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Biochar – synergies and trade-offs between soil enhancing properties and C sequestration potential

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Abstract

The characterisation of biochar has been predominantly focused around determining physicochemical properties including chemical composition, porosity, and volatile content. To date, little systematic research has been done into assessing the properties of biochar that directly relate to its function in soil and how production conditions could impact these. The aim of this study was to evaluate how pyrolysis conditions can influence biochar's potential for soil enhancing benefits by addressing key soil constraints, and identify potential synergies and restrictions. To do this, biochar produced from pine wood chips (PC), wheat straw (WS) and wheat straw pellets (WSP) at four highest treatment temperatures (HTT) (350°C, 450°C, 550°C and 650°C) and two heating rates (5°C min⁻¹ and 100°C min⁻¹) were analysed for pH, extractable nutrients, cation exchange capacity (CEC), stable-C content and labile-C content. HTT and feedstock selection played an important role in the development of biochar functional properties while overall heating rate (in the range investigated) was found to have no significant effect on pH, stable-C or labile-C concentrations. Increasing the HTT reduced biochar yield and labile-C content while increasing the yield of stable-C present within biochar. Biochar produced at higher HTT also demonstrated a higher degree of alkalinity improving biochar's ability to increase soil pH. The concentration of extractable nutrients was mainly affected by feedstock selection while the biochar CEC was influenced by HTT, generally reaching its highest values between 450°C – 550°C. Biochar produced at >550°C showed high combined values for C stability, pH and CEC while lower HTTs favoured nutrient availability. Therefore attempts to maximise biochar's C sequestration potential could reduce the availability of biochar nutrients. Developing our understanding of how feedstock selection and processing conditions influence key biochar properties can be used to refine the pyrolysis process and design of “bespoke biochar” engineered to deliver specific environmental functions.

Introduction

Applying biochar to soil has been proposed to improve soil fertility (Chan & Xu, 2009; Atkinson *et al.*, 2010) while sequestering carbon (Lehmann, 2007; Sohi *et al.*, 2010; Ippolito *et al.*, 2012; Manyà, 2012) and reducing or suppressing the release of greenhouse gases such as CO₂, N₂O and CH₄ (Spokas & Reicosky, 2009; Zhang *et al.*, 2010; Bruun *et al.*, 2011). Due to the large variety of biomass potentially available for conversion to biochar, as well as different pyrolysis technologies (thermal, microwave etc.) and possible processing conditions (temperature, heating rate, vapour residence time etc.), an infinite range of biochar types could be created. These will differ in their physicochemical properties and functional performance (Verheijen *et al.*, 2009; Enders *et al.*, 2012; Ronsse *et al.*, 2013). While the influence of production conditions on the physicochemical properties of biochar has been widely covered (Williams & Besler, 1996; Antal & Grønli, 2003; Demirbas, 2006; Shackley & Sohi, 2010; Enders *et al.*, 2012; Angin, 2013) little has been reported on the corresponding effects on biochar functional properties (Atkinson *et al.*, 2010; Rajkovich *et al.*, 2011; Crombie *et al.*, 2013; Mašek *et al.*, 2013). Functional properties are those which could contribute to soil water holding capacity, crop nutrient availability, carbon storage, cation exchange capacity, favourable pH, etc.

Biochar has been consistently shown to be recalcitrant (Spokas, 2010; Enders *et al.*, 2012; Crombie *et al.*, 2013) when applied to soil which is its most important property in terms of C sequestration potential. Although having high levels of resistance, biochar is still gradually mineralized to CO₂; otherwise, soil organic matter (SOM) would be dominated by biochar accumulated over long time scales (Masiello, 2004; Cheng *et al.*, 2006; Lehmann *et al.*, 2008). Therefore the absolute longevity of biochar in soil cannot be quantified by one number as biochar is not one consistent homogeneous state (Hedges *et al.*, 2000). Different fractions and pools of biochar will decompose at different rates under different conditions

determined by method of production, feedstock material, as well as climate and soil properties. This makes the quantification of stability and degradation rates extremely important to the environmental and economic feasibility of biochar production. Direct measurements of stability on the timescale of decades or even a century is not possible leading to the development of laboratory based assessment tools for the rapid screening of fresh biochar (Hammes *et al.*, 2007; Cross & Sohi, 2011, 2013; Harvey *et al.*, 2012; Crombie *et al.*, 2013).

After low temperature pyrolysis, biochar may contain an unconverted or partially converted biomass fraction, known as labile-C, which is rapidly mineralized on addition to soil. The mineralization of labile-C results in a small short term CO₂ flux (Zimmerman, 2010; Bruun *et al.*, 2011; Calvelo Pereira *et al.*, 2011; Cross & Sohi, 2011; Jones *et al.*, 2011) and could be responsible for mineralization of other soil C, i.e. priming (Hamer *et al.*, 2004; Cross & Sohi, 2011; Jones *et al.*, 2011; Lehmann *et al.*, 2011; Zimmerman *et al.*, 2011) however labile-C can also provide a readily available food source for soil microorganisms (Smith *et al.*, 2010). However this stimulated microbial activity occurs over a short time period (Cheng *et al.*, 2006) with long incubation tests actually showing decreased or no mineralization of other soil C following biochar application (Kuzyakov *et al.*, 2009; Spokas & Reicosky, 2009; Zimmerman, 2010; Cross & Sohi, 2011; Zimmerman *et al.*, 2011). In many cases the observed release of CO₂ from biochar takes place over a relatively short period of weeks or months before dissipating (Smith *et al.*, 2010; Jones *et al.*, 2011). However the inconsistency in CO₂ evolution following the addition of biochar to soil could be a result of large variability in the nature of applied biochar (feedstock, temperature, heating rate, pre/post treatment) as well as the conditions used during incubation studies (temperature, soil type, incubation time, atmosphere, pH) (Jones *et al.*, 2011; Zimmerman *et al.*, 2011) making conclusions on the positive or negative aspects of labile-C difficult.

