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Aston, Stephen (2014) *The impacts of biochar application on soil hydrology, erosion and related properties..* thesis, Swansea University.
http://cronfa.swan.ac.uk/Record/cronfa42257

THE IMPACTS OF BIOCHAR APPLICATION ON SOIL HYDROLOGY, EROSION AND RELATED PROPERTIES

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2014

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Submitted to Swansea University
in fulfilment of the requirements
for the Degree of Doctor of Philosophy

Stephen Aston (student no. 405537): The impacts of biochar application on soil hydrology, erosion and related properties, Submitted to Swansea University in fulfilment of the requirements for the Degree of Doctor of Philosophy, © 2014

ABSTRACT

Biochar production and application to soil can mitigate climate change and improve soil quality. This thesis investigated the influence of biochar preparation methods and application rates on the hydrological and erosional characteristics of biochars themselves and the soils to which they were applied.

Biochar hydrophobicity was influenced by feedstock and decreased with increasing highest treatment temperature (HTT). Biochar did not influence soil wettability and the effect of HTT on biochar porosity was more important for soil water-holding capacity than its effect on hydrophobicity. HTT affected biochar yield, cation exchange-capacity and provision of fungal substrates. HTT also significantly influenced the effect of biochar on soil suction.

Smaller feedstock particles produced biochars that were slightly more hydrophobic than those produced from larger particles. The effects of biochar application on the properties of sandy loam were influenced by biochar particle size, because larger particles had less effect on bulk density and had slower water uptake.

A low biochar application rate (5 g kg^{-1}) had no effect on the aggregate stability of a silt loam and did not affect the hydrological and erosional response of the soil under simulated rainfall. Application rates of 25 and 50 g kg^{-1} reduced aggregate stability, which led to surface sealing and overland flow generation occurring more readily. However, there was no more erosion of these soils than those with low or zero biochar content, and the crusts formed by seal drying were much weaker than those formed on soils with low or zero biochar. Biochar was preferentially eroded from the soils, regardless of the application rate used.

HTT and particle size can have important implications both for the properties of biochar itself and for its effects on soil properties. However, biochar may only substantially influence soil hydrology and erosion when applied at sufficiently high rates.

DECLARATION

I declare that this work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree.

Signed ______________________ (Candidate)

Date 06.05.15

Statement 1

This thesis is the result of my own investigations, except where otherwise stated. All other sources are acknowledged by footnotes and/or explicit references listed in the bibliography.

Signed ______________________ (Candidate)

Date 06.05.15

Statement 2

I hereby give consent for the thesis, if accepted, to be available for photocopying and for inter-library loan, and for the title and summary to be made available to outside organisations.

Signed ______________________ (Candidate)

Date 06.05.15

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ACKNOWLEDGEMENTS

Thank you to the Department of Geography at Swansea University for awarding me a NERC Studentship (Doctoral Training Grant NE/H525154/1) without which this project would not have been possible. Thanks also go to the British Society of Soil Science, who provided financial support to enable me to present my research at international conferences.

Writing this thesis would have been impossible without the help I have received from my supervisors. To Professor Alayne Street-Perrott: thanks for encouraging me to apply to do this PhD in the first place and for taking on all the administrative hassle involved in supervising a PhD student! Your meticulous feedback as I wrote this thesis was invaluable - thank you. To Professor Stefan Doerr: thank you for all the times you've found time to chat things through and help untangle my thoughts. You have consistently gone beyond the call of duty to help me out and I've always left your office feeling more confident and motivated than I did when I arrived.

I am grateful for the assistance of all the following past and present staff of Swansea University: Dr Purazen Chingombe, who conducted the NH_4 flow analysis for determination of biochar CECs (Chapter 4); Dr Rob Bryant, for all his help with data logging for the tube furnace; Phil Bevan, for helping me find the equipment I needed; Dr Geertje van Keulen, who taught me how to use the stereomicroscope; Dr Kath Ficken, for helping me out with my many chemistry questions; Dr Paul Williams, for showing me how to use the Mastersizer; Professor Danny McCarroll, for patiently answering my numerous questions on statistical analysis and ensuring I had the time I needed to write this thesis; and all the staff who make stuff happen, in particular, Cath Gallagher, Diane Holohan, and Sara Fenn – thank you. I am indebted to all of the following people who kindly provided me with materials, information or advice along the way: Dr Ed Hodgson (IBERS), who generously supplied me with miscanthus and willow feedstocks; Huw Denman (SelectFor), who kindly supplied me with spruce feedstock; Walter Lowe (UKBRC, Edinburgh University), who produced the softwood pellet biochars used in this study (Chapters 5 and 6); Dr Carrie Masiello (Rice University), for helpful discussions on biochar hydrophobicity; Professors Anne Verhoef (Reading University), M.B. Kirkham (Kansas State University), Rifat Bulut (Oklahoma State University) and Warren Wray (Missouri University of Science and Technology) for their invaluable advice on measuring soil suction; Professor Karl Ritz (Cranfield University), for helping me to make sense of my observations of fungal growth on soils containing biochar; and Dr Rob Simmonds (Cranfield University) for his advice on the use of rainfall simulation to measure aggregate stability.

To my office buddies over the past four years - Dominic Woolf, Sujung Ahn, Hazel Rallison, Ian Mugford, Rory Clisby, Dan Jones, Phil Harries, Tadas Nikonovas and Donna Carless: Thanks for making it easy to go in to work every day and for all the times you helped me figure out methodologies, found useful papers for me, moved things for me when I was on crutches, lent me your keycards on the embarrassingly frequent occasions that I lost or forgot mine, and much more. You are all brilliant.

Mum and Dad - in every way, I wouldn't be here if it wasn't for you (obviously) – thanks for convincing me I was clever enough to do an undergraduate degree, it probably helped. Thanks Dad for being the best Geography teacher I ever had. Hopefully this thesis demonstrates that I was sometimes listening when you said things. Thanks to my physio, Abs, who is also a first-rate sister; thanks to Ben for being like a brother to me; and thanks to my personal IT support guy, Joe, who handily doubles up as another brother.

Thanks to all of my brilliant friends who I shall not list here, simply because there are too many of you and I've already written over two pages of acknowledgements which I fear may be some kind of faux pax. I'm almost entirely confident none of you will ever read this anyway. If you are reading this, sorry. You know who you are though.

Noa Eleri - thanks for helping motivate me to get this finished. Finally, to my trusty lab assistant and excellent wife, Claire – thanks for being so incredibly supportive. You are the Ph to my D.

ABBREVIATIONS USED

AMF	arbuscular mycorrhizal fungi
BECCS	bioenergy with carbon capture and storage
BNF	biological nitrogen fixation
CCS	carbon capture and storage
CEC	cation exchange-capacity
CIs	Confidence intervals
CO_2e	carbon dioxide equivalent
CROPS	crop residue oceanic permanent sequestration
DECC	Department of Energy & Climate Change
Defra	Department for Environment, Food and Rural Affairs
FTIR	Fourier transform infrared spectroscopy
GGR	greenhouse gas removal
Gt	gigatonne (one thousand million tonnes)
HTT	highest treatment temperature
IPCC	Intergovernmental Panel on Climate Change
Miscanthus	Miscanthus x giganteus
MJ	megajoule (one million joules)
MW	megawatt
OM	organic matter
Picea	Picea sitchensis (spruce)
Salix	Salix viminalis (willow)
UNFCCC	United Nations Framework Convention on Climate Change
WDPT	water drop penetration time
WHC	water-holding capacity

1 INTRODUCTION

According to the most recent Assessment Report of the IPCC, it is 33 - 66% likely that removal of greenhouse gases from the atmosphere will become necessary if we are to avoid what the United Nations Framework Convention for Climate Change described as 'unmanageable' climate change risks (Bierbaum *et al.*, 2007; IPCC, 2013). Building on the work of previous reviews, such as the Royal Society study on geoengineering the climate (Shepherd *et al.*, 2009) and the comparative global assessment of potential negative emission technologies carried out by McLaren (2012), this chapter explores some of the most prominent potential means of greenhouse gas removal. None of the methods of greenhouse gas removal proposed thus far is without challenges. Some of them sequester carbon only temporarily, others have adverse ecological impacts, some are prohibitively expensive and / or energy-intensive and others are still in the process of being developed (McLaren, 2012a).

Biochar production is a means of greenhouse gas removal (GGR) that avoids many of the challenges faced by other GGR methods. It is produced by the thermal decomposition of biomass in a contained environment with a limited supply of oxygen (pyrolysis) and normally within a temperature range between around 350°C and 800°C. The biomass used as pyrolysis feedstock contains carbon (C), which was initially removed from the air through photosynthesis. Biomass typically decomposes rapidly, releasing the carbon dioxide (CO_2) that was fixed by the plants back into the atmosphere. Conversely, biochar is highly recalcitrant and can store carbon (C) for long periods (Cheng *et al.*, 2008). Biochar may sequester carbon for several thousand years (Lehmann *et al.*, 2009) and its production can be a self-sustaining or energy-generating process (see section 3.3), providing a range of saleable services and commodities contributing to its economic viability, including positive impacts on soil properties (McCarl *et al.*, 2009). Furthermore, a review of the literature shows that biochar can deliver numerous benefits as a soil amendment. It can increase soil fertility by improving cation exchange-capacity (CEC) (Liang *et al.*, 2006), limiting leaching of nutrients (Laird *et al.* 2010a) and by directly introducing nutrients to the soil (Angst & Sohi, 2013). Biochars can provide substrates and secure habitats for soil microbiota (Gundale & DeLuca, 2006), though observations of earthworm preference for, or avoidance of, biochar-amended soils have been mixed (Van Zwieten *et al.*, 2010; Li *et al.*, 2011). In certain soils, biochar amendments can improve water-holding capacity (WHC) (Tryon, 1948; Laird *et al.*, 2010b) and aggregate stability (Liu *et al.*, 2012) when applied at sufficiently high rates.

This thesis further explores the potential of biochar as a soil amendment. This introduction is followed by two further introductory chapters. Chapter 2 briefly explains the potential need for greenhouse gas removal and offers a concise review of the literature surrounding some of the most prominent means of greenhouse gas removal proposed to date. Chapter 3 offers a review of the literature surrounding biochar, exploring the rationale for biochar production and exploring its effects on soil properties, with a particular focus on the influence of biochar on soil hydrology and erosion.

