007). A 2% formic acid-extractable P (FA-P) has been proven to be a sensitive indicator of P bioavailability in biochars (Chapter 6) (Wang et al. 2012a). Soil P tests probably, however, are more favourable than fertiliser P methods in investigating the P status of biochar-amended soils, especially when studying the residual P effect of biochar. Oxalate extractable P (P_{ox}), an index of the total sorbed P (Maguire et al. 2000), could not be used to distinguish the range in P bioavailability in biochar amended soils that was apparent by using other soil testing methods (Lookman et al. 1995). Both resin and Olsen P extraction methods indicated that P availability varied widely among types of P sources (Figure 7-1), following an order as CaP > MAe biochars > BSe biochars > SPR. This was consistent with the previously published amounts of FA-P in each P source (except SPR) (Chapter 6)(Wang

et al. 2012a). Significant linear relationships existed between FA-P and resin-P ($r=0.96$, $p<0.01$) and FA-P and Olsen P ($r=0.89$, $p<0.01$, SI Figure S7-3) for feedstock, biochar and CaP treatments. Furthermore, resin-P was able to predict the plant P uptake at 6 harvests (data of 3 harvests and 9 harvests had the similar trend) in soil treated with biochars and CaP, but Olsen P did not adequately reflect plant P uptake in soil treated with BSe and SPR (SI Figure S7-4). This was in accord with previous finding that resin-P, compared with Olsen P, was a better predictor of P bioavailability in soils fertilised with sparingly soluble P sources such as BSe biochars and phosphate rocks (Saggar et al. 1992a; Saggar et al. 1992b). The present study proposes resin-P 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. Additionally, the possible use of resin-P to evaluate the release of P from biochar amended soils to leaching or runoff waters (Sharpley 1995) also needs further research.

7.4.2 P forms and availability

It is inappropriate to definitely assign the extractable P of the sequential extraction to certain P compounds. Empirically, however, resin-P can be considered as the readily available P for plant uptake and/or inducing water eutrophication (Hedley et al. 1994; Richards et al. 1995); NaOH-Pi generally associated with amorphous/crystalline Al/Fe and NaOH-Po as P related to labile organic matter (Hedley et al. 1994; Turner and Leytem 2004; Toor et al. 2006); H_2SO_4-P is normally considered as sparingly soluble Ca-P; and residual P is basically occluded P (Turner and Leytem 2004). In this study, soil treated with feedstock and biochar applications increased the resin-P and NaOH-Pi fractions (SI Figure S7-1). In contrast, soluble CaP application increased soil resin-P (mainly), NaOH-Pi and H_2SO_4-P; and SPR elevated the level of H_2SO_4-P. Results of MAe feedstock, BSe feedstock, CaP and SPR were comparable

with those from previous studies that used the similar P sources. For example, i) Hedley et al (1994) found that mono-calcium phosphate (MCP, the CaP treatment in this study) application significantly increased concentrations of resin-P, NaOH-Pi (major) and H_2SO_4-P to a less extent; ii) biosolids and manures (hog manure and cattle manure) were also observed to increase concentrations of resin-P, NaOH-Pi (major) and H_2SO_4-P (Kashem et al. 2004); iii) furthermore, however, phosphate rock (PR)-P was mainly (~ 95.5%) recovered in a 0.5 mol L^{-1} H_2SO_4 solution (Tambunan et al. 1993). The chemical composition of the P compounds within the P sources, in part, controls the rates and forms of soil P formed as the P source and soil react. For cattle manure (MAe) used in this study, P existed mainly as Mg- and Ca-P complexes which had a Ca to P ratio of < 2 (Chapter 6) (Wang et al. 2012a), favouring the formation of very soluble P mineral (Struvite and $CaHPO_4$) (Toor et al. 2006) that could be extracted by resin and NaOH extraction (NaOH-Pi). Phosphorus existing as amorphous Al-P complexes in Al-treated biosolids (Chapter 6), explains the high recovery of P from soil in the NaOH fraction.

Generally, NaOH-Pi is less available than resin-P but more labile than H_2SO_4-P to provide P to plants (Hedley et al. 1994; Negassa and Leinweber 2009). Therefore, CaP which contributed majorly to resin-P should have the most available P; whereas sparingly soluble SPR should be the least labile, and biochars in between. This is consistent with the results obtained from resin and Olsen P extractions (Figure 7-1), bioassay (Chapter 6) and successive resin P extractions (Table 7-2), further supporting the value of using P fractionation to follow the availability of P in soils amended with biochars and other P sources.

7.4.3 Transformation of P forms

Transformations of P fractions are influenced by a number of factors, such as time, soil properties, the stage of soil development, type of P sources, rhizosphere processes (e.g. root and microbial activities) and P uptake by plants etc (Zheng et al. 2002; Negassa and Leinweber 2009). Our results showed that rye grass growth caused significant ($P<0.05$) decrease in resin-P and NaOH-Pi for all treatments except those amended with SPR (Figure 7-4). The sum of the decrease in the amount of P in each fraction was almost equal to the amount of P depleted by plants (Figures 7-4C and 7-6). Plant showed a preferential uptake of P from the most labile fraction (resin-P). However, some of P could still be extracted by resin strips after plant growth when part of moderately labile (NaOH-Pi) and stable (H_2SO_4-P) P forms had been depleted (Figure 7-4). Therefore, it is concluded that resin extractable P exists in dynamic equilibrium with a range of P fractions (Schmidt et al. 1997) and moderately or even stable P pools can supplement the "labile P pool" when the concentration of the latter is decreased.

NaOH-Po has been reported to be either a source or a sink of labile and moderately labile P (Zheng et al. 2002; Kashem et al. 2004; Negassa and Leinweber 2009). Increase in NaOH-Po requires the accumulation of soil organic matter, such primary plant roots and exudates and secondary microbial biomass (Qian et al. 2004). The lack of increment in NaOH-Po in treatments studied could be attributed to i) the low concentration of organic P in MAe and BSe feedstock and biochars (Hedley and McLaughlin 2005; Wang et al. 2012a); ii) the adequate separation of plant roots and air-dried sandy soil, which limited the input of new organic P associated with roots (Negassa and Leinweber 2009); iii) the rapid decomposition of newly produced soil organic matter if any (Negassa and Leinweber 2009); iv) the fast hydrolysis of labile Po

fraction; and; v) the change in this fraction was so small that it could not be detected by the fractionation scheme used in this study (Qian and Schoenau 2000; Negassa and Leinweber 2009).

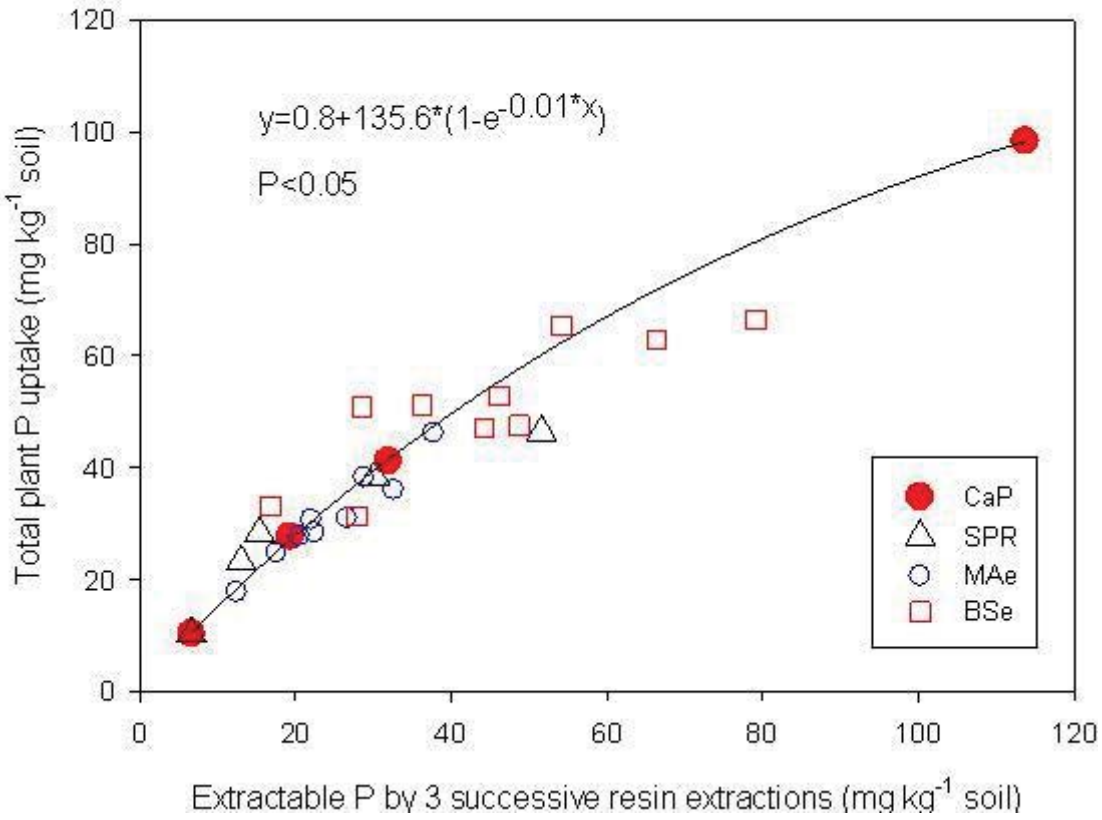

Figure 7-7. Total plant P uptake as a function of extractable P of three successive resin extractions (at T_0). Three successive resin extractions were chosen according to the amount of total plant P uptake. Data are mean of three replicates for P uptake and of two replicates for extractable P. The curve is the fit line of CaP data via a Mitscherlich-type modelling.