Many studies have reported the effectiveness of biochar in improving soil quality and crop production (Lehmann *et al.*, 2006; Liang *et al.*, 2006; Laird, 2008; Atkinson *et al.*, 2010; Van Zwieten *et al.*, 2010; Rajkovich *et al.*, 2011; Ippolito *et al.*, 2012; Spokas *et al.*, 2012; Liu *et al.*, 2013). The positive impact of biochar could be due to a range of potential reactions that remove soil-related constraints otherwise limiting plant growth: soil nutrient status and soil pH, toxins, improved soil physical properties and improved N-fertilizer use efficiency (Chan & Xu, 2009; Van Zwieten *et al.*, 2010). As biochar is produced by thermal carbonisation of biomass (virgin and non-virgin), it often contains a high concentration of C, as well as varying amounts of plant macro nutrients (phosphorous (P), potassium (K), magnesium (Mg), calcium (Ca) etc.) and micro nutrients (iron (Fe), copper (Cu), sodium (Na), zinc (Zn), chlorine (Cl) etc.) (Chan & Xu, 2009; Lehmann *et al.*, 2011). However the total concentration of nutrients within biochar is not necessarily an appropriate indicator of the content of bioavailable nutrients, as many can be bound in stable forms not readily available to plants (Chan & Xu, 2009; Spokas *et al.*, 2012). CEC is the capacity of biochar to retain cations in a plant-available and exchangeable form (e.g. nitrogen in the form of ammonium, NH_4^+). The CEC is relatively low at low (acidic) pH but increases at higher pH as well as generally being very low at low HTT with substantial improvement as temperature is increased (Lehmann, 2007). While freshly produced biochar demonstrates minimal CEC compared to SOM, biochar has shown the ability to increase its CEC upon addition to soil through abiotic and biotic oxidation and the adsorption of SOM onto its surface (Cheng *et al.*, 2006; Liang *et al.*, 2006; Lehmann, 2007). Increasing the CEC of biochar can result in reducing the leaching of nutrients (e.g. P, ammonium, nitrate, Mg and Ca) from soil, manure, slurry etc. thus increasing the potential availability of nutrients in the root zone for plant uptake and improved soil fertility (Glaser *et al.*, 2001; Chan & Xu, 2009; Major *et al.*, 2009; Clough & Condon, 2010; Angst *et al.*, 2013). Furthermore by improving the sorption ability

of biochar, the efficiency of fertilizer can be increased by absorbing it to the biochar thus improving its retention in the root zone for uptake by plants (Chan & Xu, 2009; Xu *et al.*, 2013). Increasing the N-fertilizer use efficiency can then lead to a reduction in fertilizer application rates, thus decreasing GHG emissions associated with fertilizer production, transport etc. (Major *et al.*, 2009) as well as the direct release of GHG (Zhang *et al.*, 2010). However, adding biochar to soil does not necessarily guarantee a related increase in the CEC of the soil. While some studies have shown a positive increase in soil pH and CEC following the incorporation of biochar into soil other studies have shown the opposite effect (Van Zwieten *et al.*, 2010). There are relatively few studies on the nutrient composition of biochar and its importance to soil amendment (Atkinson *et al.*, 2010; Rajkovich *et al.*, 2011; Angst & Sohi, 2013; Xu *et al.*, 2013; Zheng *et al.*, 2013) and less concerning how production conditions can influence the nutrient content of biochar and their availability (Zheng *et al.*, 2013).

This work therefore aims to establish relationships between production conditions and biochar functional properties related to its soil performance such as long-term biochar stability, labile-C concentration, pH, CEC as well as the nutrient retention. This should then improve the understanding of how selected production conditions impact the effectiveness of biochar for soil amendment while also identifying possible or impossible combinations of functional properties which ultimately determine any potential to maximise the environmental benefits of biochar while considering possible trade-offs with other biochar benefits.

Materials and methods

Feedstock

Biochar samples were produced using three types of biomass: mixed pine wood chips (PC), raw wheat straw (WS) and wheat straw pellets (WSP). The selection of feedstock was based on using biomass that possessed very different structural and chemical properties and represented feedstock readily available in the UK. All biomass was used as received with no pre-treatment steps and an initial moisture content of 4.5 wt.% (PC), 4.5 wt.% (WS) and 13.3 wt.% (WSP) obtained through gravimetric loss on drying at 105°C for 24 hr. PC (ranging 15 x 5 x 4 mm to 100 x 40 x 15 mm in dimensions) were obtained from a Farm in East Lothian, Scotland while both WS (10 x 3 x 1 mm to 90 x 5 x 4 mm) and WSP (\varnothing 6mm) were purchased from StrawPellet Ltd., Rookery Farm, Lincolnshire, England. The natural heterogeneity of the feedstock was minimized as far as possible by thoroughly mixing a volume sufficient for all experiments. The composition of PC, WS and WSP feedstock is shown in Table 1.

Experimental setup

The experimental setup was previously described in detail by Crombie *et al* (2013) and Crombie & Mašek (2014a). A fixed bed batch pyrolysis unit heated by a 12kW infra-red gold image furnace (P610C; ULVAC-RIKO, Yokohama, Japan) was used to produce all biochar samples (Fig. 1). Biomass was placed within a vertical quartz tube (50 mm diameter) with a sintered plate positioned for the sample. A glassware condensation system was developed for the collection and separation of condensable and non-condensable volatiles. The remaining non-condensable gases were collected in a 200 litre multi-layered gas bag (JensenInert Products, Coral Springs, Florida). The gas composition was analysed using a quadrupole mass spectrometer (HPR-20 QIC, Hiden Analytical, Warrington, UK) and reported in Crombie & Mašek (2014).