The subsequent six chapters of this thesis report experiments conducted to address some of the research gaps identified in Chapter 3. The objectives of this thesis were to investigate how the preparation of biochars (i.e. use of different pyrolysis temperatures, feedstocks and particle sizes) can influence their effect on soil hydrology and related properties, and how different biochar application rates influence soil hydrology and physical breakdown during rainfall. These objectives were achieved by addressing three main strands of enquiry:

i. How do feedstock type and highest treatment temperature (HTT) influence biochar hydrophobicity, CEC and yield?
ii. In what ways do the HTT and particle size of biochar amendments influence their effects on soil hydrological properties?
iii. How do different biochar application rates influence the hydrological and erosional response of soil during simulated rainfall?

In Chapter 4, the influence of HTT and feedstock on biochar hydrophobicity, yields and CEC are examined. Chapter 5 explores the extent to which HTT influences the effects (in the short-term) that biochar amendments have on soil properties, focusing particularly on moisture retention. Chapter 6 employs the same methodologies as those used in Chapter 5 to investigate the extent to which particle size influences the effects that biochar amendments have on soil properties, again with a focus on moisture retention. Finally, in Chapters 7 and 8, simulated rainfall is used to investigate the effect of different biochar application rates on soil hydrology and erosion. Chapter 9 presents the conclusions arising from the five experimental chapters, discusses their potential implications and makes suggestions for further research.

2 GREENHOUSE GAS REMOVAL

2.1 Introduction

International policy discussion on mitigating anthropogenically enhanced global warming has been framed around limiting warming to an increase of 2°C above pre-industrial levels, a figure widely held to represent an upper limit that warming must not exceed if we are to avoid 'unmanageable' climate change risks with irrevocable consequences (Commission for European Communities, 2007; Bierbaum *et al.*, 2007; Meinshausen, 2009; UNFCCC, 2009).

Apart from water vapour, carbon dioxide is by far the most significant of anthropogenic greenhouse gases. According to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, greenhouse gas emissions in 2011 were the CO_2 equivalent (CO_2e) of 38 gigatonnes (Gt). Cumulative anthropogenic emissions reached 1,947 Gt CO_2e in 2011 (IPCC, 2013). In order to have more than a 50% chance of not exceeding 2°C warming relative to pre-industrial levels, cumulative emissions will have to be limited to less than 4,437 Gt CO_2e (IPCC, 2013). There is a 33 - 66% chance that it will be necessary to remove greenhouse gases from the atmosphere to stay within this limit (IPCC, 2013). Increasing numbers of countries (112 currently) now support a more conservative warming limit of 1.5°C, which would require an atmospheric CO_2 concentration of 350 ppm (350.org, 2013). Every part per million corresponds to 7.8 Gt CO_2 (Socolow *et al.*, 2011). On current emission trends, returning atmospheric CO_2 to 350 ppm by the year 2100 would require removal of 20 - 50 Gt CO_2 per annum for 50 to 75 years

(McLaren, 2012b). Reducing atmospheric CO_2 concentrations will also mitigate other direct consequences of elevated atmospheric CO_2 such as ocean acidification, which cannot be addressed by geoengineering techniques that do not reduce atmospheric CO_2 (Shepherd *et al.*, 2009).

Scientists and engineers have proposed several methods of removing greenhouse gases from the atmosphere, often referred to as negative emissions technologies, most of which are focused on capture of CO_2, rather than other more potent, but less prolific greenhouse gases such as methane or nitrous oxide. The most prominent of these methods of carbon sequestration are discussed below. For the sake of brevity, other greenhouse gas removal methods with significant potential, such as use of timber in construction, carbon negative cement, hempcrete and wetland creation are not examined here.

2.2 Bioenergy with carbon capture and storage

Commonly referred to in the literature as BECCS, this approach to carbon sequestration involves combining two technologies commonly associated with mitigation efforts: bioenergy and carbon capture and storage (CCS). Bio-energy crops take up CO_2 as they grow and can then be burned to release energy directly, or converted to liquid fuels such as ethanol. 80-90% of the CO_2 released during these combustion or conversion processes can be captured using CCS (IPCC, 2005), resulting in a net sequestration of carbon.

It has been proposed that by 2050, a net total of 0.8 - 3.2 Gt CO_2 could be pumped into geological storage annually through use of BECCS, assuming a biomass supply of 126 exajoules (EJ) a year (Koornneef et al., 2011). This would necessitate an upscaling by two orders of magnitude of the international trade of solid and liquid biofuels, which in 2006 was about 0.9 EJ (Heinimö & Junginger, 2009). There is considerable variability in projections of global biomass potential due to differences in how comprehensively different resource categories are included and uncertainties and sensitivities in the parameters used to project the availability of resources needed for biomass production. Assessments of the global biomass potential availability range three orders of magnitude, from 50 to 1,500 EJ a year, the variations being largely due to different forecasts of land availability and yield improvement for both food and energy crops (McGlashan *et al.*, 2012). Koornneef *et al.* (2012) estimated that the economic potential of BECCS could be as high as 3.5 Gt CO_2 y^{-1}, but this assumes a CO_2 price of €50 per tonne. In contrast, prices under the European Union Emission Trading System (the world's largest carbon market) in early 2014 were only around €5.

The challenges for BECCS are not only economic; its widespread implementation could place significant strain on natural resources. According to Berndes (2008), a large-scale expansion of energy crop production could lead to a large increase in evapotranspiration, potentially as large as the present evapotranspiration from global cropland, which could enhance already stressed water situations in some countries. However, this would of course depend on the nature of the initial vegetation replaced by energy crop production. Smith & Torn (2013) estimate that removal of 3.7 Gt CO_2 annually using switchgrass BECCS would have a nitrogen requirement equivalent to 44% of global N fertiliser production in 2009, and require 2 million km^2 of land (20 times the current US area under bioethanol production). Demand for biofuels plantations has in the past resulted in 'land-grabbing', considered by some to have negative environmental and social impacts, particularly for farmers in developing countries (Zoomers, 2010; Borras *et al.*, 2011). Conversion of natural forests to pine or eucalyptus monocultures has increased in recent decades with deleterious effects for biodiversity (Zurita *et al.*, 2006). Bioenergy projects can convert native habitats to cropland directly or indirectly, by displacing cropland or rangeland, resulting in land clearance elsewhere (Lapola *et al.*, 2010). Simulations conducted by Lapola *et al.* (2010) have shown carbon emissions arising from land use changes for biofuel crops can outweigh the emissions savings made by replacing fossil fuels with biofuels (though it should be noted that these simulations were for bioenergy without CCS). A further challenge for BECCS is its dependence on sites for geological storage of CO_2 (see section 2.5).

2.3 Forestation

Canadell & Raupach (2008) estimated that efforts aimed at reforestation and reduced deforestation could achieve sequestration of up to 5.5 Gt CO_2 $year^{-1}$, assuming carbon sequestration and avoidance prices of between US$ 20 and 100 per tonne of CO_2. This would offset 2 - 4% of projected emissions increases over the same period (Canadell & Raupach, 2008). Lenton (2010) estimated that foresting an area of 2.64 million km^2 could store 0.77 - 1.54 Gt CO_2 per year.

However, although carbon sequestration rates of temperate forests are high, the net climate forcing of temperate forests is uncertain as they have lower albedo than croplands and many climate model simulations indicate that trees warm surface air temperature relative to crops (tropical forests also have relatively low albedo but this is offset by strong evaporative cooling) (Bonan, 2008; Arora & Montenegro, 2011). In any case, the primary production the terrestrial biosphere is expected to decrease with increasing global temperatures (despite the effect of CO_2 fertilization), reducing their capacity as carbon sinks (Woodward, 2007). Moreover, any carbon sequestered by forests may be vulnerable to future climate change or reversal by burning (Jones *et al.*, 2013).

Forestation projects could be problematic in terms of land and water resources. Projections indicate that rising world population and changing diets may require an additional 2m km^2 of land (an area more than 8 times the size of the UK) devoted to food production by 2050 (Tilman *et al.*, 2011). Without significant agricultural intensification, almost 10 million km^2 (an area larger than the US) may be required (Tilman *et al.*, 2011). Large forestation projects could therefore lead to a significant gap between land demand and availability, leaving the world's growing population unable to feed itself. Smith & Torn (2013) estimated that tropical forestation could increase local evapotranspiration from 50% of mean annual precipitation to 75%, placing significant strain on local water resources. However, it should also be noted that increased evapotranspiration would tend to result in an increase in low elevation cloudiness which would increase planetary albedo and therefore have a cooling effect on global temperatures (Ban-Weiss *et al.*, 2011).

2.4 Reduced tillage

Much research has been focused on the potential for reduced tillage to result in soil carbon sequestration (Follet, 2001; West & Post, 2002; Lal, 2004). When natural grassland or forest is converted to cropland, as much as 50% of the soil carbon is lost, primarily because annual tilling increases decomposition rates by aerating, or exposing, undecomposed organic matter - around 55 GtC has been lost historically in this way (Pacala & Socolow, 2004). A review of data from the National Soil Inventory of England and Wales obtained between 1978 and 2003 showed carbon was lost from soils across England and Wales over the survey period at a mean rate of 0.6% yr^{-1} (Bellamy *et al.*, 2005). However, a more recent survey by Emmett *et al.* (2007) was unable to confirm this loss, finding no net change in carbon concentration between 1978 and 2007. Pacala & Socolow (2004) estimated that if conservation tillage practices had been applied to all cropland globally in 2004 in conjunction with enforced adoption of credible soil conservation methods, 12.5 - 25 Gt C could be stored by 2054. This represents 7 - 14% of the 175 GtC capture and sequestration Pacala & Socolow (2004) claim is necessary to limit atmospheric CO_2 concentrations at 500 ± 50 ppm.