Successive resin extractions can be used to mimic P uptake by plant roots (as reflected in Figure 7-7) (Indiati 1998), assuming that the effect of biotic P transformation occurring in rhizosphere are negligible. A P fractionation was also conducted on the soils following 7 successive resin extractions (data not shown). The results showed that P successively desorbed via resin strips originated from NaOH-Pi fraction of original soil treated with CaP and biochars, which provided further evidence

of the transformation between labile and moderately labile P pools. Theoretically, all sorbed P (approximately equates to P_{ox} , as aforementioned) in soils should be releasable, although over different timeframes. However, our findings showed that $Q_{max\text{-}T0}$ was smaller than P_{ox} and the amount of P added (Table 7-2). This was attributed to i) the strong affinity of P for soil particles, consistent with apparently irreversible fixation of P in soil (Lookman et al. 1995) and; ii) possible underestimation of removed P by resin strips due to the adhesion of molybdate unreactive particulate P to the resin membrane (Lookman et al. 1995).

Compared with feedstock and lower temperature biochars, MAe-550 and BSe-550 showed the lowest % $Q_{max\text{-}T0}$/total P added. The reasons might be i) a part of P was trapped or blocked in the well-developed pore structures of biochar (Kercher and Nagle 2003), which was not accessible for DI water extraction; ii) these biochars showed high P adsorption capacity (Chen et al. 2011) and more P was likely to be irreversibly fixed; and iii) chemical structure of P bearing minerals (Adams and Campbell 1973; Gilkes and Palmer 1979) changed by thermal dehydration. Loss of hydroxyl groups of minerals [e.g. crandallite $CaAl_3(PO_4)_2(OH)_5{\cdot}(H_2O)$ loses most of the structural OH groups around 530°C (Frost et al. 2012)] would induce Al-phosphate or Fe-phosphate complex transforming from an outer sphere mode to an inner-sphere mode, and the latter generally has a higher stability and lower solubility. However, further study needs carrying out to test these speculations.

Two P pools (one is fast-release pool and the other one is slow-release pool) were calculated from the 2-component modelling (Table 7-2) of CaP and biochar fertilised soils but not SPR fertilised soil, where P dissolution, instead of desorption, was the rate-limiting step of P release. Generally, $(Q_{fast\text{-}T0,\ sample} - Q_{fast\text{-}T0,\ Control})/(Q_{max\text{-}T0,\ sample} - Q_{max\text{-}T0,\ Control})$ values (data not shown) followed a decreasing order of CaP ≥ MAe > BSe,

which was consistent with their bioavailability sequence. For CaP and MAe treatments, $Q_{fast\text{-}T0}$ accounted for >50% of the plant P uptake (estimated according to Equation (7-3) by inputting data from Table 7-2 and plant P). $Q_{slow\text{-}T0}$ would become increasingly important with time accounting for up to 40% of plant P uptake during 9 month of plant growth. For BSe treated soil, however, $Q_{fast\text{-}T0}$ accounted only 20% to 30% of $Q_{max\text{-}T0}$ and plant had to take up P from both P pools even at the early stages of plant growth. This further explained the relatively low availability of P in BSe treatment. The sum of ($Q_{max\text{-}Th}$ + plant P uptake) was slightly higher than $Q_{max\text{-}T0}$ (Figure 7-6), probably because of the accumulation of measurement errors.

7.5 Conclusion

Biochar technology has many benefits in environmental management, such as C sequestration, waste management, soil improvement and energy production. High quality biosolids and animal wastes represent an adequate feedstock for production of biochars. Biochar generally contains larger concentration of P than the feedstock from which it is produced. Our results showed that the type of feestock played a key role in controlling P bioavailability in biochars while pyrolysis temperature did so to a less extent when this was below 450 °C. Biochars had a lower availability than readily soluble P fertilisers but a higher availability than sparingly soluble rock phosphates. Generally, biochar P contributed to the readily available resin-P and moderately available NaOH-Pi fractions, and some equilibrium was likely to exist between these two fractions, both of which provided P for plant uptake. In a plant-sandy soil system as used in this study, depletion of P in resin-P and NaOH-Pi fraction was attributed to plant uptake rather than conversion into less available P forms (e.g. from NaOH-Pi to H_2SO_4-P).

Understanding the agronomic value of P in biochar and its environmental fate (as with any P fertiliser or manure) is essential for making appropriate recommendations with respect to dose, frequency and timing of application. For this, standard techniques for fertiliser analysis of total P and available P (e.g., 2% formic acid extraction, Chapter 6) (Wang et al. 2012a) should be carried out. If biochar is applied successively, the measurement of changes in the 0.1 M NaOH-Pi fraction seems a good method to estimate the residual available biochar P in the sandy soil used in this study. This may be applicable to a wider range of soils but requires confirmation with further research on contrasting soils under more realistic conditions.

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CHAPTER 8. OVERALL SUMMARY AND RECOMMENDATIONS FOR FUTURE RESEARCH

8.1 Overall summary

The current urgent need for sustainable and efficient waste management and sustained GHG emission mitigation strategies in New Zealand (and Globally) has led to the interest in the production of biochar from human and animal wastes. Biochars can have a wide range of properties, dependent on the nature of feedstocks, pryrolysis conditions and post-pyrolysis treatments. This range of properties leads to large uncertainties in previous studies of the effects of biochar applications on the surrounding ecology, and the productivity of particular crops under specific pedoclimatic conditions. It is essential to well-characterise biochars prior to land application and incorporation into soils. This thesis has presented results on the C stability and nutrient availability values of biochars produced from animal and human wastes under different pyrolysis temperatures. Special attention has been paid to the development of methodologies to adequately characterise biochars. All the information obtained will support the future development of the biochar technology to recycle nutrients and stabilise carbon from agricultural and municipal organic wastes.

8.1.1 Carbon in biochars

The C aromaticity of pyrolysis products, generated from both types of feedstocks, BSe and MAe, increased with pyrolysis temperature (250, 350, 450 and 550°C, indicating increasing C stability (Chapter 3, published as Wang T, Camps-Arbestain M and Hedley M 2013 Predicting C aromaticity of biochars based on their elemental composition. Org. Geochem. doi 10.1016/j.orggeochem.2013.06.012). Increasing aromaticity was associated with decreasing atomic H/organic C (H/C_{org}) ratio (Chapter 5), volatiles/(volatiles + fixed C) ratio (Chapters 5 and 6), C mineralisation rate (Chapter 5) and % $K_2Cr_2O_7$ oxidisable C (Chapter5).

According to the IBI Guidelines (IBI 2012), an upper H/C_{org} 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 is 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 (Chapter 5). Note that both organic H (H_{org}) and organic C (C_{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. This led us to develop a methodology to determine the carbonate-C in biochars, as shown in Chapter 4.

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 $CaCO_3$ standard (average recovery>96% with a relative experimental error <10% of carbonate-C). The acid treatment with a filtration step over-estimated the carbonate-C content (averagely by a 4-fold increment) due to the loss of dissolved/fine particulate organic C during the filtration. The acid fumigation method was suitable for biochars containing high amount of carbonate-C (>0.3% wt) and when the isotopic signature needs to be determined. TGA methods were reliable when calcite was the main carbonate form in biochars, but were found to be inadequate for samples containing considerable amount of whewellite and other carbonate-bearing minerals that decompose at < 600°C. As more than half of the samples studied (58%) contained< 0.4 % carbonate-C (and 38 % of these contained no detectable carbonate-C), a low-cost screening method was developed in order to identify the biochars that required

carbonate-C analysis. For this purpose, two methods were proposed: (i) an effervescence test using a 20% ethanol-1 M HCl water solution; and (ii) a graphic method by plotting the fixed C to total C ratio (fixed C/C) vs. H/C.

Aromaticity of biochar C can be extremely useful for the prediction of the mean residence time (MRT) of biochar C in soils. Solid state ^{13}C NMR spectroscopy associated with BD or DP techniques are generally used to quantitatively characterise aromatic C in biochars. However, these techniques are costly and time-consuming, and not always available. Therefore, based on data from literature and those from our study, simple models were examined to predict C aromaticity of biochars based on their elemental composition and fixed C content (Chapter 3). Using the content of C_{org}, H_{org}, N and O, the aromaticity of biochars can be estimated accurately (prediction error <8.5% of the measured value) without expensive NMR analysis.

8.1.2 Availability of N in biochars

A paper on this topic has been published (Chapter 5. Wang T, Camps Arbestain M, Hedley M and Bishop P 2012 Chemical and bioassay characterisation of nitrogen availability in biochar produced from dairy manure and biosolids. Org. Geochem. 51, 45-54). Biochars produced from MAe and BSe feedstocks at four pyrolysis temperatures (250, 350, 450 and 550 °C) were used for this study. Samples were treated with a 6 M HCl solution to fractionate labile N, which is considered the fraction of N that would be available in a short term; and with 0.167 M $K_2Cr_2O_7$ acid solution to determine potentially available N in the long term. An incubation study of samples 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 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 became more stable as pyrolysis temperature increased. As organic N is an integral part of the biochar structure, the availability of this N also depends on the lability of biochar C and this was reflected in similar changes in HCl hydrolysable N, volatile C, mineralised C, dichromate oxidisable C and N as a function of pyrolysis temperature. Therefore, a compromise needs to be reached if the production of a biochar with stable C and available N is targeted. The ratio of volatile C (representing labile C) to total hydrolysable N (THN) could be used as a useful indicator of whether net N mineralisation or immobilisation of N in biochar will occur. Given that the % labile C was low in biochars produced at high temperatures (450 and 550°C), those samples may only induce N immobilisation at the early stages of biochar application.

8.1.3 Availability of P in biochars

This section comprises two chapters (Chapters 6-7), one of which has been published (Chapter 6.Wang T, Camps-Arbestain M, Hedley M and Bishop P 2012 Predicting phosphorus bioavailability from high-ash biochars. Plant Soil 357, 173-187) and the other has recently been submitted (Chapter 7. The fate of phosphorus of ash-rich biochars in a soil-plant system). The same biochar samples that were used in Chapter 5, "The N availability study" were used for this research.