For each pyrolysis experiment a standard volume of feedstock (approx. 200mm bed depth) was used, resulting in a different mass of starting material used for each biomass type: 40g for PC, 15g for WS and 120g for WSP. For experiments carried out using the higher heating rate ($100^{\circ}\text{C min}^{-1}$) the mass of WSP material was reduced to 60g so that rapid gas release did not exceed the handling capacity of the condensation system. Each type of feedstock was exposed to highest treatment temperatures (HTT) of 350°C , 450°C , 550°C and 650°C and two heating rates of $5^{\circ}\text{C min}^{-1}$ and $100^{\circ}\text{C min}^{-1}$. Heating at temperatures below 350°C would be considered to be torrefaction rather than pyrolysis while pyrolysis above 650°C could have resulted in insufficient char yields required for analysis. The selection of $100^{\circ}\text{C min}^{-1}$ and $5^{\circ}\text{C min}^{-1}$ heating rates were made to compare a higher heating rate, typical of rates used for industrial-scale slow pyrolysis, with a lower heating rate close to the lower extreme for slow heating, providing adequate time for sufficient heat transfer. All runs were performed using one standard carrier gas flow rate (0.33 L min^{-1}) of nitrogen (N_2) and holding time at HTT (20 min). The collection and storage of the different pyrolysis products was described in Crombie *et al.* (2013). No pyrolysis run could be performed for WSP biomass at 350°C and $100^{\circ}\text{C min}^{-1}$, due to aborted pyrolysis runs which resulted in an insufficient amount of remaining homogenous WSP material.

Biochar functional analysis

This analysis focused on two key properties of biochar related to its function in soil, namely biochar C stability (stable-C%) and content of labile C (labile-C%) (Cross & Sohi, 2011, 2013). In addition to these two assays biochar samples were also analysed for pH and extractable nutrients.

Stable carbon and labile carbon

Stable-C was assessed using an oxidative ageing method previously described (Cross & Sohi (2013)). Any temporary protection to oxidation provided by physical macrostructure was removed by milling prior to ageing. Biochar containing 0.1 g C was treated with 7 ml of 5% hydrogen peroxide at room temperature, before being heated at 80°C for 48 hr. Oxidative ageing was performed in triplicates for each sample. While the stable-C tool uses chemical oxidation to mimic the oxidative degradation of biochar caused by peroxidase enzymes, this technique cannot completely replicate environmental processes. By focusing on the oxidation of biochar the process does not account for the degradation of biochar through hydrolysis steps which are likely to occur within the environment. Furthermore biochar samples were milled prior to oxidation as a means of removing any physical protection to the oxidation process, which could potentially lead to an underestimation of the environmental stability of biochar. Stability could also be further underestimated by failure to account for the potential stabilisation of biochar with soil minerals.

Labile-C content was determined as the evolution of CO₂ during a two week incubation of biochar (1 g) in sand (9.5 g) at 30°C, inoculated with a soil extract (Cross & Sohi (2011)). Each biochar set consisted of 4 replicates and one control blank to correct for the CO₂ gained during preparation of the vials, the flask headspace and re-drying of soda lime prior to weighing. The incubation of biochar was performed using a sand medium as opposed to soil, so that the measurement of labile-C was not compounded by soil mineralisation. While this allowed for measuring the labile-C content of biochar it also fails to include soil specific differences which could be faced in the environment.

Nutrient extraction analysis

Biochar samples were analysed to determine the concentration of extractable Ca, K, Mg, Na, P and CEC. A full description of the analytical procedure for determining the extractable bases and CEC can be found in the supplementary material. Due to the low density of WS biomass, an insufficient amount of biochar was obtained following pyrolysis to allow for the nutrient extraction analysis to be performed, hence this analysis was only carried out using PC and WSP biochar.

CEC and extractable nutrients

Biochar CEC was assessed using the ammonium acetate method (Faithfull, 1985) where ammonium was extracted from biochar with acidified potassium chloride and quantified colorimetrically. The concentrations of extractable ions were determined by dry ashing, dissolving in hydrochloric acid and analysing by ion chromatography.

Total and extractable phosphorous

Biochar total phosphorous content was determined by ashing at 550°C for 4 hours followed by aqua regia digestion under heating (BS EN 13650, 2001). The remaining residue was then analysed using ICP-OES. Extractable P was estimated using the Olsen P method (Olsen *et al.*, 1954; BS7755-3.6, 1995).

pH

Biochar pH was assessed using the procedure of Rajkovich *et al.* (2011). Biochar pH values were obtained using a ratio of 1.0 g of biochar in 20 ml of deionized water. Before pH measurements were taken the samples were shaken (Orbital Multi-Platform Shaker PSU-20i, Grant instruments Ltd, Shepreth, Cambridgeshire, UK) for 1.5h to ensure sufficient equilibration between biochar surfaces and solution. The pH measurements were taken using

a bench top pH probe (Mettler-Toledo FE20, Mettler-Toledo, Columbus, OH, USA) and performed in triplicate.

Statistical analysis

The pyrolysis experiments were designed and performed based on a ‘fully crossed design’ to investigate the effect of each production parameter on the response variables (Box *et al.*, 2005). Using this type of experimental design meant that each combination of experimental conditions was only performed once. This design was possible as preliminary tests ($n = 3$) showed very good reproducibility of HTT ($s = 0.15$), heating rate ($s = 0.36$), time at peak temperature ($s = 0.10$) and char yield ($s = 0.25$). The monitoring of the pyrolysis process was such that any discrepancies in the process conditions would be detected and the run and results discarded. Analysis of variance (ANOVA) was applied through a general linear model using Minitab 16 statistical software and significance of results were calculated at a significance level of $P < 0.05$ for all materials and production conditions. Correlations were performed using Spearman rank method where $R < 0.35$ was taken to indicate weak correlations, 0.36 to 0.67 to be moderate correlations, 0.68 to 0.90 strong correlations and > 0.9 to be a very strong correlation (Taylor, 1990).

Results

The focus of this work was the assessment of biochar functional properties. Results for pyrolysis product distribution as well as biochar physiochemical properties are reported in supplementary material (Table S1).

Biochar functional properties

The progression of large scale biochar application to soil has been limited by uncertainties over the response of crops to biochar in the soil. Carbon sequestration, CEC, nutrient content and availability and pH were identified as important properties to investigate and relate to production parameters.