The literature surrounding reduced tillage can be ambiguous, with titles such as "Conservation Tillage for Carbon Sequestration" (Lal & Kimble, 1997) imprecisely suggesting that reduced tillage directly results in soil removing atmospheric carbon. When soil is tilled, soil carbon is oxidised, and removal of crop residues to facilitate easier tillage means organic carbon is removed that could otherwise be assimilated into the soil through humification (Lal, 2004). However, removing crop residues from a field does not necessarily mean organic carbon cannot be assimilated into soil elsewhere. Also, whilst reducing tillage does reduce the amount of carbon released into the atmosphere by oxidation, it does not directly increase the amount of new soil carbon (Burras *et al.*, 2001; Sundermeier *et al.*, 2005). Rather, increased soil carbon associated with conservation tillage is a result of indirect carbon sequestration from decomposition of crop residues left in-situ (rather than being removed for easier tillage), in conjunction with reduced oxidation of soil carbon, resulting in a lower rate of loss (Burras *et al.*, 2001; Sundermeier *et al.*, 2005). There is no conclusive evidence that reducing tillage increases direct sequestration by chemical reactions converting carbon dioxide into soil inorganic carbon compounds (Burras *et al.*, 2001; Sundermeier *et al.*, 2005). Any carbon sequestration associated with conservation tillage practices could actually be achieved without conservation tillage, because crop residues can conceivably be temporarily removed before tillage then returned as mulch afterwards.

Harbinson (2001) argued that carbon emissions savings achieved through reduced tillage might actually be cancelled out by production, transport and application of the herbicides needed in place of tillage. This argument is countered somewhat by writers who point to the reduced CO_2 emissions resulting from reduced use of farm machinery (Koga *et al.*, 2003; Lithourgidis *et al.*, 2005) and also by the fact that in horticultural systems, weeds are often suppressed using mulching rather than herbicides. A large proportion of the carbon that accumulates in soils through conservation tillage is labile and could easily be lost through soil disturbance (Jacinthe & Lal, 2006). In soils with a carbon content of greater than 100 g kg^{-1}, the rate of loss has been found to be 2 % yr^{-1} (Bellamy *et al.*, 2005). Strand & Benford (2009) argue that soil sequestration is inefficient and temporary because after 20 years, less than 10% of the original crop residue carbon remains in the soil, and once at equilibrium, even this is matched by a loss. Furthermore, whilst there is still debate as to the precise effect of climate change on global soil carbon stocks, it has been speculated that as global temperatures increase, soil respiration may be accelerated, enhancing carbon decomposition (Davidson and Janssens, 2006). Reducing tillage does not so much sequester carbon as reduce oxidation of soil carbon and might therefore be better understood as means of reducing agricultural carbon emissions rather than as a means of carbon sequestration.

Calculating atmospheric CO_2 removal by conservation tillage is challenging and there is no conclusive evidence that it increases carbon storage in all soils (Powlson *et al.*, 2012; Stockmann *et al.*, 2013). Furthermore, carbon storage associated with reduced tillage might be counteracted by increased soil emissions of nitrous oxide, a highly potent greenhouse gas (Powlson *et al.*, 2012). It has been estimated that implementation of conservation tillage practices could enable a peak storage of 0.77 Gt CO_2 per year (Thomson *et al.*, 2008). However, soils would eventually become carbon-equilibrated, so this rate could not be sustained (Stockmann *et al.*, 2013).

2.5 Direct air-capture

Several methods have been proposed for capturing CO_2 directly from ambient air using chemical sorbents such as sodium hydroxide or polymer based ion-exchange resins (Stolaroff *et al.*, 2008; Lackner, 2009). These sorbents would then be heated or washed to release CO_2 which would be pressurised and injected into geological storage. Cost estimates for direct air capture methods vary dramatically (from 30 to >600 US dollars per tonne of CO_2 captured), partly because some methods would adapt existing technology from scrubbing towers (Socolow *et al.*, 2011; Holmes & Keith, 2012; Mazzotti *et al.*, 2013), while others would utilise novel technology that is less well-established but may have the potential to become cheaper and more efficient in the long-term (Lackner, 2009). Either way, even the most optimistic cost estimates far exceed current carbon prices. In 2013, under the European Union Emissions Trading Scheme (EU ETS), the world's largest carbon market, carbon prices were €4 t^{-1} CO_2, equivalent to US $5 t^{-1} CO_2. (World Bank, 2014). Models developed by Thomson Reuters Point Carbon, suggest that CO_2 prices for 2030 may range from €40-50 t^{-1} CO_2 (Ferdinand, 2014).

An additional challenge (and cost) to direct air capture methods (and also BECCS) is geological storage. Cost estimates for geological storage of CO_2 span two orders of magnitude depending on the storage site location (DECC, 2012). Geological storage projects in Europe have been abandoned because of public opposition arising from fears about safety and inadequate involvement of local stakeholders (Brunsting *et al.*, 2011). Should these challenges be overcome however, direct air capture would be highly scalable and would theoretically be capable of sequestering several Gt CO_2 annually (McLaren, 2012a), assuming sufficient geological storage availability.

2.6 Ocean fertilization

Iron is a necessary trace element for photosynthesis, but it is highly insoluble in seawater and its low availability limits phytoplankton growth in the high nutrient-low chlorophyll regions of the oceans such as the North-East and Equatorial Pacific. Large phytoplankton blooms can therefore be created by introducing iron to the upper-ocean in iron-deficient waters. Iron would enhance phytoplankton productivity and lower levels of dissolved CO_2 in the upper-ocean, which could lead to carbon levels being restored through a flux of atmospheric CO_2, reducing atmospheric CO_2 levels (Jones & Young, 1997). When the phytoplankton die, a proportion would sink to the deep ocean, storing the carbon they hold there. However, the efficacy by which ocean fertilization would sequester CO_2 is poorly constrained (Buesseler, 2008). An alternative means of enhancing phytoplankton growth is the use of vertical pipes that utilise wave energy to pump nutrient-rich waters from below the thermocline into the relatively nutrient-poor waters at the ocean surface, promoting algal blooms (Lovelock & Rapley, 2007).

Ocean fertilization is considered by its proponents to have multiple benefits besides carbon sequestration. Increasing the productivity of plankton through ocean fertilization could increase fish stocks, contributing to much-needed global protein production (Jones & Young, 1997). Ocean fertilization might be considered a dual-pronged approach to climate change mitigation as phytoplankton (such as the coccolithophorid *Emiliania Huxleyi*) produce dimethyl sulphide, which is oxidised in the atmosphere to sulphur dioxide which can form sulphate aerosols that increase Earth's albedo, causing cooling (Wingenter *et al.*, 2004). However, the production of cloud-forming particles from dimethyl sulphide is highly episodic, so assessing the potential impact of ocean fertilization on albedo is difficult (Wingenter *et al.*, 2004).

Despite its supposed benefits, ocean fertilization is yet to be accepted by the scientific community as a viable means of CO_2 sequestration. The efficiency of iron fertilization in sequestering atmospheric carbon remains largely unknown (Aumont & Bopp, 2006). Buesseler *et al.* (2008) note that modelling studies have suggested that ocean iron fertilization would be unlikely to sequester more than several hundred million tons of carbon per year and would thus be unable to make more than a minor contribution to emissions mitigation. Furthermore, there is currently little understanding of the intended and unintended ecological and biogeochemical impacts of iron ocean fertilization which are spread over a large area by oceanic circulation, making long-term assessment and verification problematic (Buesseler *et al.*, 2008). The energy costs of iron fertilization are likely to be high as it would involve shipping to rather distant regions of the ocean in some cases. Most commentators stress that ocean iron fertilization cannot be considered a viable means of generating carbon offsets until there is stronger evidence that ocean iron fertilization effectively removes atmospheric CO_2, retains carbon in the ocean for a quantifiable period, and has predictable and acceptable environmental impacts (Buesseler *et al.*, 2008; Shepherd *et al.*, 2009). There is currently an international moratorium on major ocean iron fertilization until scientists better understand the potential risks and benefits of manipulating the oceanic food (Secretariat of the Convention on Biological Diversity, 2009).

2.7 Ocean liming

Ocean liming would involve heating limestone ($CaC0_3$) until it breaks down into CO_2 (which must be captured and pumped into geological storage) and lime (CaO), which would be released into the surface waters of the ocean (Renforth *et al.*, 2013). The lime would react with CO_2 dissolved in seawater to form bicarbonate (H_2CO_3) and thus enable the seawater to absorb additional atmospheric CO_2 to replace that removed by formation of bicarbonate (Renforth *et al.*, 2013). As limestone is abundantly available, the only limiting factors for ocean liming are energy for calcining limestone, vessels and port facilities, and the availability of geological storage for the CO_2 released during calcining which must be captured and stored (see section 2.5).

Ocean liming would deliver the co-benefit of increasing ocean alkalinity, counteracting the effect of elevated CO_2 concentrations in lowering ocean pH (Paquay & Zeebe, 2013). However, the ecological effects of heightened local alkalinity following ocean liming have not yet been discussed in the literature, nor have the onshore effects of the process, which would include extensive quarrying. Cost estimates for ocean liming range from US$ 72 to US$ 159 t^{-1} CO_2 sequestered (Renforth *et al.*, 2013; Paquay & Zeebe, 2013), but these figures are highly uncertain. Using ocean liming to capture 3.7 Gt CO_2 annually would probably require an industry larger than the current global cement industry (McGlashan *et al.*, 2012).

2.8 Oceanic burial of crop residues

"Crop residue ocean permanent sequestration (CROPS)" as it was branded by Strand & Benford (2009), can be simply defined as the removal of crop residues for deep ocean burial. Strand & Benford (2009) stated that CROPS is 92% efficient in sequestration of crop residue carbon and could potentially capture 15% of the current global CO_2 annual increase, using existing infrastructure and technology to confine the carbon for millennia. However, Karlen *et al.* (2009) argued that CROPS could have harmful consequences as crop residues provide multiple services in agricultural systems - including protection against soil erosion, food sources for many organisms, enhanced water infiltration, retention and release, enhanced nutrient cycling and improved soil structure - all of which are critical for sustaining the soil resources upon which we depend for food, livestock feed, fibre and biofuel feedstocks. Nutrients lost through removal of crop residues would have to be replaced by fertilizers and costly, specialised equipment with additional operator time would also be required, resulting in a high opportunity cost associated with harvesting crop residue (Karlen *et al.*, 2009). The potential loss of phosphate is also particularly serious in view of the ongoing depletion of phosphate resources. Karlen *et al.* (2009) also pointed out that the transportation costs and CO_2 released through combustion of transportation fuels pose a significant threat to the credibility of CROPS as a viable means of sequestration. Furthermore, unless sufficient material were deposited to create anoxic conditions (this in itself constituting a major ecosystem perturbation), organic material would be slowly decomposed and the carbon and nutrients returned to shallow waters, disrupting growth and nutrient cycling in the ocean ecosystem (Shepherd *et al.*, 2009).