All samples were pyrolysed with the final kiln temperatures kept below 700°C (the temperature at which P starts to volatilise), so P in feedstock was fully recovered and enriched in the biochars. In order to determine the bioavailability of P in biochars, various methodologies were employed, 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 agreed in that P bioavailability diminished following the order of dihydrogen phosphate (CaP) > MAe biochars> BSe biochars > Sechura phosphate rocks (SPR). Based on data of plant P uptake and extractable P, 2% formic acid extractable P (FA-P) was found to be a sensitive indicator of P bioavailability in biochars according to a Mitscherlich-type modelling ($y=y_0 + a - a \cdot e^{-bx}$). In addition, resin-P was considered 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 extraction. P availability in biochars produced at 550°C was lower than in those produced at lower temperatures and this was attributed to (i) noticeable amount of P can be fixed in biochars due to the well-developed pore structures and large surface area; and (ii) labile non-crystalline P may be re-crystallised into stable P forms owing to thermal treatment. Therefore in biochars with a considerable P fertiliser value (as MAe and BSe biochars in this thesis), more attention should be paid to the pyrolysis temperature region of 450–550°C to achieve a compromise between P availability and C stability.

For a further understanding of biochar P availability and its transformation in soils, P forms in biochar-amended soils were investigated according to the Hedley fractionation procedure. Generally, biochar P contributed to the readily available resin-P and moderately available NaOH-Pi fractions, and some equilibrium was likely to exist between these two fractions, both of which provided P for plant uptake. In a plant-sandy

soil system, as used in this study, depletion of P in resin-P and NaOH-Pi fraction was attributed to plant uptake rather than conversion into less available P forms (e.g. from NaOH-Pi to H_2SO_4-P).

In summary, high-ash biochars with high P concentrations are 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 of biochars, so that dose, frequency and timing of application are correctly established..

8.1.4 Highlights of this thesis

- A model was developed to predict C aromaticity of biochars based on their elemental composition (Chapter 3)
- A method was obtained to determine carbonate-C in biochars (Chapter 4)
- Stability of C and N in biochars was shown to increase as pyrolysis temperature increased (Chapters 3 and 5)
- High-ash biochars with high P concentrations have the potential to be used as slow-release P fertilisers. 2% formic acid extractable P could be used as an indicator of P availability in biochars (Chapters 6 and 7)
- Biochar production can be used to recover P from organic wastes of good quality (i.e. low in heavy metal); however, over-application of specific P-rich biochar can also induce P accumulation in soils. Dose, frequency and timing of application can be correctly established if information on available P in biochars is known (Chapter 7)

8.2 Recommendations for future research

The economic feasibility of biochar technology determines the likelihood of its implementation and future development. At present, production and soil application of biochar solely for GHG abatement may not be economically attractive, as the current C trading price is rather low (4.72€/t CO_2 on March 28th, 2013, according to EU Emission Allowances, http://www.eex.com/en/Market%20Data/Trading%20Data/Emission%20Rights/EU%20Emission%20Allowances%20%7C%20Spot). However, the price of C trading is expected to increase as the public acceptance of the social cost of global warming increases (Lehmann 2007) and when the world economy recovers from global financial crisis (Nazifi 2013). Additionally, the potential benefits from biochar production and application (e.g. energy production, soil improvement and reclamation, waste management and other environmental benefits) merit biochar for further investigation.

The following aspects may need special attention.

- **Precise knowledge on biochar C stability and its benefits needs results from long-term experiments under more realistic field conditions.**

  Biochar was proposed as a GHG mitigation strategy due to the high stability – and thus longevity – of biochar C compared to that of the biomass from which it is produced. However, the length of time biochar can remain in soil and benefit soil functions it is still disputed. Existing estimations of the mean residence time (MRT) of biochar C are generally based on data from short-term incubations under controlled conditions in the laboratories. This may under-estimate the stability of biochar as only labile C can be degraded during the early stage of C decomposition (Singh et al. 2012). Therefore, long-term incubations in the laboratories and/or under field conditions need to be designed and conducted in the future. Inter-laboratory comparisons and/or international

collaborations may be necessary to work out the interactions of biochar and soil organic matter on a case-by-case basis, as both the properties of biochars and soils vary widely. Furthermore, some properties of biochar, e.g. the cation exchange capacity (CEC), will evolve with pedogenesis and necessitate further study. In addition, the effects of biochar on plant growth and soil quality may also be dependent on time scale. For example *Terra Preta* (~800 years old before present) have proven to be very fertile soils in this regard, although it should be kept in mind that *Terra Preta* are not only soils rich in charcoal but also abundant in human and animal wastes and therefore not directly comparable to solely biochar-amended soils.

- **Producing biochars for soil remediation and restoration.**

  As it is not economically feasible to produce biochar specifically for C sequestration, the potential added values of biochar should be explored further. Specific biochar have a large surface area and high hydrophobicity, which can be used to remediate polluted sites dominated by hydrophobic organic contaminants. However, whether biochar application can help the restoration of soil quality (especially on microbial diversity and structure) needs further investigation. Areas that are investigated first require a high return per unit biochar used.

- **Enriching nutrients in biochars from wastewater treatment.**

  In this thesis, I have demonstrated that P enriched in biochar can be available for plant uptake. However, many biochars produced from wood biomass may contain very low content of P and N. In New Zealand, the municipal wastewater and farm effluents, rich in P and N and low in toxic metals, may be a good source to combine with biochar for further soil amendment.

- **Environmental risks may arise from multiple/over-applications of biochars.** Negative environmental impacts associated with nutrients, metals, metalloids and organic pollutants in biochars after its first application to soil at low doses are likely to be minimal (Freddo et al. 2012). However, over- and multiple-applications of biochar may cause nutrient (e.g. P) and heavy metal (e.g. Cd in BSe biochars) accumulation in soils, which can lead to environmental problems such as water eutrophication and toxic metal pollution. Therefore, environmental risk assessments associated with multiple/over-applications of biochars should be conducted in future studies.

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APPENDIX

Appendix I. Supporting information for Chapter 3 (S3)

Materials and methods

HF treatment and elemental analysis

~2 g biochars were shaken with 10% HF for 2 h and centrifuged to remove the supernatant at room temperature. The procedure was repeated for 4 times (Gonçalves *et al.*, 2003; Rumpel *et al.*, 2006). This method was found in our preliminary study as effective as 2%HF-HCl mixture to remove ash in biochars. The residues were filtered through a Whatman No 542 filter paper, rinsed with DI water and dried at a 60°C oven. Total C, H and N in original biochar and treated samples were determined using an elemental analyser (Elementar, Vario MACRO, Germany). All the analyses were conducted in duplicates.

Table S3-1. An overview of published data on biochar elemental composition, aromaticity, ash content and fixed C content. $f_{a\text{-}pre}$ is predicted f_a and $f_{a\text{-}exp}$ is the measured f_a by DP-NMR techniques. Non-grey-shaded data were used for calibrating Model 2 as discussed in Chapter 3.

No.	Reference	samples	Elemental composition (daf)				ash (dry)	FC (daf)	atomic ratio		$f_{a\text{-}exp}$	$f_{a\text{-}pre}$		
			C%	H%	O%	N%	%	%	H/C	O/C		M1	M2	M3'
1	(Cao et al., 2012)	maple wood (MW)	53.90	6.90	37.70	0.00	1.00	N.A.	1.53	0.52	0.10	0.04	-0.07	N.A.
2		MW 300	61.30	5.60	31.80	0.00	0.80	N.A.	1.11	0.39	0.41	0.48	0.45	N.A.
3		MW 350	74.10	4.70	18.50	0.00	2.20	N.A.	0.77	0.19	0.71	0.74	0.77	N.A.
4		MW 400	76.10	4.10	17.60	0.00	1.70	N.A.	0.64	0.17	0.83	0.82	0.83	N.A.
5		MW 500	84.70	3.30	9.70	0.00	1.80	N.A.	0.47	0.09	0.93	0.89	0.92	N.A.
6		MW 600	88.20	2.60	6.50	0.00	2.20	N.A.	0.35	0.06	0.96	0.94	0.96	N.A.
7	(McBeath et al., 2011; Kaal et al., 2012)	Chestnut wood (CW) 200	50.30	5.60	44.20	0.10	N.A.	N.A.	1.33	0.66	0.14	0.27	0.07	N.A.
8		CW 250	54.30	5.30	40.10	0.10	N.A.	N.A.	1.16	0.55	0.29	0.44	0.30	N.A.
9		CW 275	64.10	4.30	31.40	0.20	N.A.	N.A.	0.80	0.37	0.72	0.72	0.68	N.A.
10		CW 300	69.50	4.00	26.10	0.20	N.A.	N.A.	0.69	0.28	0.78	0.79	0.77	N.A.
11		CW 350	73.40	3.20	23.00	0.30	N.A.	N.A.	0.52	0.24	0.88	0.87	0.87	N.A.
12		CW 400	78.10	3.00	18.50	0.30	N.A.	N.A.	0.46	0.18	0.89	0.90	0.90	N.A.
13		CW 500	87.10	2.70	9.80	0.30	N.A.	N.A.	0.36	0.08	0.99	0.93	0.95	N.A.
14		CW 600	93.80	1.90	3.90	0.30	N.A.	N.A.	0.24	0.03	1.00	0.96	0.98	N.A.
15		CW 700	95.10	1.10	3.30	0.50	N.A.	N.A.	0.14	0.03	1.00	0.98	0.99	N.A.
16		CW 800	96.00	0.70	2.40	0.70	N.A.	N.A.	0.08	0.02	1.00	0.99	1.00	N.A.
17		CW 900	96.50	0.30	2.20	0.80	N.A.	N.A.	0.04	0.02	1.00	0.99	1.00	N.A.
18		CW 1000	96.30	0.20	2.50	1.00	N.A.	N.A.	0.03	0.02	1.00	0.99	1.00	N.A.
19	Baldock and Smernik, 2002	Pine wood (PW) 70	46.90	5.90	44.90	0.10	0.20	N.A.	1.52	0.72	0.17	0.06	-0.17	N.A.
20		Pine wood (PW) 150	46.90	5.70	43.90	0.10	0.30	N.A.	1.45	0.70	0.20	0.14	-0.09	N.A.