Long-term biochar stability

The most accurate method of assessing the C sequestration potential of biochar could possibly be through long-term field experiments monitoring stability and degradation over time; however this is not feasible over a period of 100 years or more. In this work we used an oxidation approach (Cross & Sohi, 2013) to determine stable-C content (biochar C basis) and yield of stable-C (feedstock C basis). The results plotted in Fig. 2a show that HTT was the main factor ($P < 0.0001$) determining the concentration and yield of stable-C together with feedstock ($P < 0.026$). On the other hand, no effect was observed for heating rate ($P > 0.05$), in the range investigated. Increasing the pyrolysis HTT generally resulted in an increase in stable-C present within biochar. At $\text{HTT} < 450^\circ\text{C}$ the slower heating rate produced higher stable-C concentrations compared to $100^\circ\text{C min}^{-1}$ however at higher HTT this trend disappeared as temperature played the dominant role (Antal & Grønli, 2003; Crombie *et al.*, 2013; Crombie & Mašek, 2014a).

The results further showed that the efficiency of conversion of feedstock carbon into stable carbon (stable-C yield) increased with HTT (Fig. 2b), therefore indicating that high HTT improved the C storing potential of biochar, reaffirming the same trend seen for different feedstock in Crombie & Mašek (2013). The variation in stable-C yield from $350 - 650^\circ\text{C}$ was considerably lower than that experienced for stable-C concentration with the average difference being $10.7 + 4.57\%$ compared to $42.1 + 11.4\%$ for stable-C content.

Lower variation in the yield of stable-C as HTT is increased can have a large impact on the economic and environmental case for biochar production, especially when pyrolysis at higher temperatures could provide additional energy and C sequestration benefits (Crombie & Mašek, 2014a). Although there is a significant effect of HTT and feedstock on the stable-C content and yield, the extent of this influence varies at different heating rates. Both parameters are largely significant when using heating rate of $100^{\circ}\text{C min}^{-1}$ ($P < 0.019$), but only HTT shows statistically significant effect ($P < 0.037$) when applying the lower heating rate ($5^{\circ}\text{C min}^{-1}$) ($P < 0.037$), while feedstock type is not ($P > 0.147$). The lower heating rate would increase the duration of chemical reactions occurring during pyrolysis and could result in more time for the dominating effect of HTT to influence the biochar stability causing similar stable-C yields to be obtained for PC, WS and WSP biochar produced at 650°C .

Biochar labile-C content

Biochar labile-C content is mainly affected by the HTT ($P < 0.0001$) and feedstock ($P < 0.028$) selection, as shown in Fig. 3a, while heating rate had no statistically significant effect. As the pyrolysis HTT was increased from 350°C to 650°C the labile-C content in biochar dropped dramatically for WS and WSP feedstock while PC labile-C content also dropped between 450°C and 650°C . The trend for PC biochar labile-C content was difficult to determine as HTT was increased from 350°C to 450°C due to a large standard deviation for that biochar sample. All biochar samples produced at 650°C , with the exception of WS, showed a labile-C content of $< 0.11\%$. WS biochar produced at 650°C contained a labile-C concentration of 0.31% which was unexpectedly high but not statistically different to the labile-C content (0.18%) of WS biochar produced at 550°C . The initial release of CO_2 when biochar is added to soil could be due to microbial decomposition of an easily degradable C fraction remaining in higher concentrations within low HTT biochar due to incomplete conversion (Cheng *et al.*, 2006; Zimmerman, 2010; Bruun *et al.*, 2011; Calvelo Pereira *et al.*,

2011). There was a clear difference in the concentration of labile-C present within biochar produced from the different feedstock at 350°C with the largest being WSP (1.34 %) followed by WS (0.94 %) and lastly PC (0.18 %). Biochar made from grasses has generally been found to degrade faster than wood biochar and has a higher initial CO₂ flux (Zimmerman *et al.*, 2011).

Similar to labile-C concentration, the labile-C yield (feedstock C basis) of biochar decreased with increasing HTT (Fig. 3b). Biochar produced at > 550°C contained a labile-C yield of < 0.14 %, and all biochar samples produced from PC, WS and WSP showed a labile-C yield of < 0.17 %, < 0.66 %, < 0.77 % respectively. Overall this pathway for the release of CO₂ represents only a small fraction of biochar C and therefore does not compromise the C sequestration potential. The observed increase in stable-C yield and decrease in labile-C yield with increasing HTT emphasises that pyrolysis at higher temperatures can sequester more C by increasing the C fraction stable over long periods of time while at the same time reducing the C fraction susceptible to rapid decay. However, further studies into the positive impacts of labile-C (e.g. food source for microorganisms) on soil processes is needed to gain a better understanding of the desired threshold for biochar labile-C content.

Biochar nutrient concentration

The concentrations of feedstock and biochar extractable nutrients were determined through ammonium acetate extraction and shown in Table 2 and Table 3 respectively. The extraction procedure was originally designed for analyzing soil samples and so analyzing biochar has demonstrated some limitations of the technique such as a higher concentration of nutrients being extracted from biochar compared to feedstock. This effect can also be due a dramatic change in physical (surface area, pore volume etc.) and chemical (surface charge, nutrient form etc.) properties following the pyrolysis process.

Extractable nutrients

The mineral content of biochar consists largely of nutrients such as P, K, Ca, Mg, Cl, Na etc. which can cause a catalytic effect during pyrolysis affecting the yields, composition and properties of char, condensable liquids and gas co-products including the reactivity and ignition properties of chars (Antal & Grønli, 2003; Sonoyama *et al.*, 2006; Mašek *et al.*, 2007; Brown, 2009; Enders & Lehmann, 2012). As the majority of feedstock nutrients are retained in the ash fraction of biochar, and the ash concentration of biochar increases with rising HTT, a strong positive correlation can be seen between ash content and the amount of extractable K ($R^2 = 0.713$, $P = 0.003$) while moderate correlations are also evident for Ca ($R^2 = 0.632$, $P = 0.011$), Na ($R^2 = 0.601$, $P = 0.018$) and Mg ($R^2 = 0.541$, $P = 0.037$). The amount of extractable nutrients was also considerably higher for the high ash WSP biochar compared to the relatively low ash PC biochar (Table 3). Due to this clear correlation of ash content with nutrient composition the selection of feedstock was deemed to be the determining factor in the final biochar concentration of K ($P = 0.005$) and Na ($P = 0.014$) however Ca ($P = 0.070$) and Mg ($P = 0.139$) overall were not influenced by feedstock selection (for the types investigated). Although the influence of feedstock is clear, it is not surprising as only two types of feedstock, which differ greatly in origin and composition, were used for the comparison.