2.9 Enhanced weathering

When silicate minerals dissolve in seawater or rainwater, CO_2 is drawn in to the resultant solution, forming carbonate ions, which can be incorporated into the shells or skeletons of certain aquatic organisms, a portion of which sinks into the deep ocean when the organisms die (Hartmann *et al.*, 2013). This process can be described by the following simplified equation for enhanced weathering of olivine:

$$Mg_2SiO_4 + 4CO_2 + 4H_2O \rightarrow 2Mg^{2+} + 4HCO_{3-} + H_4SiO_4$$
$$\rightarrow 2MgCO_3 + SiO_2 + 2CO_2 + 4H_2O$$

Enhanced weathering would involve applying finely ground, silicate-containing rocks to soils (Schuiling & Krijgsman, 2006) or seawater (Köhler *et al.*, 2013) to augment this process in order to reduce atmospheric CO_2 levels. Köhler *et al.* (2010) estimated that global use of enhanced weathering might annually capture up to 3.7 Gt CO_2 if the difficulties of spreading silicate minerals in remote, densely forest areas could be overcome. This method is currently conceptual as the weathering rates achieved in laboratory experiments are yet to be replicated in field trials, where weathering is typically 2 - 4 orders of magnitude slower (White & Brantley, 2003). Moreover, enhanced weathering is not without its risks. Release of elements such as Si, P and K during mineral dissolution could result in an inadvertent ocean fertilization effect, disrupting oceanic ecosystems (Köhler *et al.*, 2013). Use of enhanced weathering on agricultural land could also have a fertilization effect, but might also result in crop uptake of toxic metals (Hartmann *et al.*, 2013).

2.10 Summary

If we are to be certain that global warming will not exceed 2°C above pre-industrial levels, greenhouse gas removal may become necessary. Several methods of carbon sequestration have been proposed. Some of these methods sequester carbon only temporarily, others might have adverse ecological impacts, some are prohibitively expensive and / or energy-intensive and others are still in the process of being developed.

Although forestation has significant potential for carbon sequestration, its net climate forcing is uncertain and forest productivity is in any case expected to decline as temperatures increase, while forestation projects will face growing competition for land and water resources and population increases. Reduced tillage could help increase soil carbon storage, but the efficacy of carbon sequestration through conservation tillage remains unclear. Direct air-capture methods would be capable of removing and securely storing large volumes of carbon dioxide, but are unlikely to become economically viable under foreseeable carbon market conditions. Ocean fertilization is a means of carbon sequestration that could have beneficial side-effects such as increased fish stocks, but its efficacy and ecological impacts remain unclear. Ocean liming could sequester large volumes of CO_2, but its ecological impacts are yet to be explored. Furthermore, along with direct air-capture and BECCS, ocean liming is dependent on the successful development of geological CO_2 storage, which is costly and politically sensitive. The potential economic and ecological costs of CROPS seem to outweigh its limited carbon sequestration potential. Enhanced weathering has significant carbon sequestration potential, but only if the rates of weathering observed in field trials can be dramatically increased.

An additional means of greenhouse gas removal that has not been discussed in this chapter is the production of biochar. Although biochar does share some of the challenges faced by the greenhouse gas removal methods described above, there are many that it might avoid. The potential of biochar is explored in detail in the following chapter.

3 BIOCHAR FOR GREENHOUSE GAS MITIGATION AND SOIL IMPROVEMENT: A REVIEW

3.1 Introduction

The application of biochar to soil has been proposed as a novel approach to establish a substantial long-term sink for atmospheric CO_2 in terrestrial ecosystems (Lehmann et al., 2006). Biochar is generally considered to comprise biomass-derived char produced specifically for application to soil (Sohi *et al.,* 2010). Increased crop yield is a frequently reported benefit of applying biochar to soil and meta-analysis has shown a small but statistically significant benefit of biochar application on crop productivity, with a grand mean increase of 10% (Jeffery *et al.,* 2011). It should be noted however, that the results for each analysis within the meta-analysis covered a wide range, from -28% to 39%, and were dependent on the biomass used to produce biochar, the application rate and nature of the soil to which biochar was applied (Jeffery *et al.,* 2011).

Recent research on biochar was instigated by the discovery of *terra preta* soils in the Amazon. These anthropogenic soils have textures, mineralogy and other geochemical signatures similar to those of adjacent soils but are often distinguishable by their higher contents of ceramic and lithic artefacts and also by their characteristic black colour which contrasts with the Ferralsols typical of the area (Dawit *et al.,* 2007). Compared to adjacent soils, these anthrosols have been shown to have accumulated much higher levels of fertility over time under non-agricultural use. The terra preta soils have come to be known as Amazonian Dark Earths and are estimated to have developed between 500 and 9000 years B.P. through human activity including biomass burning and nutrient deposition on pre-Columbian Amerindian settlements. It has been suggested that soils could be enhanced today in a similar manner through the use of biochar (Lehmann & Joseph, 2009a).

Biochar is produced by the thermal decomposition of biomass in a sealed environment with a limited supply of oxygen (pyrolysis) and normally within a temperature range between around 350°C and 800°C. Many studies also include biomass heated to temperatures between 200 and 300°C within their definition of biochar, but for the purposes of this literature review, such products are considered to be torrefied material (Zheng *et al.*, 2012; Atienza-Martínez *et al.*, 2012) rather than biochar. Mok *et al.* (1992) found that structural degradation of cellulose only began at around 300°C; for woody species the threshold was higher (312 - 322°C), while for herbaceous plants the threshold was slightly lower (291 - 299°C). These temperature ranges broadly correspond the endothermic (< 280°C and > 350°C) and exothermic (> 350°C) phases of biomass pyrolysis (Evans, 2008).

Biochar differs from charcoal in that it is specifically produced as a means of carbon sequestration and as a soil amendment, and therefore it can be produced from any biomass feedstock, whereas charcoal tends to be produced from woody feedstocks. The biomass used as pyrolysis feedstock contains C, which was initially removed from the air through photosynthesis. Biomass typically decomposes rapidly, releasing the CO_2 that was fixed by the plants back into the atmosphere. Converseley, biochar is highly recalcitrant and is thus able to store C for long periods (Liang *et al.*, 2008; Lehmann *et al.*, 2008).

The physio-chemical properties of biochar are difficult to define as they are dependent on the organic material and charring conditions used. The crucial property of biochar is its high C content, which largely comprises sheets of aromatic compounds characterised by rings of six C atoms linked together without oxygen or hydrogen atoms which are otherwise more plentiful in living organic matter (Lehmann & Joseph, 2009a). Graphite comprises aromatic rings arranged in perfectly stacked and aligned sheets, but pure graphite is not formed to any significant extent within the temperature ranges used to produce biochar. Pyrolysis instead yields rather more irregular (turbostratic) arrangements of C that contain O, H, and sometimes minerals, depending on the feedstock (Lehmann & Joseph, 2009a; Downie *et al.*, 2009). The crystalline particles comprising biochar enlarge and become more ordered with increases in highest treatment temperature (HTT) (Downie *et al.*, 2009).

Several of the challenges faced by other means of greenhouse gas removal discussed in the previous chapter are not shared by biochar. Firstly, biochar's sequestration of carbon is not dependent on geological CO_2 storage. Secondly, rather than having high energy-costs, biochar production can release energy as a co-product. Thirdly, although negative impacts are possible when biochar is applied to soil, it often has positive ecological impacts. Fourthly, biochar production has potential as a commercially viable enterprise as it produces saleable commodities and is therefore not purely reliant on emissions trading. Finally, unlike many other sequestration technologies, which are at the concept or pilot stages of development, biochar production is an old technology that can be adopted at various scales and used today. The viability of biochar for CO_2 sequestration is examined in greater detail below. Beginning by exploring the biochar as a means of greenhouse gas mitigation and the relative energy efficiency of biochar production, this review then briefly discusses the energy efficiency of biochar production, its potential as a waste-management tool and the economic viability of biochar production. However, the majority of this review is devoted to investigating the emerging body of knowledge regarding the effects of biochar amendments on soil nutrient dynamics, biota, hydrology and erosion.

3.2 Biochar for greenhouse gas mitigation

Woolf *et al.* (2010) estimated that without endangering food security, habitat or soil conservation, production of biochars and their application to soil could directly sequester 1.8 - 3.3 Gt CO_2 per year, whilst also avoiding an additional 1.8 - 3.3 Gt CO_2e of net global emissions of CO_2, N_2O and CH_4, equating to 12% of current anthropogenic CO_2e emissions. It should, however, be acknowledged that such a widespread implementation of biochar technology could share some similar challenges to those of BECCS and forestation methods of greenhouse gas removal (see Chapter 2).

3.2.1 Carbon sequestration in biochar

The physical, chemical and biological stability of biochars are of fundamental importance to their use as a carbon sequestration technology, as this will determine how long C applied to the soil as biochar will remain sequestered in the soil and also how long it can influence pedospheric greenhouse gas emissions (Lehmann *et al.*, 2009).

The chemical recalcitrance of biochar persists over long periods. A study of black carbon in the Amazonian Dark Earths found there were no differences in aromaticity between biochar particles of ages between 700 and 7000 years (Liang *et al.*, 2008). In Kenya, a study of the first 100 years of biochar exposure to soil found that whilst surfaces of biochar particles were oxidised rapidly within 5 years, below this 10nm thick surface layer the O:C ratio remained unchanged (Nguyen *et al.*, 2008). This indicates that whilst biochar does decompose to a degree, the stability of the remaining biochar persists over long periods. Radiocarbon dating of charcoal found in high proportions in the Amazonian Dark Earths indicates that it originated between 500 and 7000 years ago (Lehmann *et al.*, 2009). Other studies have found soil charcoal deposits up to 9500 years old in central Guyana (Hammond *et al.*, 2007) and deposits over 23,000 years old in Costa Rica (Titiz & Sanford, 2007). It should be noted, that these findings may be indicative only of the recalcitrance of certain portions of charcoal, as it is possible that other portions were degraded prior to dating.