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21		Pine wood (PW) 200	50.90	4.30	41.30	0.10	0.30	N.A.	1.01	0.61	0.38	0.57	0.42	N.A.
22		Pine wood (PW) 250	58.00	2.40	34.00	0.20	0.50	N.A.	0.51	0.44	0.83	0.88	0.83	N.A.
23		Pine wood (PW) 300	58.40	2.20	31.50	0.30	0.70	N.A.	0.45	0.40	0.84	0.90	0.86	N.A.
24		Pine wood (PW) 350	61.90	2.80	26.30	0.20	0.80	N.A.	0.54	0.32	0.82	0.86	0.84	N.A.
25		PW 450	77.90	3.40	14.40	0.70	N.A.	N.A.	0.52	0.14	0.93	0.87	0.89	N.A.
26		Brewer 1	74.40	4.00	19.90	1.50	60.30	64.60	0.65	0.20	0.81	0.81	0.83	0.83
27		Brewer 2	72.60	4.60	21.30	1.40	56.70	59.80	0.76	0.22	0.75	0.75	0.76	0.79
28		Brewer 3	67.80	6.00	25.10	1.10	44.70	45.40	1.06	0.28	0.60	0.53	0.54	0.64
29		Brewer 4	66.60	5.50	26.50	1.30	47.60	48.70	1.00	0.30	0.62	0.58	0.59	0.70
30		Brewer 5	85.00	0.40	13.30	1.60	74.30	79.90	0.06	0.12	0.85	0.99	1.00	0.90
31		Brewer 6	87.30	2.90	7.60	2.10	61.70	82.40	0.40	0.07	0.92	0.92	0.95	0.91
32		Brewer 7	76.40	4.50	18.10	1.00	50.90	65.70	0.70	0.18	0.78	0.78	0.80	0.83
33		Brewer 8	92.20	4.30	2.30	1.10	55.80	73.10	0.56	0.02	0.87	0.86	0.90	0.76
34		Brewer 9	85.20	3.80	9.90	1.00	50.50	71.70	0.54	0.09	0.87	0.86	0.90	0.81
35		Brewer 11	83.20	0.90	14.70	0.90	67.90	77.50	0.13	0.13	0.84	0.98	0.99	0.89
36		Brewer 13	83.80	2.80	11.90	1.50	53.00	84.80	0.40	0.11	0.94	0.92	0.94	0.97
37	(Brewer et al.,	Brewer 14	81.50	3.50	14.20	0.80	23.90	75.60	0.52	0.13	0.85	0.87	0.90	0.89
38	2011)	Brewer 15	85.10	2.60	11.80	0.50	7.00	81.30	0.36	0.10	0.88	0.93	0.95	0.92
39		Eucalyptus wood (EW) 400 activated	71.06	3.17	25.49	0.28	2.24	59.51	0.53	0.27	0.85	0.87	0.85	0.80
40		EW 550 activated	86.90	2.68	9.99	0.43	5.33	78.17	0.37	0.09	0.99	0.93	0.95	0.86
41		EW 400 non-activated	70.97	3.43	25.36	0.23	2.73	59.86	0.58	0.27	0.83	0.85	0.83	0.81
42		EW 550 non-activated	87.36	2.73	9.46	0.45	6.33	81.86	0.37	0.08	0.99	0.93	0.95	0.90
43	(Singh et al., 2012)	Eucalyptus leaves (EL) 400 activated	71.36	3.93	22.78	1.93	7.42	63.46	0.66	0.24	0.82	0.81	0.81	0.85

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44		EL 550 activated	78.25	3.18	16.52	2.05	9.26	69.71	0.49	0.16	0.92	0.89	0.90	0.86
45	(Mercedes Maroto-Valer et al., 1998)	coal	87.80	4.40	6.10	1.70	8.70	N.A.	0.60	0.05	0.87	0.84	0.88	N.A.
46		pcc-1	88.20	4.00	6.20	1.60	8.80	N.A.	0.54	0.05	0.91	0.86	0.90	N.A.
47		pcc-2	89.70	3.20	5.70	1.40	9.20	N.A.	0.43	0.05	0.97	0.91	0.94	N.A.
48		biochar	81.00	3.10	15.60	0.30	<0.10	N.A.	0.46	0.14	0.97	0.90	0.91	N.A.
49		ct-ti	92.10	2.70	4.30	0.90	N.A.	N.A.	0.35	0.04	0.99	0.93	0.96	N.A.
50		ctp-ti	92.90	3.40	2.70	1.00	N.A.	N.A.	0.44	0.02	0.99	0.91	0.94	N.A.
51	(Zimmermann et al., 2012)	B1998	82.75	2.44	10.05	0.16	5.50	N.A.	0.35	0.09	0.92	0.93	0.95	N.A.
52		B2008	91.74	1.71	7.83	0.04	3.10	N.A.	0.22	0.06	0.93	0.97	0.98	N.A.

daf: dry and ash-free;
N.A.: data not available
M: model

Table S3-2. Quantitative NMR spectral analysis of biochars from DP spectra (adopted from Brewer *et al.*, 2011)

Biochar #	Carbonyls		Aromatics			Alkyls					
Moieties	C=O	COO	$CO_{0.75}H_{0.5}$	$C_{non\text{-}pro}$	C–H	$HCO_{0.75}H_{0.5}$	$CH_{1.5}$	CH_3	total O	C=O double bonds	θ
ppm	210–183	183–165	165–145	145–70	145–90	90–50	50–25	25–6			
1	3	5	12	44	26	2	4	4	23.50	8.00	0.34
2	4	4	11	39	25	7	5	5	25.50	8.00	0.31
3	4	6	11	27	23	21	6	5	40.00	10.00	0.25
4	4	5	11	30	21	17	7	6	35.00	9.00	0.26
5	2	4	6	69	10	4	4	2	17.50	6.00	0.34
6	1	1	7	56	29	3	2	2	10.50	2.00	0.19
7	4	5	13	45	21	5	4	4	27.50	9.00	0.33
8	3	4	10	55	21	2	2	3	20.00	7.00	0.35
9	2	3	9	53	25	3	2	3	17.00	5.00	0.29
11	2	5	7	68	9	4	4	2	20.25	7.00	0.35
13	1	1	7	53	34	1	2	1	9.00	2.00	0.22
14	2	2	11	52	22	3	3	4	16.50	4.00	0.24
15	2	3	9	57	22	2	2	3	16.25	5.00	0.31
average									21.42	6.31	0.29

a. C non-pro non-protonated aromatic carbon, error margins ± 2%

b. All values are % of total ^{13}C signal. $CO_{0.75}H_{0.5}$ moieties assume a 1:1 ratio of alcohols and ethers. $CH_{1.5}$ moieties assume a 1:1 ratio of CH_2 and CH groups

c. total O=1* (C=O) + 2*(COO) + 0.75*($CO_{0.75}H_{0.5}$) + 0.75*($HCO_{0.75}H_{0.5}$)

d. C=O double bonds = 1* (C=O) + 1*(COO); therefore, θ = [1* (C=O) + 1*(COO)]/[1* (C=O) + 2*(COO) + 0.75*($CO_{0.75}H_{0.5}$) + 0.75*($HCO_{0.75}H_{0.5}$)]

A5

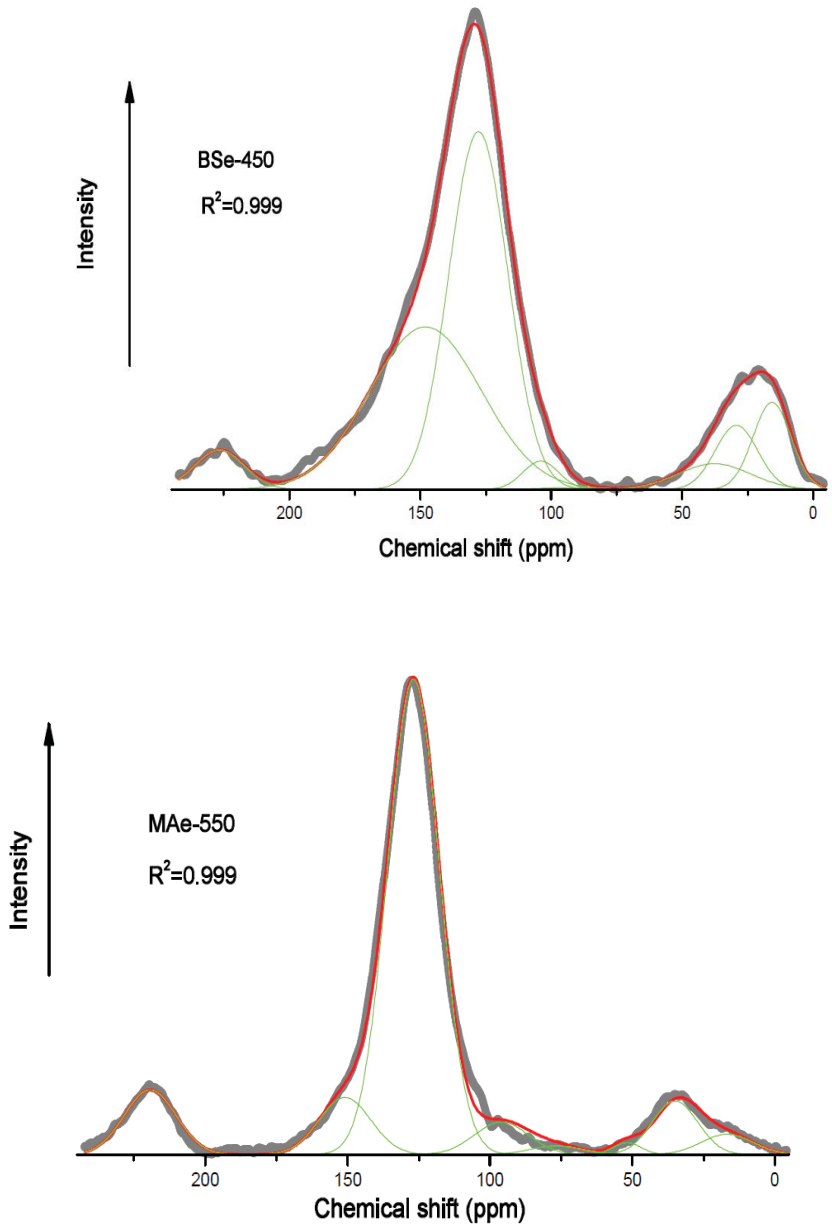

Figure S3-1. Fitted deconvolution components of DP NMR spectra of BSe-450 and MAe-550