The concentrations of Ca, K, Mg and Na extracted from WSP biochar generally peak at 450°C for both heating rates with increased HTT resulting in equal or lower concentrations of nutrients. The concentration of extractable nutrients from WSP biochar was substantially smaller when the higher heating rate was applied. This could be due to a loss of biochar structure and decrease in pore volume caused by a combination of a high heating rate and ash content (Downie *et al.*, 2009). A lack of structure in biochar produced using higher heating rates has been attributed to the melting of the cell structure and the blocking of pores (Downie *et al.*, 2009). Increasing the heating rate of pyrolysis reduces the time that volatiles have to be

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discharged during pyrolysis leading to a shorter time for pore development as well as increasing the accumulation of volatiles between and within particles (Lua *et al.*, 2004; Angin, 2013). For PC biochar, the highest amount for nutrient extraction occurred at 450°C when using the low heating rate, however pyrolysis of PC at a higher heating rate resulted in increasing nutrient extraction with increasing HTT. This led to the peak nutrient extraction for Ca, K and Na all occurring at 650°C. The ash content of PC biochar is considerably lower than WSP biochar therefore the expected loss of structure due to the presence of ash would be minimal.

Phosphorus

Total biochar P and extractable P concentrations are also shown in Table 3. Firstly to assess the yield of P extracted from the initial feedstock sample, the amount of extractable P (biochar weight basis) from biochar was expressed as a percentage of the extracted feedstock P. Secondly the amount of extractable biochar P was further expressed as a percentage of the total biochar P (biochar weight basis) to determine the proportion of P remaining within the biochar sample. For the range of process conditions investigated, the yield of extractable P as a function of extracted feedstock P peaked at 350°C for PC biochar and 450°C for WSP for both heating rates while the yield of extractable P as a function of total biochar P also peaked under the same conditions. The extractable P concentration for WSP biochar at 450°C actually exceeded the total P measurement for that biochar sample. This can be caused by a lack of repeated analysis or limitations of the total P extraction method. WSP was previously seen to contain a higher amount of extractable Ca, K, Mg and Na compared to PC biochar; this trend applied also to P. It is desirable to retain as many nutrient elements in biochar as possible. For some elements a proportion are lost by vaporisation during pyrolysis (K, Na, S, N etc.) with over half of their content being released at temperatures below 500°C (Mašek *et al.*, 2007; Chan & Xu, 2009; Enders *et al.*, 2012). A lack of P volatilization compared to other nutrients

as HTT is increased could be the reason for a rise in total P as pyrolysis HTT is increased.

Although total biochar P concentration increases with HTT, P availability can decrease due to P being trapped in less available forms at higher temperatures (Chan & Xu, 2009).

To maintain content and availability of crop nutrient elements the preferred temperature of pyrolysis, based on the results of this work, would be between 450°C – 550°C which falls within the range put forward by Chan & Xu (2009) (400°C – 500°C). The exact conditions for improved nutrient properties may well differ between feedstock.

Cation exchange capacity (CEC)

In addition to the extracted nutrient concentrations, the CEC of biochar samples were also determined and shown in Table 3. In the HTT range 350°C to 650°C, biochar CEC increased between 450°C – 550°C for both feedstocks at both heating rates. This was consistent with trends reported previously (Lehmann, 2007). However, as HTT was increased to 650°C, CEC decreased for all samples (except WSP biochar produced using 100°C min⁻¹) potentially due to a reduction in surface area attributed to higher pyrolysis HTT. As the biochar structure becomes more aromatic at higher pyrolysis temperatures, large amounts of acid-base surface functional groups (Chan & Xu, 2009; Lehmann *et al.*, 2011) are lost altering the charge of biochar (Novak *et al.*, 2009; Lehmann *et al.*, 2011) therefore influencing the nutrient retention ability of cations and anions determined by CEC and anion exchange capacity (Chan & Xu, 2009).

Biochar pH in solution

Some studies have indicated that ash content of feedstock in conjunction with pyrolysis intensity could influence the final pH of biochar samples (Glaser *et al.*, 2002; Lehmann *et al.*, 2011; Enders *et al.*, 2012; Novak *et al.*, 2013; Ronsse *et al.*, 2013). Enders *et al.* (2012) suggested that a large proportion of the ash in high-ash feedstock contains

carbonates which could cause a liming effect. While the production conditions of feedstock and HTT are well covered throughout these studies the impact of heating rate has not been covered. HTT ($P < 0.0001$) and feedstock selection ($P < 0.0001$) were both seen to influence the final pH value of biochar while heating rate only influenced the pH value of PC biochar. As the HTT of pyrolysis increased so too did the biochar pH (Fig. 4) indicating that higher HTT results in biochar with increased alkalinity. Studies have shown that under less intense pyrolysis conditions (reduced HTT and heating rate) more labile and oxygenated carbon with high acid-base surface functional groups are retained in the char, however as the intensity of pyrolysis increased more acidic groups (e.g. carboxyl) became deprotonated to the conjugate base consequentially causing a rise in the pH of biochar in solution (Chan & Xu, 2009; Ronsse *et al.*, 2013; Zheng *et al.*, 2013). The pH of biochar has been associated with having a liming effect on soil acidity thus increasing the soil pH following the addition of biochar (Van Zwieten *et al.*, 2010; Biederman & Harpole, 2013; Liu *et al.*, 2013; Novak *et al.*, 2013). When heating rate of $100^{\circ}\text{C min}^{-1}$ was used the pH of PC biochar increased with HTT while the pH values of WS and WSP were not affected ($P > 0.05$) by HTT. Applying the higher heating rate of $100^{\circ}\text{C min}^{-1}$ can increase the rate at which volatiles are released from biochar thus affecting the rate that the deprotonation of the acidic groups within biochar occurs resulting in similar pH values over the temperature range 450°C – 650°C compared to $5^{\circ}\text{C min}^{-1}$.