Lehmann *et al.* (2008) compared annual production of black carbon by savannah fires to measured char stocks for various soils in North Australian woodlands. Assuming the most likely and conservative scenarios of the proportions of char produced per unit biomass burned, the extent and frequency of biomass burning and biomass production, evidence suggests the mean residence time of char in the dryland conditions of Northern Australia is between 1300 and 2600 years (Lehmann *et al.*, 2008). However, whilst the above data provide some indication of the potential stability of biochar, they provide no evidence of biochar's actual decomposition rates. Furthermore, few studies have investigated the stability of biochar under mid-latitude and temperate climatic conditions. Gomez *et al.* (2014) observed increased CO_2 emissions from temperate soils with increasing biochar application rate, but this could only be partially explained by priming - microbial utilization of biochar carbon.

Carbon budgeting of biochar suggests that its average stability is much greater than that of plant litter. Forbes *et al.* (2006) estimated global production of black carbon (produced by incomplete combustion of biomass or fossil fuels) to be between 0.05 and 0.27 Gt C y^{-1}. This is less than 0.5% of the global net primary production by land plants, estimated by Sabine *et al.* (2009) to be about 57 GtC y^{-1}. However, a study of soils selected from long-term research plots in five widely different agricultural areas of the USA found that charcoal constituted between 10 and 35% of the total organic carbon in the soils (Skjemstad *et al.*, 2002), and a previous study of four different soil types in Australia found charcoal constituted up to 30% of total soil carbon (Skjemstad *et al.*, 1996). Combined, these studies indicate that biochar has a significantly slower rate of decomposition than plant litter.

It is important to note that differences in biochar stocks over time should not be interpreted only in terms of decomposition or mineralization to CO_2, as biochar can also be removed from soil by leaching or erosion (Olson and Tryterud, 2000; Czimczik *et al.*, 2003; Rumpel *et al.*, 2006; Lehmann *et al.*, 2009; Major *et al.*, 2010). Consumption by subsequent fires has also been considered a major mechanism of black carbon losses from soil (Preston & Schmidt, 2006; Czimczik & Masiello, 2007), but recently published data indicate that losses by fires are actually likely to be small (Santín *et al.*, 2013).

The effect of biochar application on soil organic matter is debated, with some studies indicating increased mineralization (positive priming) and others indicating a decrease in C metabolism, causing increased stabilization of soil organic carbon (negative priming). For example, Cross and Sohi (2011) found that carbon mineralization was often higher in biochar-amended soil but demonstrated that this was due to swift utilization of a small, labile proportion of the biochar rather than a positive priming effect on native soil organic matter. In fact, for grassland soils, biochar actually had a negative priming effect (Cross and Sohi, 2011). Conversely, although Farrell *et al.* (2013) observed a substantial reduction in positive priming of biochar amended soils after 15 days of incubation, it nonetheless remained persistent throughout 74 days of incubation. Observations of enhanced losses of boreal forest litter in the presence of black carbon had led some commentators to speculate that the carbon sequestration potential of biochar might be significantly offset or even negated by losses of non-pyrogenic soil organic carbon (Wardle *et al.*, 2008; Lehmann & Sohi, 2008). However, it has since been demonstrated that the potential effect of increased labile organic carbon decomposition is negligible, even when assuming that (i) the priming effect is the largest recorded in any published study and (ii) ther priming effect persists in the long-term (Woolf & Lehmann, 2012).

Zimmerman (2010) found that carbon release from year-long abiotic incubations of biochar was 50-90% that of microbially inoculated incubations, indicating that abiotic processes were consistently responsible for about half the oxidation of black carbon during the year. These conclusions contrast with those of Cheng *et al.* (2009) who examined changes in surficial functional-group chemistry following 4-month incubations at 30°C and found that abiotic processes were more important than biotic processes. However, Zimmerman (2010) argued that BC loss via mineralisation (oxidation to CO_2) probably occurs at different rates and by different processes to the oxidation of the BC surface to O-containing functional groups. It is also noteworthy that the two experiments used different microbial inoculants and are therefore not directly comparable. Cheng *et al.* (2006) state that increases in hydrophilicity brought about by abiotic oxidation could also facilitate higher levels of microbial oxidation.

Lehmann (2007a) argued that quantification of the long-term stability of biochar will require long-term observations that are impractical for traditional experiments. As biochars consist of recalcitrant aromatic ring structures and more easily degradable aliphatic and oxidized carbon structures, a portion of a given biochar particle may indeed be mineralized very rapidly in a short-term experiment, but an extrapolation of data produced by such an experiment to the whole biochar could lead to erroneous projections (Lehmann, 2007a). Furthermore, whilst surface oxidation may be initiated within timescales as short as a few months (Cheng *et al.*, 2006), even after hundreds of years it can remain restricted to the outer areas of a particle, meaning that quantification of the decomposition of fresh biochar through short-term experiments may lead to overestimation of long-term decay (Lehmann, 2007a).

Zimmerman (2010) demonstrated that increasing pyrolysis temperature has an exponential effect on the long-term stability of the resultant material to both abiotic and microbial decay. For example, the difference between the half-lives of material pyrolysed at 250°C and 400°C was ~20%, but there was an order of magnitude difference between the stability biochars produced at 525°C and 650°C (Zimmerman, 2010). Mašek *et al.* (2013) also found that the concentration of stable (not susceptible to thermal and chemical oxidation) biochar increased with increasing pyrolysis temperature. However, actual yield of the stable biochar fraction is almost independent of pyrolysis temperature (Mašek *et al.*, 2013).

3.2.2 Influence of biochar on soil greenhouse gas emissions

There is evidence to suggest that greenhouse gas emissions from soil may be significantly reduced by biochar application. Rondon *et al.* (2005) reported that applying biochar at a rate of 20 t ha^{-1} to an acid savannah soil in eastern Colombia led to a 50% reduction of nitrous oxide (N_2O) emissions and an almost complete suppression of methane (CH_4) emissions. Spokas & Reicosky (2009) examined the effect of 16 different biochars on the greenhouse gas emissions of 3 different soils and found that the effect of biochar amendments is highly dependent on the biochar and the soils used. However, in the majority of cases, biochar additions reduced CO_2 and CH_4 emissions or had no effect, while N_2O emissions were almost always suppressed (Spokas & Reicosky, 2009). Suppression of N_2O emissions following biochar application was also reported by, *inter alia*, Yanai *et al.* (2007) and Zhang *et al.* (2010). However, Zhang *et al.* (2010) also found that biochar application led to increased CH_4 emissions. The mechanisms by which the emissions are reduced remains unclear (Gaunt & Lehmann, 2008). It is evident that further research is necessary to identify the exact mechanisms by which these emissions suppressions occur and under what conditions they can be expected.

Biochar application may also indirectly reduce greenhouse gas emissions through its effect of reducing nutrient leaching (see section 5.4.3). If less agricultural nutrients are lost through leaching, fertilizers will not have to be applied so often, reducing the emissions associated with fertilizer production, transport and application.

3.3 Energy efficiency of biochar production

Whereas many other proposed means of greenhouse gas removal have large energy requirements, biochar production can be a self-sustaining, energy generating process. The pyrolysis process releases syngas containing combustible gases. In advanced, continuous feed pyrolysers, these gases can be combusted to dry incoming feedstock and also to heat the pyrolysis kiln itself (Best Energies Inc., 2006; Brown, 2009). If the pyrolysis process is optimized for syngas production, the energy yield is 50% of the energy contained in the feedstock and if pyrolysis is optimized for biochar production, the energy yield is 38% of the energy contained in the feedstock (Gaunt & Lehmann, 2008).

Using Switchgrass (*Panicum virgatum*), *Miscanthus*, forage corn, wheat straw and corn stover as feedstocks, energy output from pyrolysis optimized for energy production ranges from 3.0 - 9.1 MJ MJ^{-1} (Gaunt & Lehmann, 2008). If pyrolysis is optimised for biochar production, energy output is about 30% lower, ranging from 2.3 - 6.9 MJ MJ^{-1} (Gaunt & Lehmann, 2008). However, this lower energy output still compares favourably with ethanol production from corn which yields 0.7 - 2.2 MJ MJ^{-1} (Patzek & Pimentel, 2005; Metzger, 2006) and is likely to remain competitive with future cellulosic ethanol technologies which projections estimate will yield ~4-6 MJ MJ^{-1} (Hammerschlag, 2006).

3.4 Biochar for waste management

3.4.1 Agricultural and food-processing wastes

Agricultural and food-processing wastes can lead to pollution of ground and surface waters and can therefore present a significant burden to agricultural and food processing industries which face increasing regulatory pressure to reduce their environmental impacts (Matteson & Jenkins, 2007). The following examples illustrate a wide range of problematic wastes that could conceivably be utilised for biochar production:

Manure management practices have traditionally recycled plant nutrients through land application, but in the US there is an increasing trend toward so-called concentrated animal feeding operations whose manure production often exceeds local crop and pastureland nutrient demands (Cantrell *et al.*, 2007). Over-application of animal manure can result in emissions of ammonia (contributing to acid rain) and GHGs, spread of pathogens, release of hormones and other pharmaceutically active compounds and eutrophication of water resources (Cantrell *et al.*, 2007). Several studies have shown that biochar produced from manure can have beneficial agronomic impacts (Chan *et al.*, 2008; Tagoe *et al.*, 2008; Shinogi *et al.*, 2008).

Cassava (*Manihot esculenta*) is a staple food across large parts of sub-Saharan Africa, South-East Asia and Latin America. Fresh cassava peels contain toxic levels of hydrocyanic acid (364.2-814.7 ppm) and are normally left to rot in the open, resulting in health hazards (Tewe, 1992; Oboh, 2006). Cassava peel accounts for 10-13% of the wet weight of a cassava tuber (Oboh, 2006; Oyebimpe *et al.*, 2006) though this figure can be much higher if cassava is peeled by hand. In Nigeria, roughly 10 million tonnes of cassava tubers are peeled for processing every year (Oboh, 2006), meaning that ~1 million tonnes of cyanogenic waste is produced. Sudaryanto *et al.* (2006) found that cassava peel is an ideal feedstock for production of activated carbon, indicating that it may also be a suitable feedstock for biochar production.

Following the BSE (bovine spongiform encephalopathy) and foot and mouth crises, fallen livestock in the UK can no longer be buried or burned in the open by farmers themselves due to the risk of disease spread through groundwater or air pollution (Defra, 2009). Carcasses must instead be taken to or collected by an approved knacker, incinerator, renderer or hunt kennel (Defra, 2009). Bonemeal has been used to produce biochar that passes all standard tests for ecotoxicity and is safe for soil application at the recommended rate of 0.4 - 1 t ha^{-1} (IBI, 2009).