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Appendix II. Supporting information for Chapter 4 (S4)

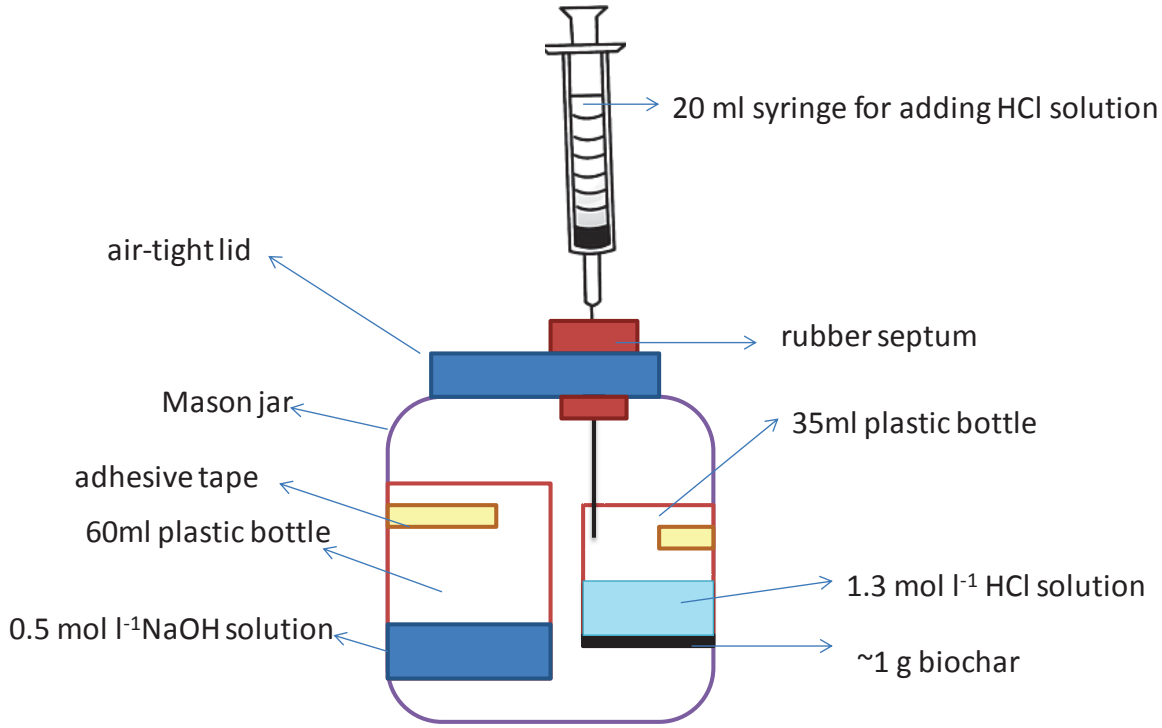


Figure S4-1. An apparatus used for trapping CO_2 evolved from biochar after addition of HCl solution

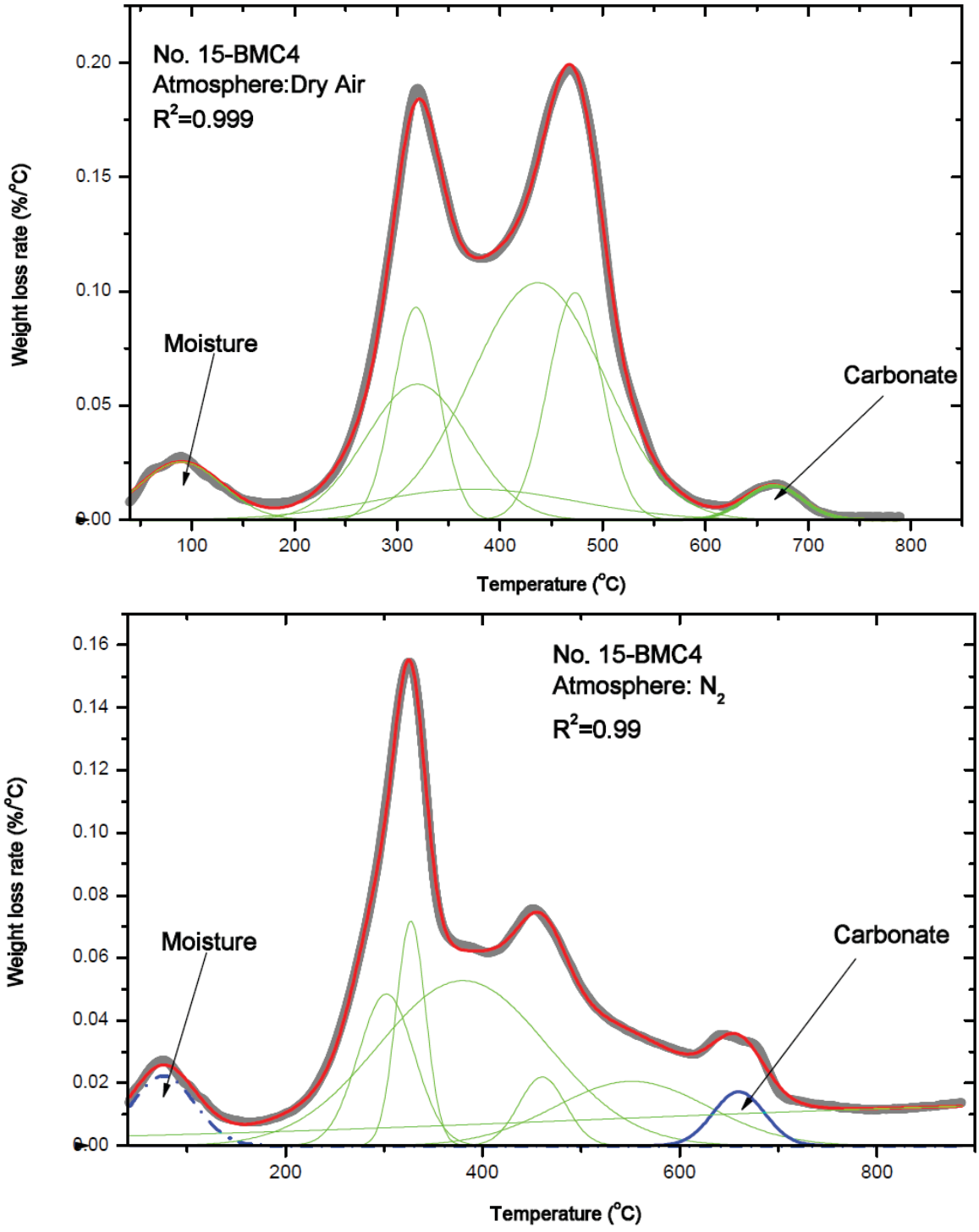


Figure S4-2. Examples of deconvolution of peaks associated with carbonate decomposition