Differences in pH can also be observed between the biomass types: pH of biochar derived from woody biomass was consistently lower compared to straw based biochar. The higher pH values of WS and WSP biochar over PC biochar can be strongly correlated ($R^2 = 0.891$, $P < 0.0001$) to the larger ash concentration of wheat biochar compared to wood. The influence of ash can be clearly seen when comparing the values for PC biochar (ash = 0.7 – 5.9 %, pH = 5.5 – 9.1) to that of WS (ash = 10.9 – 27.6 %, pH = 8.6 – 11.2) and WSP (ash = 14.4 – 23.7 %, pH = 8.6 – 11.6). Increasing the alkaline nature of biochar can increase the

ability of biochar to improve crop productivity, however a number of variables such as soil type and climate also need to be considered (Czimczik & Masiello, 2007), as application of biochar with a very high pH can also have negative effects on soil such as micronutrient deficiencies (Chan & Xu, 2009).

Discussion

Identifying a combination of production conditions which could maximise the soil enhancing and C sequestering properties of biochar would be practically impossible due to the impact that processing conditions can have on several biochar properties simultaneously. For that reason a fine balance needs to be found between the C mitigation potential of biochar and identifying the functions relevant to the soil constraint being addressed i.e. soil pH, nutrient retention, microbial activity etc. To aid in the identification of these relationships Fig. 5 (a matrix plot diagram) and Fig. 6 (combination of scatterplot diagrams) were used to show the ranges in which biochar functional properties can be varied by adjusting key production parameters. In the following section each biochar sample is identified by feedstock-HTT-heating rate e.g. PC-650-5 would refer to biochar produced from PC, using the HTT of 650°C and the heating rate of 5°C min⁻¹.

Carbon stability versus degradability

If the desired outcome of pyrolysis is to increase the fraction of stored C and minimise the degradable C fraction, then this can be achieved through applying higher pyrolysis temperatures (HTT >550°C)(Crombie *et al.*, 2013; Mašek *et al.*, 2013; Crombie & Mašek, 2014a), i.e. WS-550-5, WS-650-5, WS-550-100, WS-650-100, WSP-550-5, WSP-650-5, WSP-550-100, WSP-650-100, PC-650-5 and PC-650-100 (Fig. 5a). Where the concentration of labile-C is an important key soil property a HTT < 450°C would result in higher labile-C

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concentration however at the expense of long-term C sequestration. Few stable biochar samples contained relatively “high” labile-C content when comparing the entire data set. However WS-450-5 and WSP-450-100 both contained a labile-C content > 0.45 % and stable-C concentrations above 72 %. WSP-450-100 in fact contained a labile-C concentration of 0.70 % and stable-C content of 81.8 % demonstrating a good combination of relatively high values of both stable-C and labile-C. While labile-C provides an energy source for microbial communities that promote soil aggregation, high-concentrations of labile-C could result in biological immobilisation of soil N which could become problematic if biochar is applied in large quantities. It is important to note that stable-C accounts for the long-term stability of C (> 100 years) while relatively non-stable labile-C demonstrates the short term decomposition of biochar C (two week incubations). Therefore combining stable-C and labile-C does not account for the total C present within biochar, indicating a third fraction of intermediate stability (2 weeks < Int-C < 100 years) (Crombie & Mašek, 2014a). It is important to consider this additional C fraction when assessing the C sequestration potential of biochar as it bridges the gap between the two extremes for biochar C stability and therefore can influence trade-offs between C mitigation and other important benefits (greenhouse gas emissions, soil enhancement etc.).

Carbon stability versus liming value

It has been well documented that biochar of high alkalinity has been effective at increasing fertility of acidic soils (Van Zwieten *et al.*, 2010; Biederman & Harpole, 2013; Liu *et al.*, 2013; Novak *et al.*, 2013). The cluster seen in Fig. 5b, representing biochar samples WS-550-5, WS-650-5, WS-550-100, WS-650-100, WSP-550-5, WSP-650-5, WSP-550-100 and WSP-650-100, have high stable-C content and an alkaline pH. Within this smaller group the difference in stable-C content ranged from 90.5 – 100 % and pH from 10.2 – 11.6. A second group of biochar samples which showed less favourable but still relatively high values

of stability (81.7 – 88.9 %) and pH (9.1 – 10.4) consisted of PC-650-5, PC-650-100, WSP-450-100. Although PC-650-100 was identified as having a high stable-C concentration (88.9 %) its pH value of 9.14 was lower than the WS and WSP biochar produced at $\text{HTT} > 550^\circ\text{C}$. However a pH of this value could still potentially provide an effective soil response depending on site specific soil properties. Furthermore, as labile-C decreases linearly with increasing HTT any attempt to maximise the pH of biochar and stable-C concentration would result in a reduction in the labile-C content e.g. WSP-650-5 biochar produced the highest biochar pH while also contained the second lowest labile-C concentration (Fig. 5d). Any reduction in HTT led to a reduction in pH and an increase in the concentration of labile-C. While it was clearly identified that increasing the severity of pyrolysis resulted in higher pH values and C stability, for soil amendment biochar with a high pH value may not be preferable. Too high a pH has been shown to cause micronutrient deficiencies (Chan & Xu, 2009). Therefore determining the ideal pH value for biochar will undoubtedly be influenced by the initial pH of the soil and the effect that biochar pH has on the overall agronomic impact of biochar.

Carbon stability versus cation exchange capacity

Non-linear progression of CEC with HTT made production conditions that maximise both stable-C concentration and CEC difficult to define (Fig. 5c). The surface area and CEC of biochar has typically been shown to decrease when made at $\text{HTT} > 550^\circ\text{C}$ and to maximise the CEC value, pyrolysis should be performed at temperatures between $500^\circ\text{C} - 550^\circ\text{C}$ (Lehmann, 2007). However CEC for PC and WSP biochar reached its highest values between 450°C and 550°C , depending on the applied heating rate. Therefore, this indicates that the preferred pyrolysis temperature could actually fall between 450°C and 550°C . Too high a temperature can cause greater surface area, increased aromatic structure and loss of negative charge and therefore decrease the CEC (Novak *et al.*, 2009; Lehmann *et al.*, 2011)

When comparing the biochar CEC with stable-C concentration (Fig. 5c) some biochar samples show a high value for CEC but low stable-C content (WSP-450-5) or vice versa (WSP-550-5). Biochar produced from WSP at 650°C using 5°C min⁻¹ (WSP-650-5) demonstrated the highest CEC while also containing a high stable-C concentration of 99.5 %. With the exception of WSP-650-5, the CEC of biochar tended to be higher at HTT < 550°C. Despite the importance of CEC, due to the fact that in general the initial CEC of fresh biochar is low, the importance of this parameter for optimisation is limited. It is the ability of biochar to acquire high CEC upon addition to soil, as a result of abiotic and biotic oxidation (Cheng *et al.*, 2006; Xu *et al.*, 2013) that is more relevant. Therefore while the initial CEC of biochar may be relatively low compared to SOM, the long term influence of CEC on nutrient retention may be an important functional property to monitor.