3.4.2 Household, municipal and industrial wastes

Commentators have expressed concerns regarding the use of household, municipal or industrial wastes for biochar production because they may contain organic pollutants or heavy metals that could cause environmental contamination (Lehmann *et al.*, 2006; Lehmann & Joseph, 2009b). However, green urban wastes and certain clean industrial wastes such as those from paper mills could also be effectively managed through use as feedstock for pyrolysis, thus avoiding the problem of declining availability of landfill (Lehmann & Joseph, 2009b).

Sewage sludge could be used as biochar feedstock. Shinogi *et al.* (2003) found biochar produced from sewage sludge did not contain harmful levels of heavy metals. Conversely, Hossain *et al.* (2010) found that while biochar produced from wastewater sludge did contain high concentrations of heavy metals, uptake of the trace metals by cherry tomato plants indicated that their bioavailability was below the maximum permitted concentrations for food in Australia. Plant uptake of heavy metals is dependent on the specific physico-chemical properties of the soil and the plant species involved (Kidd *et al.*, 2007), so it may be the case that if the biochar used by Hossain *et al.* (2010) had been applied to different soil and/or with different plant species, the crops produced could have contained unsafe heavy metal concentrations. The sewage sludge biochar produced by Shinogi *et al.* contained cadmium concentrations of 1.3 mg kg^{-1} and zinc concentrations of 500 mg kg^{-1}, while the biochar produced from wastewater sludge by Hossain *et al.* contained cadmium concentrations of 4.7 mg kg^{-1} and zinc concentrations of 3300 mg kg^{-1}. Neither Shinogi *et al.* or Hossain *et al.* explain the precise composition of the sewage sludge and wastewater sludge used in their respective experiments, but these differences in heavy metal concentrations suggest that the composition of two sludges may have been very different. For example, while the sewage sludge used by Shinogi *et al.* might have been obtained from a separate sewerage system carrying only domestic black water, the wastewater sludge used by Hossain *et al.* might have been obtained from a combined sewerage system carrying urban storm water run-off and industrial effluent in addition to domestic waste water. Clearly while there is potential for sewage sludge to be used as feedstock for biochar production, the suitability of sludges to be managed in this way must be determined on a case-by-case basis.

3.5 Economic viability of biochar production

According to McCarl *et al.*, (2009) the economic viability of large-scale biochar production could arise from a combination of saleable energy commodity yields, marketing of biochar as a soil additive, other saleable chemical products and the trading of emissions offsets generated by displacing use of fossil fuels, reducing emissions from use of agricultural inputs and sequestering carbon. However, the authors neglect to mention that farmers could conceivably generate further emissions offsets simply by applying biochar to the soil, as various studies have indicated that application of biochar can reduce emissions of non-CO_2 GHGs from the soil. Furthermore, McCarl *et al.* do not highlight the possibility that biochar projects could potentially generate income through gate fees arising from provision of disposal services that could, for example, deal with municipal sewage or food processing wastes.

The fact that co-production of biochar and bioenergy through slow pyrolysis is likely to remain competitive with future ethanol technologies (see section 3.3) gives some indication of its commercial viability. Nonetheless, Lehmann (2007b) calculated that biochar sequestration in conjunction with bioenergy from pyrolysis will not become "economically attractive" until the value of avoided carbon dioxide emissions reaches US $37 per tonne, more than five times current carbon trading prices in the EU. However, this in itself is dependent on recognition of biochar projects as qualifying for carbon offsets. It is difficult to evaluate the calculation offered by Lehmann (2007b) as it is unclear what income sources for biochar production the author has taken into account.

McCarl *et al.* (2009) conclude that at an electricity sale price of US$ 80 MW h^{-1}, a biomass pyrolysis plant will be unprofitable based only on energy sales. However, a full evaluation of profitability must also consider income from biochar sales, emissions trading and sales of other chemicals (McCarl *et al.*, 2009). Income from gate fees (see section 3.4) and offsets generated by avoided soil emissions (see section 3.2.2) could also be added to this list. As to whether it is more profitable to use biochar as a soil amendment or as an energy source, McCarl *et al.* (2009) concluded that the economic value of biochar applied to the soil is close to its value as an energy source. However, the economics of biochar production are highly dependent on the cost of feedstock and the pyrolysis system used (Brown *et al.*, 2011).

There are doubts as to the viability of industrial-scale commercial production of biochar, but the economics of pyrolysis technology at the household, farm and community level must be evaluated separately and by a very different set of criteria (Joseph, 2009). Joseph (2009) argues that assessment of small-scale biochar projects - particularly in the context of rural areas or developing countries - must be carried out within a framework recognising the need for projects to be people-centred and participatory, economically, environmentally and institutionally sustainable, and emphasising partnership between all stakeholders, including biochar users, producers, researchers, extension workers, all levels of government and where relevant, donor organisations. There are currently few, if any, such assessments of small-scale biochar projects in the literature. Further research will be necessary to determine and enhance the viability of small-scale biochar production.

3.6 The influence of biochar on soil nutrient dynamics

The terra preta (dark earth) soils in the Amazonian region are much more fertile than other soils in the area, having high contents of carbon (C), phosphorus (P), calcium (Ca), magnesium (Mg), zinc (Zn) and manganese (Mn), along with larger amounts of stable soil organic matter (Kern *et al.*, 2003; Glaser *et al.*, 2001). It is thought that use of biochar as a soil amendment could produce similar effects.

3.6.1 Cation exchange-capacity

Amazonian Dark Earths (ancient anthrosols developed through biomass burning and nutrient deposition) contain up to 70 times more black carbon than other soils in their vicinity, indicating the presence of incompletely combusted organic matter (Glaser *et al.*, 2001). This high black carbon content can give Amazonian Dark Earths a greater potential cation exchange-capacity (CEC) than adjacent soils, increasing their nutrient retention (Liang *et al.*, 2006). For example, at the Hatahara archaeological site near Manaus, an Amazonian Dark Earth was found to have a CEC of 211.3 mmol kg^{-1}, whereas CEC of the adjacent soil was less than half of that at 88.4 mmol kg^{-1} (Liang *et al.*, 2006). Similarly, at the Lago Grande archaeological site (also near Manaus), an anthrosol had a CEC of 222.4 mmol kg^{-1}, almost four times greater than that of the surrounding soil, which had a CEC of just 59.2 mmol kg^{-1} (Liang *et al.*, 2006). Biochar can potentially be used to enhance the ability of soils to retain plant-available nutrients in cation form in a similar way (McHenry, 2009).

Several authors have attributed the high CECs of biochar in soil to the presence of oxidised functional groups (such as carboxyl, phenolic or hydroxyl groups) on the surfaces of biochar particles (Liang *et al.*, 2006; Preston & Schmidt, 2006; Cheng *et al.*, 2008; DeLuca *et al.*, 2009; Joseph *et al.*, 2009). If functional groups are also primarily responsible for the CEC of biochar before it is applied to soil, then biochar CEC would be expected to decrease as HTT is increased; studies using Fourier Transform Infrared (FTIR) spectroscopy (see Antal & Grønli, 2003) and Boehm titrations (Chun *et al.*, 2004, Guo and Rockstraw, 2007) have indicated that concentrations of functional groups are progressively reduced as HTT is increased. However, when Boehm titrations are used to characterise acidic groups on biochar surfaces, erroneous results can be produced due to the presence of bio-oil or ash (Tsechabsky & Graber, 2014). There is evidence to suggest that functional group concentrations can in fact increase with increasing HTT. Using X-ray photoelectron spectroscopy, Nishimiya *et al.* (1998) found that while carboxyl groups were present on biochars produced at 300°C, they were around 30-60% more concentrated on the surfaces of biochars produced at 400, 600 and 800°C.

The results of other investigations of biochar CEC also suggest that it is not controlled exclusively by the elimination of functional groups with increasing pyrolysis temperature. Lehmann (2007a) found that, overall, CEC increased with increasing HTT; the CEC of biochar produced at 500°C was almost three times higher than that of biochar produced at 350°C. There was little difference between biochars produced at temperatures of 500, 550, 600 and 750°C, but the CEC of biochar produced at 800°C was ~40% higher (Lehmann, 2005). Mukherjee *et al.* (2011) found that the CECs of biochars produced from oak and pine feedstocks at 400 and 650°C were similar. For biochars produced from grass, the CEC of biochar at 650°C was much higher than that produced at 400°C, even though for each feedstock type, functional groups decreased dramatically between 400 and 650°C (Mukherjee *et al.*, 2011). Yuan *et al.* (2011) found that the CEC of biochars produced from canola straw and corn straw at 500°C were significantly higher than those of biochars produced at 300 or 700°C, but for soybean straw and peanut straw biochars, CEC was highest using HTTs of 300 and 700°C respectively.

The CEC of freshly produced biochar is relatively low; only aged biochar shows high CEC (Lehmann, 2007a; Liang *et al.*, 2006). Cheng et al. (2008) found that charocal deposits found in soils at historical charcoal furnace sites in North America had a mean CEC of 1644 mmol kg^{-1} C, whereas freshly produced biochar had a CEC of just 1.7 mmol kg^{-1} C. Cheng *et al.* (2006) incubated biochar for four months at 30°C and 70°C and found that the CEC increased by 53% and 538% respectively, which suggests CEC will naturally increase quickly in very warm conditions or over long periods of time. In their study of the ADEs, Glaser *et al.* (2000) used ^{13}C nuclear magnetic resonance spectroscopy which showed that oxidation of pyrogenic C had, over time, produced carboxylic groups on the edges of its aromatic backbone, thus increasing its nutrient retention capacity. Further research is necessary to investigate the lengths of time necessary for oxidation to increase biochar CEC, particularly in temperate climates (Lehmann, 2007a).