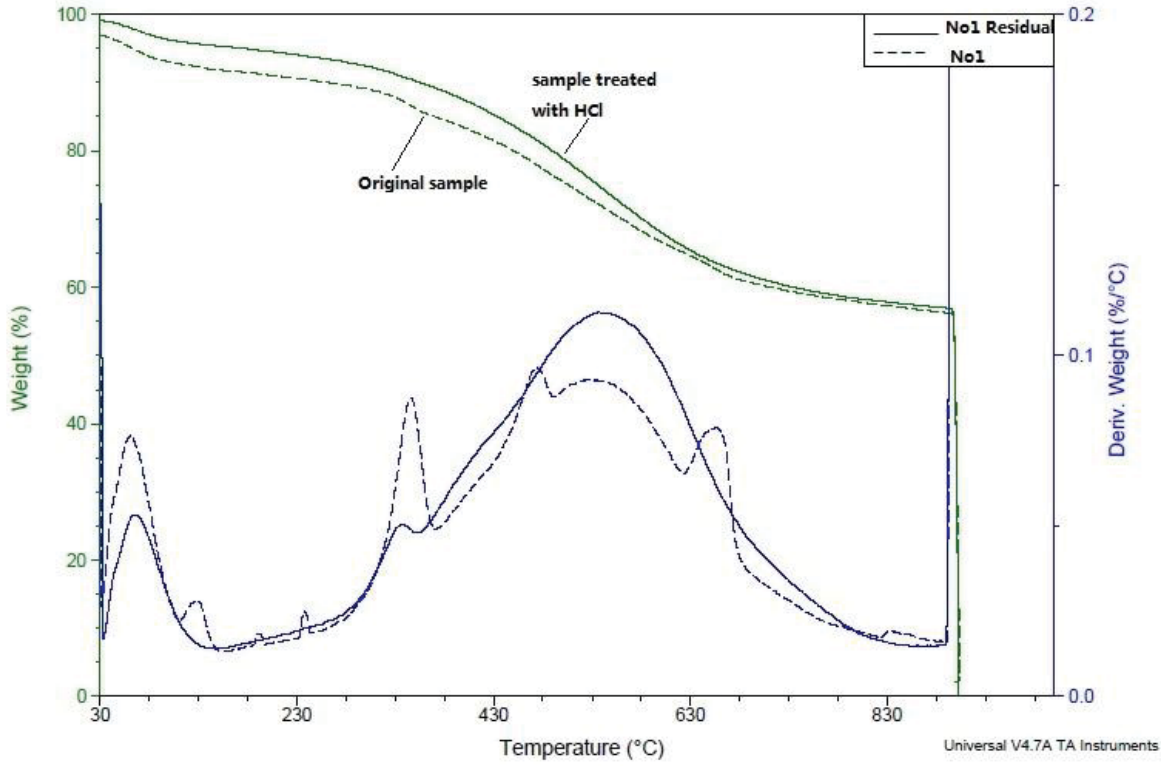


Figure S4-3. TG/DTGA curves of sample No1 and its residual after acid treatment

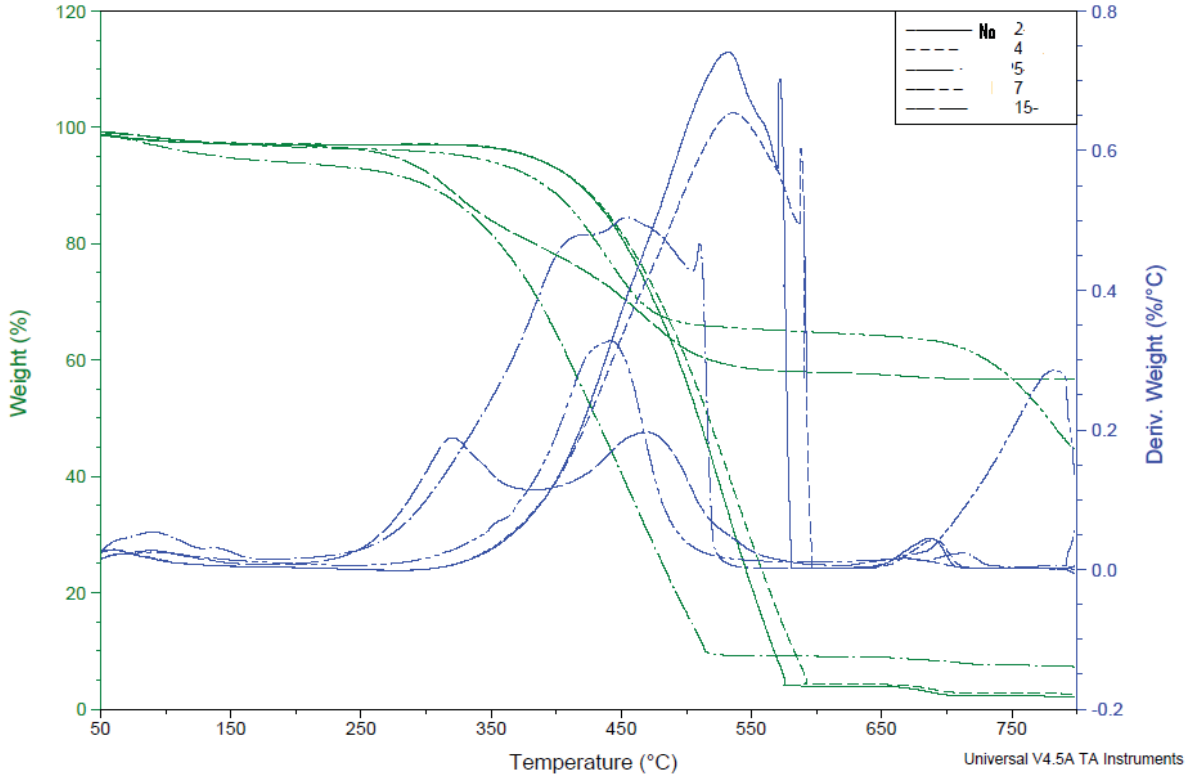


Figure S4-4. TG/DTG curves of selected samples. Samples were run in an air atmosphere.

Table S4-1. Decomposition temperature zones of common carbonate minerals and compounds

Minerals	Decomposition temperature zones (°C)	Reference
Minerals		
dolomite	600-800	(Samtani et al. 2002)
magnesite	500-650	
calcite	600-800	
synthetic calcite	520-595	
synthetic strontianite	750-850	(Frost et al. 2009)
synthetic witherite	>900	
ankerite	700–800	
wollastonite	400-800	(Vassileva and Vassilev 2005)
larnite	500-900	
siderite	500-600	
Pure compounds		
$BaCO_3$	1300	
$CdCO_3$	500	
$CaCO_3$ (aragonite)	825	
$CaCO_3$ (calcite)	825	
$Ca[Mg(CO_3)_2]$	730	
$CuCO_3$	200	
$FeCO_3$	not stable	(Dean 1999)
$PbCO_3$	340	
Li_2CO_3	1300	
$MnCO_3$	>200	
K_2CO_3	>900	
Na_2CO_3	>858	
$SrCO_3$	1100	
$ZnCO_3$	300	

References

Dean J A 1999 Lange's handbook of chemistry. McGRAW-HILL, INC.

Frost R L, Hales M C and Martens W N 2009 Thermogravimetric analysis of selected group (ii) carbonateminerals — implication for the geosequestration of greenhouse gases. J. Therm. Anal. Calorim. 95, 999-1005.

Samtani M, Dollimore D and Alexander K S 2002 Comparison of dolomite decomposition kinetics with related carbonates and the effect of procedural variables on its kinetic parameters. Thermochim. Acta 392–393, 135-145.

Vassileva C G and Vassilev S V 2005 Behaviour of inorganic matter during heating of bulgarian coals: 1. Lignites. Fuel Process. Technol. 86, 1297-1333.

Appendix III. Supporting information for Chapter 5 (S5)

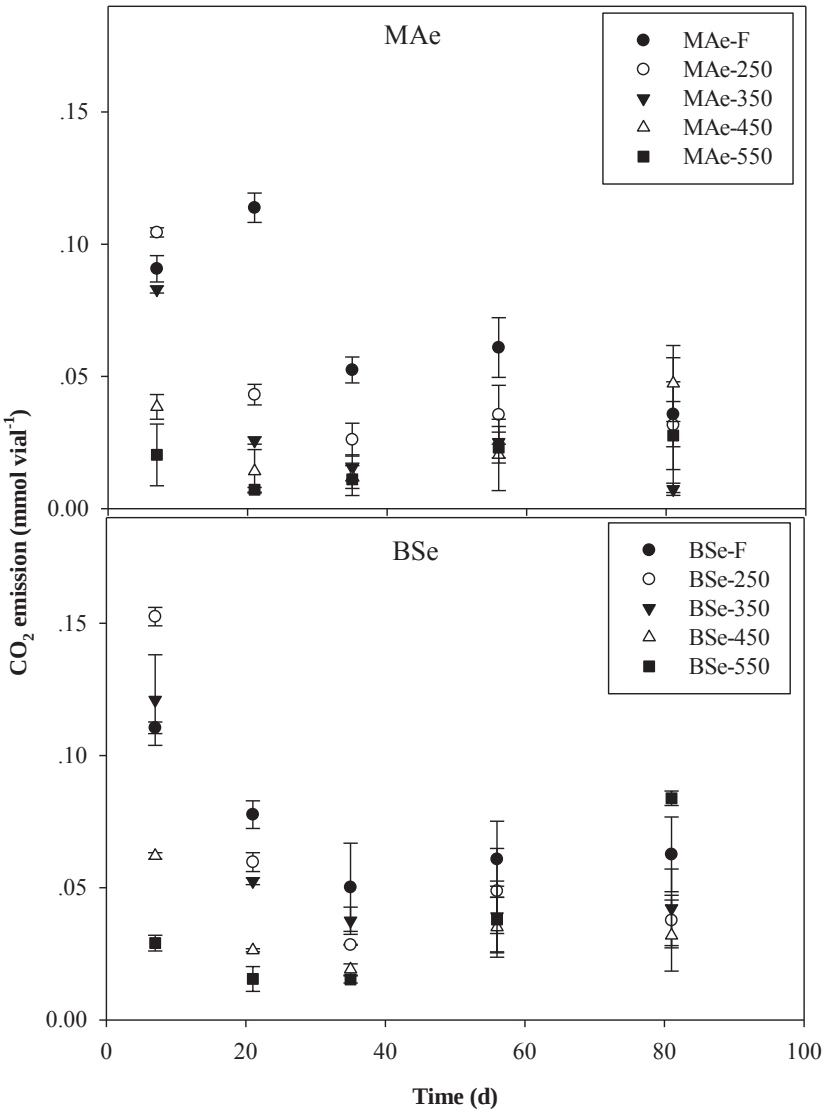


Figure S5-1. CO_2 evolution at different sampling times. The data are the cumulative CO_2 evolved at specific sampling intervals.