Carbon stability versus extractable crop nutrients

Most biochar produced from virgin biomass contains a relatively limited amount of nutrients, and therefore cannot be compared to conventional fertilisers. Nevertheless, the ability of biochar to release nutrients is an important one. The concentration of available plant nutrients in biochar was determined by ammonium acetate extraction. While the high temperature pyrolysis (> 550°C) of WS and WSP biomass has consistently shown a high C storage potential, high alkalinity, low labile-C concentration as well as high values of CEC, the concentration of extractable biochar nutrients was highest at 450°C. As HTT is increased from 200°C to 500°C the greater production of volatile material can enhance pore (macro-, meso- and micro-) development leading to increased pore volume and surface area (Downie *et al.*, 2009; Angin, 2013). Above 500°C, structural re-ordering, pore widening, pore blockage and melting or fusing of ash seems to predominate resulting in decreased pore volume and surface area (Downie *et al.*, 2009; Fu *et al.*, 2011) reducing the extractability of plant nutrients. Therefore any beneficial properties obtained at higher HTT may be at a cost of crop

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nutrient availability. The stable-C concentration of biochar samples was compared to the concentrations of extracted Ca, Mg, K, Na, P and total P in Fig. 6a,b,c,d,e,f respectively and WSP-450-5 was consistently associated with the highest extractable amounts of Ca (100 %), K (100 %), Mg (69.9 %), Na (80.2 %) and P (100 %) as well as the second highest CEC (72.5 $\text{cmol}_c \text{kg}^{-1}$) of any biochar. While the processing conditions used to produce this biochar did give a high pH (9.9) the stable-C content was relatively low (58.9 %) compared to other biochar samples investigated. This highlights the trade-off between C storage versus enhancing soil quality (Jeffery *et al.*, 2013). While WSP-450-5 was associated with the largest amount of extractable nutrients it was not the only biochar to show positive results for this functional property. The highest extractable P content was found in WSP-550-5 which also contained a stable-C concentration of 98.2 %. This again demonstrates the increased availability of nutrients from biochar produced at $\text{HTT} > 550^\circ\text{C}$. Two further biochar samples (WSP-650-5 and WSP-550-100) also showed a potentially positive combination of extractable P ($> 44.5 \%$) and stable-C concentration ($> 99.5 \%$). All other biochar samples either contained too low a concentration of stable-C or extractable P. WSP-650-5 also demonstrated a high stable-C (99.5 %) concentration in conjunction with high extractable Ca (51.7 %) and K (100%) concentrations. When excluding WSP-450-5 (due to low stability) the remaining biochar samples displayed extractable Mg $< 22 \%$ while the majority of Na values fell below 41 %.

Due to its content of N, P and K, biochar can serve as a low grade fertilizer (Glaser *et al.*, 2002; Novak & Busscher, 2013) with potential to improve soil quality. Free bases such as K, Ca and Mg can not only increase soil pH but also provide readily available nutrients for plant growth (Glaser *et al.*, 2002; Novak & Busscher, 2013). However, biochar is potentially more important as a soil conditioner and can support nutrient transformation in soil rather than acting purely as a source of nutrients (Glaser *et al.*, 2002). However these nutrient

transformations can also result in negative effects on plants, including N deficiency caused by N immobilization (Chan & Xu, 2009; Atkinson *et al.*, 2010) where microorganisms are stimulated by the labile fraction of biochar to decompose available N in soil (NH_4^+ and NO_3^-) or from SOM if the available N concentration in soil is low. A high mineralisation rate has been attributed to a larger labile C fraction present within biochar making low temperature biochar more likely to cause the activation of soil microorganisms (DeLuca *et al.*, 2009; Nelissen *et al.*, 2012). However the bulk of the remaining organic C present within biochar does not lead to mineralisation-immobilization reactions because of its highly recalcitrant nature (Chan & Xu, 2009). Biochar has also been seen to adsorb NH_4^+ and NH_3^- from soil solution and thus reduce the availability of inorganic N (DeLuca *et al.*, 2009).

C stability versus soil enhancement and energy output

The lower stable-C fraction of WSP-450-5 demonstrated that focusing pyrolysis to produce biochar with properties favouring nutrient extraction could affect the C sequestration potential of the related biochar; therefore enhancing both functional properties could prove to be impossible without directly affecting the other property. Although the proportion of extractable nutrients increased between 450°C – 550°C it was actually seen that biochar produced from higher HTT provided the better overall result when combined with the other functional properties of biochar.

Although the energy content of pyrolysis co-products was not covered within this study, previous studies into the energy balance of the system concluded that applying higher pyrolysis HTTs actually resulted in increased C storage in addition to a larger amount of energy available within liquid and gas products (Crombie & Mašek, 2014a, 2014b). When considering the conclusions reported in these studies in conjunction with the results of this work, pyrolysis at HTT > 550°C can produce biochar with long-term stability, high alkalinity,

high biochar CEC, and deliver good concentrations of nutrients to soil, while providing additional heat and power generation potential through the utilisation of liquid and gas co-products.