3.6.2 **Biochar as a nutrient source**

Chan & Xu (2009) compiled a summary of the total elemental composition of 14 different biochars recorded by various studies. The C content of biochar ranged between 172 g kg^{-1} and 905 g kg^{-1} (Chan & Xu, 2009). There is an even greater range in the cases of total N (1.8 g kg^{-1} to 56.4g kg^{-1}), total P (2.7 g kg^{-1} to 480 g kg^{-1}) and total K (1.0 g kg^{-1} to 58 g kg^{-1}) (Chan & Xu, 2009). The high variability of biochar composition can result from the varying initial elemental composition of different feedstocks. For example, biochars produced from feedstocks of animal origin (e.g. sewage sludge or broiler litter) have higher P content than biochars produced from plant feedstocks such as wood (Chan & Xu, 2009). The variable composition of biochar also depends on the conditions under which it was produced. Chan & Xu (2009) reported that one study they reviewed reported total N contents of 6.0 g kg^{-1} and 7.5 g kg^{-1} for two biochars made from poultry litters at 450°C, while another study reported total N contents of 20 g kg^{-1} for another biochar produced from at 700°C poultry litter. Chan & Xu (2009) therefore speculated that production conditions significantly determine the N content of biochar as there is greater N loss at higher pyrolysis temperatures. Indeed, a later study by Hossain *et al.* (2011) demonstrated that the N content of a wastewater sludge biochar decreased with increasing pyrolysis temperature. Conversely, micronutrients increased with increasing temperature (Hossain *et al.*, 2011).

The total elemental nutrient content of biochar does not necessarily reflect the availability of those nutrients to plants, especially for organically bound nutrients such as N and S, which must be mineralised in order to become bioavailable. Angst & Sohi (2013) used sequential leaching to assess the potential of sycamore wood (*Acer pseudoplatanus*) biochar to supply crop nutrients. Cumulatively, most or all of the biochar's potassium contents were released during leaching, but at most one-third of the total magnesium in the biochar was released (Angst & Sohi, 2013). Cumulative release of the biochar's phosphorus content ranged from partial to complete, but in all cases the release was slow and relatively even over six extractions, suggesting that with further leaching all phosphorus might have eventually been released (Angst & Sohi, 2013).

3.6.3 The influence of biochar on nutrient availability

The elemental composition of biochar itself can have indirect effects on nutrient availability. For example, phosphorus is an important element for nodule metabolism in legumes. Application of P-rich biochars (e.g. those derived from poultry manures or bonemeal) can therefore enable legumes to compensate for limited N availability through increased biological nitrogen fixation (BNF) (Chan *et al.*, 2008; Tagoe *et al.*, 2008). Biochar application can therefore indirectly increase N availability. A study of the effects of biochar applications on BNF by common beans (*Phaseolus vulgaris L.*) in Columbia found that biochar additions of 30 g kg^{-1} increased BNF by 49% compared to the unamended control (Rondon *et al.*, 2007). Adding an additional 30 g kg^{-1} increased BNF by another 29% but with a total biochar addition of 90 g kg^{-1} the BNF dropped to just 30% above the control (Rondon *et al.*, 2007). The significant improvement of BNF with moderate biochar addition rates is likely to be largely due to increased availability of boron and molybdenum which are known to increase BNF (Rondon *et al.*, 2007).

In some cases, biochar application can actually lead to reductions of available nutrients, particularly nitrogen (Warnock *et al.*, 2007). Application of plant-derived biochar may reduce the availability of soil nitrogen due to its effect on the soil C:N ratio. The effect of biochar application can therefore be highly dependent on pre-existing soil fertility and fertilizer management (Asai *et al.*, 2009; Tenenbaum, 2009; Rondon *et al.*, 2007).

Several authors have attributed positive plant responses to biochar application to the ability of biochars to increase and / or maintain soil pH. For example, Van Zwieten *et al.* (2010) applied a paper mill sludge biochar to an acidic soil and observed a 30-40% increase in wheat height resulting from biochar carbonates counteracting the toxic effects of exchangeable aluminium.

3.6.4 Nutrient leaching

Application of biochar to soil can reduce leaching of agricultural pollutants. Laird *et al.* (2010a) observed significant reductions in nutrient leaching with increasing biochar application rate, even though the biochar amendments themselves added substantial amounts of nutrients to the soil. Singh *et al.* (2010) also found that biochar amendments reduced ammonium leaching by 55 - 94% depending on the soil involved and the feedstock and HTT used to produce the biochar. Yao *et al.* (2012) produced twelve biochars using four feedstocks and three HTTs. Nine of these were able to adsorb ammonium but most showed little or no ability to adsorb nitrate or phosphate (Yao *et al.*, 2012). However, it should be noted that the CECs of freshly produced biochars such as those in the latter study tend to be relatively low (Lehmann, 2007a). Biochar CEC can increase substantially as it is oxidised in the soil (Cheng *et al.*, 2008), meaning that biochar may become more effective at limiting nutrient leaching over time. There is nonetheless evidence to suggest otherwise. Lehmann *et al.* (2003) found that although an Amazonian Dark Earth had much higher water percolation than a Ferralsol from the same region, cumulative leaching of mineral N, K, Ca and Mg in the ADE was just 24, 45, 79 and 7%, respectively, of that found in the Ferralsol. However, when both soils were fertilised with inorganic nutrients, leaching in the ADE exceeded that found in the Ferralsol (Lehmann *et al.*, 2003).

3.7 Soil biota

The porous structure of biochar is thought to provide a secure habitat for microbiota; hyphae and bacteria that colonize biochar particles may be protected from soil predators such as collembolan, mites, protozoans and nematodes (Gundale & DeLuca, 2006; Warnock *et al.*, 2007; Tenenbaum, 2009). Rondon *et al.* (2007) reported that biochar is an excellent support material for Rhizobium (nitrogen-fixing bacteria) inoculants. Biochar can increase the ability of arbuscular mycorrhizal fungi (AMF) to assist their host in resisting infection by plant pathogens (Matsubara *et al.*, 2002). Several studies have shown that biochar application can have a positive effect on AMF, resulting in greater availability of nutrients and moisture for host plants, but some have observed negative effects on the abundance of AMF (Warnock *et al.*, 2007). Steiner *et al.* (2008) reported that pyrolysis condensates introduced to the soil by biochar application provided a substrate that promoted microbial activity. DeLuca *et al.* (2006) found that biochar can alleviate factors inhibiting the activity of the nitrifying microbial community in forest soils. Similarly, Zackrisson & Nilsson (1992) observed a complete elimination of the phytotoxic effect of allelochemicals inhibitory to microorganisms themselves by adding activated carbon to the soil, which adsorbed the allelochemicals.

Earthworm behaviour studies have demonstrated that earthworm behaviour in response to biochar application can differ according to the HTT used to produce the biochar, the soil to which the biochar is applied, and the application rate. An earthworm behaviour study conducted by Chan *et al.* (2008) found that worms preferred soil amended with biochar produced at

450°C to soil amended with biochar produced at 550°C or unamended soil (the application rates were not specified). A later study by the same research group showed that in an acidic Australian ferrosol, worms preferred a soil containing a biochar amendment to the control, but in a calcarosol, biochar amendments made no difference (Van Zwieten *et al.*, 2010). Li *et al.* (2011) found that although earthworms didn't avoid artificial soils (wetted to 85% of the control treatment's water-holding capacity) containing 10 g kg^{-1} of biochar, they did avoid soil with 100 and 200 g kg^{-1} biochar. However, when the soil containing 100 g kg^{-1} of biochar was wetted to it full water-holding capacity, there was no statistically significant difference in worm avoidance compared to the control (Li *et al.*, 2011). After 28-day incubations in soils amended with different biochar concentrations, worms experienced significantly more weight loss in soils containing 100 and 200 g kg biochar compared to soils without biochar, but an application rate of 10 g kg^{-1} did not significantly affect worm weight loss and none of the application rates affected reproduction (Li *et al.*, 2011).

3.8 Impacts on soil hydrology and erosion

3.8.1 Moisture retention

One of the oft-cited benefits of applying biochar to the soil is increased moisture retention. The high water-holding ability of charcoal has been known for many years. Morley (1927, p.15) wrote in the first issue of The National Greenkeeper that *"charcoal acts as a sponge in the soil, absorbing and retaining water..."*, and in a later edition asserted that *"As…an absorber of* *moisture, charcoal has no equal.*" (Morley, 1929, p.11). An increase in the water-holding capacity (WHC) of a soil will diminish the occurrence of saturated overland flow events, significantly reducing erosion (Verheijen *et al.*, 2010).

3.8.1.1 Biochar porosity

The ability of biochar to retain moisture is thought to be due to its porous structure giving it a high specific surface area. Glaser *et al.* (2002) found that Amazonian Dark Earths had specific surface areas three-times higher than those of surrounding soils, and 18% higher water-holding capacity (WHC). The greater the porosity of biochar, the more water it will be able to hold (Joseph *et al.*, 2009). However, the pore size distribution of biochar will determine the extent to which that water is mobile in soil and its availability to plants. Data on the relative percentage of different pore sizes under different production scenarios are scarce (Joseph *et al.*, 2009). Further research is necessary to identify which feedstocks and specific pyrolysis parameters will produce biochars that improve soil WHCs, but more specifically, biochars with maximized volumes of pores of diameters between 0.2 and 30 μm which hold plant-available water (Kumar & Shivay, 2008).

Observations of biochar specific surface area and porosity with increasing HTT have varied. Several studies have observed increases in pore volume and specific surface area with increases in HTT up to 500-600°C (depending on the feedstock), then decreases in porosity and specific surface area with subsequent increases in HTT (Lua *et al.*, 2004; Chun *et al.*, 2004; Lehmann, 2007a; Chen *et al.*, 2008; Chen & Chen, 2009; Angin, 2013). These patterns have been attributed to enhanced evolution of volatiles with increases in HTT between 400 and 500°C, followed by widening or coalescence of pores < 0.002 μm in diameter and / or the sealing off of some pores by plastic deformation and sintering of ash and volatile fractions at HTTs above 500°C, which seal off some of the pores (Lua *et al.*, 2004; Fu *et al.*, 2011; Angin, 2013). However, some authors have reported linear increases (Uchimiya *et al.*, 2011; Chen *et al.*, 2012), another observed linear decreases (Muradov *et al.*, 2012), whilst another observed fluctuating porosity with increasing HTT (Karaosmanoğlu *et al.*, 2000).