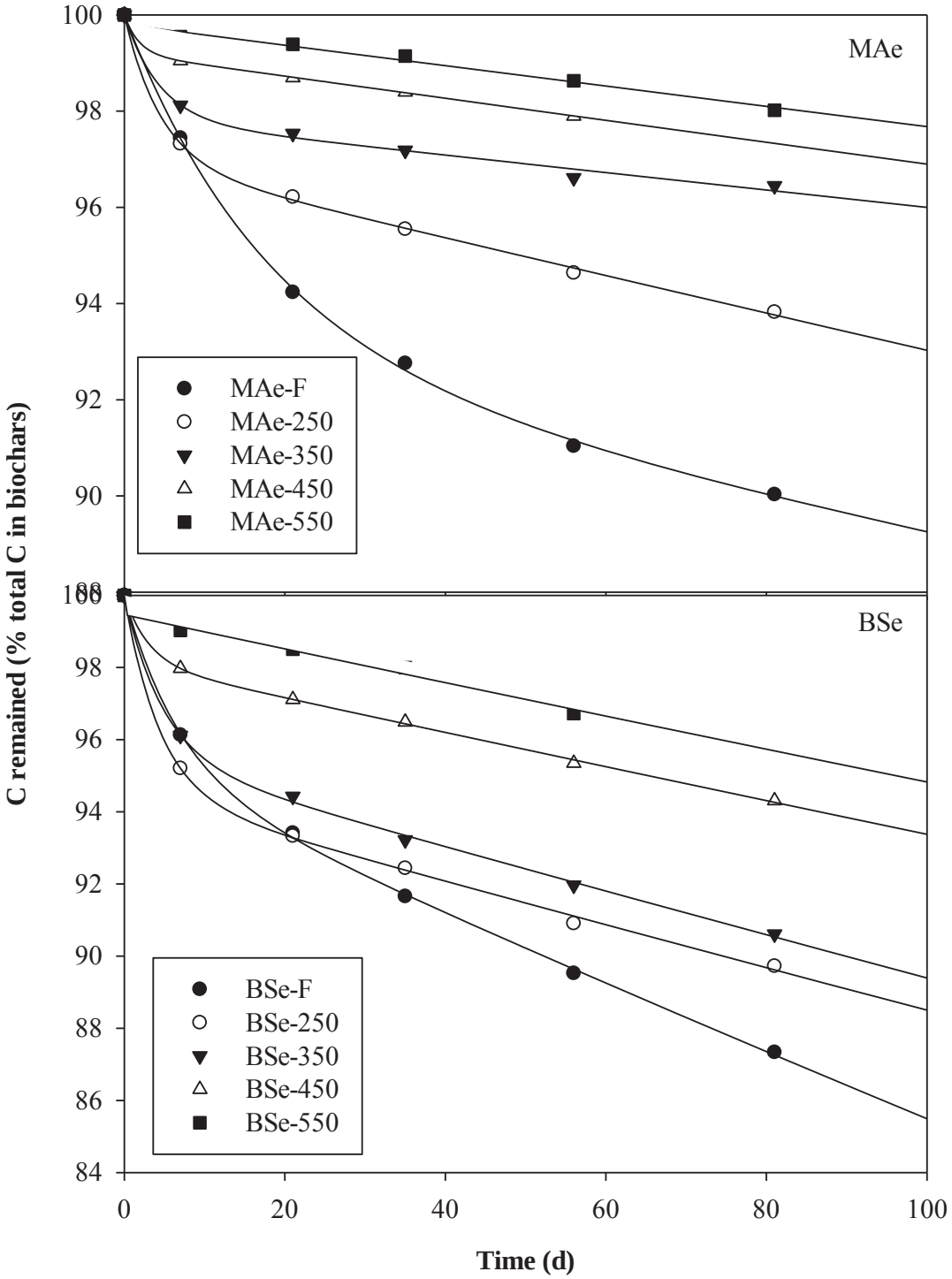
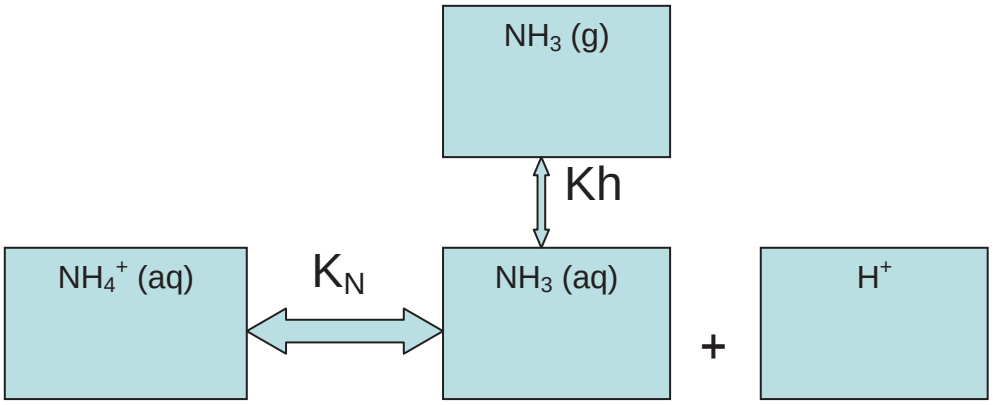


Figure S5-2. A 2-component decay model for C decomposition in biochars.

Modelling ammonia volatilization from the biochar-sand mixtures in a sealed jar



(S5-1)

In a sealed jar, the relationships between NH_4^+ (aq) and NH_3 (aq), NH_3 (aq) and NH_3 (g) are shown in Formula (S5-1), from which we can get the following equations (Sommer and Olesen, 2000), assuming the activity constant of NH_4^+ (aq) to be 1 (when concentration of NH_4^+ is low in the sand pore water)

$$[TotalNH_4(aq)] = [NH_3(aq)] + [NH_4^+(aq)] \quad \text{(S5-2)}$$

$$[NH_3(aq)] = \frac{[TotalNH4]}{1 + [H^+]/K_N} \quad \text{(S5-3)}$$

$$[NH_3(g)] = K_H[NH_3(aq)] = \frac{14K_h}{RT}[NH_3(aq)] \quad \text{(S5-4)}$$

where

K_N is the equilibrium constant of reaction between NH_4^+ (aq) and NH_3 (aq);

K_H and K_h are the Henry's law constants based on concentration and partial pressure respectively;

R is the gas constant and T the absolute temperature.

K_N and K_h can be estimated according to the following equations (Beutier and Renon, 1978).

$$\ln(K_N) = -177.95292 - 1843.22/T + 31.4335\ln(T) - 0.0544943T \quad \text{(S5-5)}$$

$$\ln(K_h) = -160.559 - 8621.06/T - 25.6767\ln(T) + 0.035388T \quad \text{(S5-6)}$$

Therefore, at 32 ^{o}C, $K_N = 9.19119\times10^{-10}$ and $K_h = 0.022546851$.

The free volume of the sealed jar (subtracting the volumes of vials and samples) is ca. 900 ml. The total NH_3 volatilization can be neglected in a sealed jar, as shown in Figure S5-3, when the total amount of N is 100 mg l^{-1}.

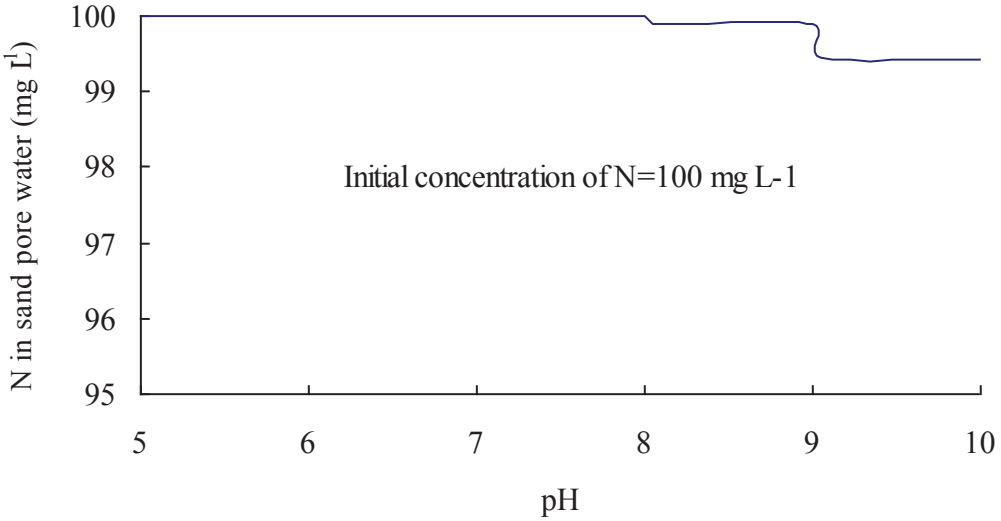


Figure S5-3. N concentration in sand pore water as a function of pH in a sealed jar

References

Beutier, D., Renon, H., 1978. Representation of NH_3-H_2S-H_2O, NH_3-CO_2-H_2O, and NH_3-SO_2-H_2O vapor-liquid equilibria. Industrial & Engineering Chemistry Process Design and Development 17, 220-230.

Sommer, S.G., Olesen, J.E., 2000. Modelling ammonia volatilization from animal slurry applied with trail hoses to cereals. Atmospheric Environment 34, 2361-2372.