In summary, the main objective of this work was to relate differences in biochar functional properties to pyrolysis process parameters while seeking combinations of functional properties that could lead to improvements to the environmental performance of biochar. The results showed that while CEC and available nutrients tended to be more favourable at lower HTTs, high temperature pyrolysis still demonstrated beneficial values for these soil enhancing properties as well as increased alkalinity and stable-C yield. Overall the differences between the functional properties of low and high heating rate biochar were not considerable. The lower heating rate may have produced biochar with marginally more beneficial properties however the process constraints imposed by slow heating (e.g. low throughput, large equipment) are unfavourable for industrial biochar production. Therefore a combination of production conditions and feedstock under which biochar with positive functional properties of high long-term C sequestration and soil enhancing capabilities was achievable.

These findings are important, and in conjunction with detailed life cycle analysis (LCA) as well as comparative studies analysing the trade-offs between different benefits i.e. C storage and electricity generation, would provide a firm basis for decisions on best biochar deployment practices. While pyrolysis on a small-scale allowed for the high level of control needed to investigate the impact of production conditions and to identify regions of major property changes, the same control may not be achievable when using industrial-scale pyrolysis. It is reasonable to assume that if biomass particles are exposed to the same thermal history and environment (within the reactor), the same type of biochar can be produced, no

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matter the scale or type of pyrolysis unit. Therefore the challenge is to design and control the conversion process to ensure the correct processing conditions. Furthermore field testing of selected biochar is required to first validate laboratory assessed functions to behaviour in soil and observe the development of functional properties with time. This work represents an important first step towards the ambitious goal of bespoke biochar, engineered to deliver specific environmental response.

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Table 1: Composition of feedstock used throughout the pyrolysis experiments expressed on dry mass basis (db).

Sample	Proximate analysis [wt.% (db)]			Ultimate analysis [wt.% (db)]							Biomass components [wt.% (db)]		
	Fixed C %	Volatile Matter %	Ash %	C %	H %	N %	O %	O: C	H: C	HHV [MJ/Kg]	Cellulose	Hemicellulose	Lignin
Pine Wood Chips	22.3	75.7	2.0	50.7	4.8	0.0	42.4	0.6	1.1	19.0	52.0	21.0	12.6
Wheat Straw Pellets	15.0	78.5	6.5	43.1	5.8	0.0	44.6	0.8	1.6	16.7	22.0	42.0	30.0
Wheat Straw Pellets	18.0	81.8	2.0	48.0	6.2	1.8	43.8	0.7	1.5	18.0	23.0	44.0	26.0

Table 2: Concentration of nutrients extracted from the PC and WSP feedstock via ammonium acetate

Sample	Extractable Nutrients [mg/kg]								CEC [cmol _c /kg]
	Ca	K	Li	Mg	Mn	Na	Total P	Extracted P	
Pine Wood Chips	787.0	787.0	0.04	162.7	73.5	422.5	146.0	174.0	51.0
Wheat Straw Pellets	1969.0	1969.0	0.06	213.7	2.6	401.1	335.0	206.0	117.0

Table 3: The ash content (dry mass basis, db), CEC and extractable nutrient concentrations of biochar produced from PC and WSP feedstock

Sample	Ash [wt.%, db]	Extractable Nutrients						CEC [cmol _c /kg]
		Extracted biochar Nutrient / Extracted Feed Nutrient [%]						
		Ca	K	Mg	Na	P	Extracted Biochar P / Total Biochar P [%]	
PC350/5	1.4	5.3	4.3	7.7	34.1	12.8	21.5	35.7
PC450/5	2.9	10.3	13.8	9.5	34.5	9.8	17.4	60.6
PC550/5	4.2	4.5	4.1	4.9	22.0	9.2	14.0	65.9
PC650/5	5.9	6.6	13.6	5.5	21.5	7.2	9.0	41.4
PC350/100	3.4	5.6	8.8	6.7	28.7	17.0	15.3	38.4
PC450/100	3.4	10.1	12.6	5.3	19.1	8.0	13.9	48.0
PC550/100	0.7	11.2	18.9	5.5	18.9	4.5	5.1	32.9
PC650/100	5.0	13.8	36.8	5.9	20.1	9.4	12.8	27.5
WSP350/5	14.4	22.8	17.2	16.5	40.7	87.0	82.1	30.7
WSP450/5	17.6	100.0	100.0	69.9	80.2	100.0	100.0	72.5
WSP550/5	20.1	24.1	84.3	12.8	53.3	89.5	85.8	27.4

WSP650/5	21.9	51.7	100.0	21.1	68.4	44.5	44.5	79.6
WSP350/100	-	-	-	-	-	-	-	-
WSP450/100	20.9	12.7	24.1	9.0	26.1	82.2	78.2	36.8
WSP550/100	21.9	8.2	22.1	5.6	24.7	65.0	61.2	60.6
WSP650/100	23.7	4.7	15.7	4.4	25.3	24.5	22.0	46.7

Figure legends

Figure 1: Small scale batch pyrolysis unit located at UKBRC

Figure 2: Environmental stability of PC, WS and WSP char expressed on (a) char carbon basis (b) feedstock carbon basis. Error bars were added to the graph to show standard deviation of stable-C %, but are not visible due to the scale of the data ($n = 3$). All values for the standard deviation of stable-C % were > 0.63 and were provided in the supplementary material (Table S2).

Figure 3: Labile C content of PC, WS and WSP biochar expressed on (a) char carbon basis (b) feedstock carbon basis. Error bars were added to the graph to show standard error of labile-C % ($n = 4$). All values for the standard deviation of labile-C % are provided in the supplementary material (Table S2).

Figure 4: Investigating the effect of temperature and heating rate on the pH of biochar. Error bars were added to the graph to show standard error of biochar pH, but are not visible due to the scale of the data ($n = 3$). All values for the standard deviation of pH were > 0.07 and were provided in the supplementary material (Table S2).

Figure 5: Matrix plot comparing biochar functional properties, (a) stable-C vs labile-C (b) stable-C vs pH (c) stable-C vs CEC (d) labile-C vs pH (e) labile-C vs CEC (f) pH vs CEC.

Figure 6: Combination of scatter plots showing the comparison of stable-C concentration with the concentration of extractable nutrients, (a) stable-C vs Ca (b) stable-C vs Mg (c) stable-C vs K (d) stable-C vs Na (e) stable-C vs P (f) stable-C vs total P.