Appendix IV. Supporting information for Chapter 7 (S7)

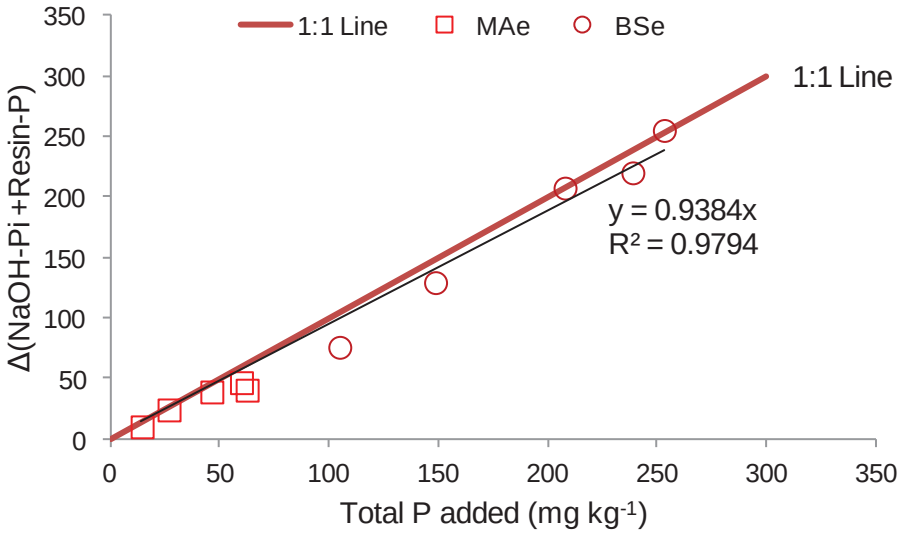


Figure S7-1. Relationship between total P added and the increment of (resin-P + NaOH-Pi) [Δ(resin-P + NaOH-Pi)] of the biochar treatments compared with the control treatment at T_0. Data are shown on the basis of dry soil weight (mg kg^{-1} soil).

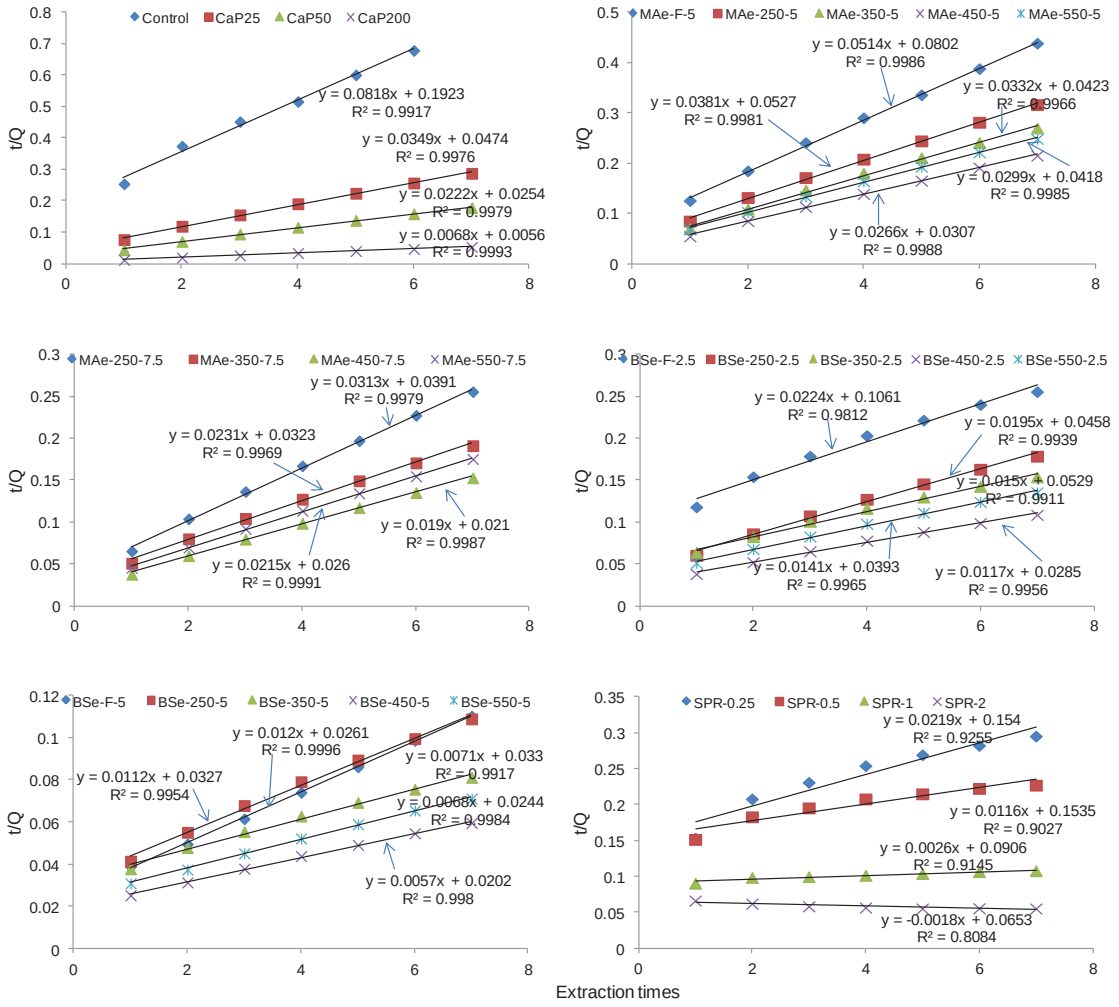


Figure S7-2. Application of the PSO (pseudo-second-order) model to estimate the maximum P release capacity of soils fertilised with different P sources

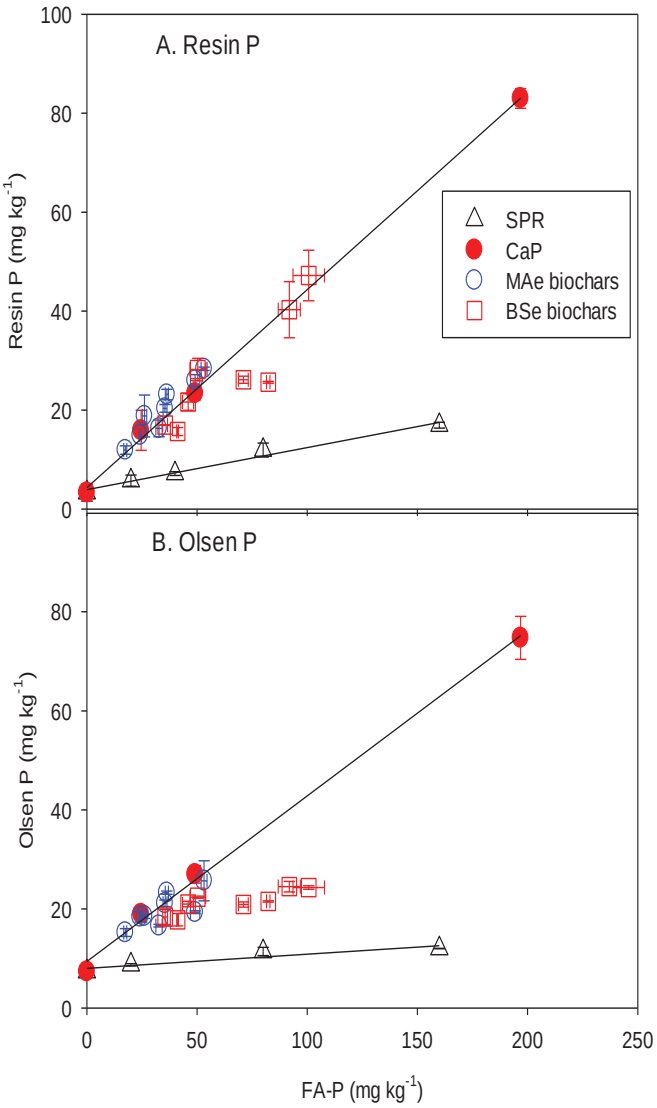


Figure S7-3. Relationships of 2% formic acid extractable P (FAs-P) (Chapter 6) to resin P and Olsen P in soil amended with BSe and MAe feedstocks and biochars, CaP and SPR. Lines are fitted lines for CaP and SPR treatments respectively.

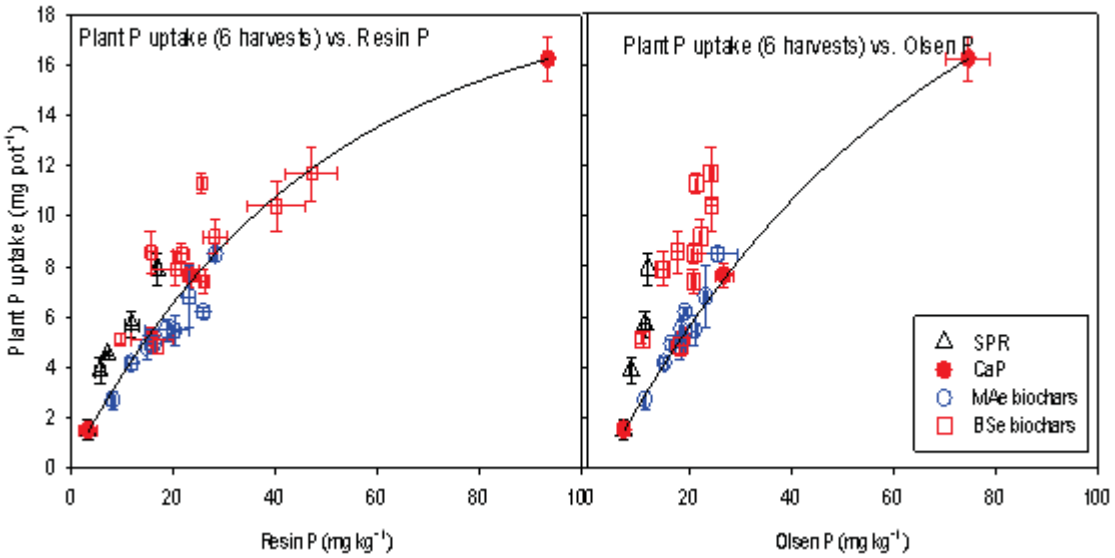


Figure S7-4. Plant P uptake (first 6 harvests) vs resin-P or Olsen P fitted by the Mitscherlich-type equation [$y=y_0 + a - a \cdot e^{-bx}$] (Chapter 6). The fit lines were based on the data of CaP treatment. The CaP model using resin-P data could be used to predict P uptake of plants grown in soil fertilised with both MAe and BSe; however, the CaP model using Olsen P data underestimated the P uptake of plants grown in soils amended with BSe biochars.