The measurements of biochar porosity discussed above were made using BET (the Brunauer, Emmett and Teller method) (Brunauer *et al.*, 1938), which is influenced by nanometre scale pores. Biochars with high proportions of nanometre-scale pores may hold large volumes of immobile water even at elevated matric potentials. According to Joseph *et al.* (2009), biochars having both a high specific surface area and a high volume of pores with diameters in excess of 50 nm can have a particularly high WHC, with plant available water residing in pores of about 10 – 80 μm. Biochars typical of this description are those derived from wood, the pores of which originate from tracheids in the feedstock material and can have diameters greater than 100 μm (Joseph *et al.*, 2009; Wildman & Derbyshire, 1991). Smaller pores will attract and retain capillary soil water for much longer periods than larger pores of diameters greater than ~20 μm (Thies & Rillig, 2009), but water is generally considered only considered 'mobile' when present in pores of sizes in the order of a few micrometers (Brady & Weil, 2008), so water held in pores of the nanometre scale will not be plant-available (Sohi *et al.*, 2010).

3.8.1.2 Impacts of biochar application on soil moisture

The effect of biochar application on soil water-holding capacity (WHC) varies with application rate. Tryon (1948) found that mixing biochar with a sandy podzolic forest soil at a rate of 45 % (by volume) increased the soil's water retention by 18 %, but such a large application rate is probably unrealistic for the average soil manager. Busscher *et al.* (2010) mixed 0, 5, 10, and 20 g kg^{-1} (equivalent to 0, 11, 22 and 44 tonnes ha^{-1}) of pecan shell biochar (produced at 700°C and ground to < 0.6 mm) with loamy sand but found no compelling evidence that biochar additions increased soil WHC. Chan *et al.* (2007) demonstrated that the WHC of an Australian Alfisol (texture not described) increased as it was mixed with increasing amounts of biochar. However, significant increases in WHC were detected only at the highest rates of biochar application used in the study, 50 and 100 t ha^{-1} (Chan *et al.*, 2007). Gaskin *et al.* (2007) found that mixing biochar with loamy sand at rates equivalent to 11 and 22 t ha^{-1} did not affect the soil's WHC, only an application rate of 88 t ha^{-1} increased WHC. However, Laird *et al.* (2010b) found that a biochar application rate of 5 g kg^{-1} significantly increased the WHC of a fine-loamy soil. Although doubling and tripling the application rate increased WHC, the increases were not statistically significant (Laird *et al.*, 2010b).

The type of biomass and the temperature at which it is pyrolysed to produce biochar can influence its effect on WHC. Novak *et al.* (2009) mixed biochars with loamy sand soil at a rate of 20 g kg^{-1} pecan shell and poultry litter biochars had no significant effect on WHC, nor did biochar produced from peanut hull using a HTT of 500°C. However, biochar produced from switchgrass and biochar produced from peanut hull at 400°C significantly increased the soil's WHC (Novak *et al.*, 2009). Lei & Zhang (2013) produced biochars from manure and woodchip at HTTs of 300, 500 and 700°C and mixed them with a loam soil at a rate of 50 g kg^{-1}. Although all the biochars increased WHC, the effect was strongest in biochars produced at higher temperatures (Lei & Zhang, 2013).

It has been demonstrated that the effect of biochar on soil moisture retention is determined to an extent by the nature of the soil with which it is mixed. Tyron (1948) applied charcoal additions of 45% (by volume) to sandy, loamy and clayey brown podzolic forest soils. As discussed above, in sandy soil, water retention increased by 18% (Tyron, 1948). However, in loamy soil, no changes in water retention were observed whilst in clayey soil, the available soil moisture actually decreased with increasing charcoal additions, which Tyron (1948) attributes to the hydrophobicity of the charcoal (Tyron, 1948). Another possible explanation could be simply that the charcoal had a lower water retention capacity than the clay it replaced. It is conceivable that the results of this experiment might have been different had the charcoal been produced from different parent material and by different pyrolysis conditions. Once optimum feedstocks and pyrolysis parameters for biochar WHC have been identified, research could be conducted to investigate again the effect of biochar application on different soil types.

The effect of biochar application on soil moisture retention may be dependent to an extent on the particle size of the biochar used. Little information is available regarding the effects of biochar particle size on soil WHC. Whilst it can be postulated that smaller particles are more likely to increase efficiency as a result of a larger surface area, it can also be theorised that particle size is a redundant parameter due to the high porosity of biochar particles (Joseph *et al.*, 2009). Lehmann *et al.* (2003) observed no relevant differences between the impacts on crop growth of biochars of < 2 mm and ~20 mm particle size, though the application method was not specified. Joseph *et al.* (2009) concluded that it was not necessary to include particle size in their biochar classification system. The specific surface area, porosity, pore-size distribution and pore connectivity will each have a significant influence on the effect that biochars have on soil water-holding capacity. High biochar porosity will increase the total amount of water stored within the soil, whilst pore sizes will determine whether this water is mobile in soil and whether it is available or unavailable to plants.

Besides the work of Lei & Zhang (2013), there are scarce data regarding the effect of the pyrolysis temperature at which biochars are produced influences their effect on soil moisture retention. Furthermore, there are no published studies on the influence of biochar particle size on soil matric suction, nor on the effect of different biochars on osmotic suction, which, combined with matric suction, determines the amount of energy plants must expend to take up water, which in turn influences crop yields (Taylor, 1952; Kirkham, 2005). Osmotic suction results from the presence of solutes in the soil solution. Water molecules cluster around solute ions or molecules meaning that their freedom of movement is reduced, so the greater the concentration of solutes, the greater the osmotic suction (Brady & Weil, 2008). Thomas *et al.* (2013) reported that biochar additions mitigated salt stress for two herbaceous plant species, suggesting that biochar can influence osmotic suction.

It is likely that there are soil-specific thresholds which biochar application must exceed to have a significant effect on soil WHC, depending on the biochar. Further research is needed to determine the minimum application thresholds to achieve significant increases in WHC for different biochars on different soils.

Biochar amendments can increase the amount of water held in the soil at the permanent wilting point (-1,500 kPa). Hardie *et al.* (2014) reported that applying biochar at a rate of 20% w/w to a sandy loam significantly increased the soils moisture content at -1,500 kPa. However, using an application rate of 5% w/w (similar to the maximum rates used in some field trials) had no effect on the soil moisture content at wilting point (Hardie *et al.*, 2014). Laird *et al.* (2010b) found that mixing biochar produced from mixed hardwoods and sieved to < 0.5 mm with a fine-loamy soil at rates of 5 – 20 g kg^{-1} increased the amount of water retained in the soil at -500 kPa. Ulyett *et al.* (2014) reported that adding biochar to a sandy loam at a rate of 60 t ha^{-1} increased the available water capacity by up to 1.3% between 0 and -50 kPa (the application method was not specified).

3.8.2 Bulk density

High soil bulk densities usually indicate a poor environment for root growth, with increased soil penetration resistance, low aeration, slow movement of water and nutrients, and accumulation of toxic gases and root exudates (Brady & Weil, 2008). Biochar can reduce soil bulk density and increase total porosity (Van Zweiten *et al.*, 2009; Laird *et al.*, 2010b; Ulyett *et al.*, 2014). Conversely, if the biochar has a low mechanical strength and disintegrates quite quickly into small particles, filling up existing pore spaces, soil bulk density may actually increase (Verheijen *et al.*, 2010). Further research is necessary to investigate how biochar soil bulk density is affected by different biochar particle sizes.

3.8.3 Biochar hydrophobicity

Several authors have reported that surfaces of newly produced biochars are hydrophobic (Lehmann *et al.*, 2009; Major *et al.*, 2009; Verheijen *et al.*, 2010), implying that hydrophobicity is eliminated as biochar ages. Verheijen *et al.* (2010) argued that hydrophobicity induced by biochar is considered to be most significant in the first years immediately following application because fresh biochar contains a larger fraction of hydrophobic groups. Similarly, Major *et al.* (2009) stated that fresh biochar with low surface oxidation is both hydrophobic and an effective sorbent of hydrophobic molecules. Nevertheless, previous research has shown that hydrophobicity is not necessarily limited to fresh biochar and can in fact persist over long periods. Briggs *et al.* (2005) found that samples of eight-year-old charcoal (produced by wildfire) taken from the soil surface and from within the soil were extremely water-repellent, having water drop penetration times in excess of 2 hours. However, this may have been due to fungal colonization of the biochar.

Observations of a reduction in biochar hydrophobicity over time may be partly due to the way amphiphilic molecules re-orient themselves while in contact with water. It is thought that where water repellency is caused primarily by soil particles being coated in amphiphilic molecules, the attraction of water to the polar (hydrophilic) ends of these molecules weakens the soil/molecule bond, eventually leading to the reorientation of the molecules and resulting in a wettable soil (Doerr *et al.*, 2000). Whilst Doerr *et al.* (2000) argued that this concept has yet to be proven and that the factors determining the length of time necessary for a breakdown of water repellency in soil are poorly understood, it may nonetheless be the case that this hypothesis can also be applied to biochar.

Major *et al.* (2009) implied that reductions in biochar surface hydrophobicity may sometimes be the result of oxidation. Cheng *et al.* (2006) artificially 'aged' fresh biochar through incubation at 70°C. Its subsequent oxidation led to the formation of acidic functional groups, suggesting that over long time periods, biochar could actually become hydrophilic (Cheng *et al.*, 2006). Conversely, Briggs *et al.* (2005) concluded that water repellency of charcoal is reduced by leaching of hydrophobic compounds from the charcoal. Clearly further research is clearly needed to identify the processes that eliminate biochar hydrophobicity and the periods of time over which this occurs. Biochar hydrophobicity can be eliminated through the utilisation of higher pyrolysis temperatures. Kinney *et al.* (2012) found that biochar hydrophobicity was greatly reduced between pyrolysis temperatures of 300 and 600°C. Biochar hydrophobicity was strongly correlated to the presence of C-H functional groups characteristic of alkyl groups in FTIR spectra, suggesting that hydrophobicity derives from aliphatic domains on the surface of low-temperature biochars. Producing biochar from pine needles, Chen *et al.* (2008) showed that aliphatic alkyl groups were completely destroyed at HTTs of 400°C. Anecdotal evidence indicates that the surface hydrophobicity of 'fresh' biochar might be reduced by the reabsorption and readsorption of condensed volatiles on the surface of biochar particles (R. Bryant, pers. comm., 3rd March 2011). However, biochar hydrophobicity may also be affected by its surface topography. The sub-mm scale surface topography of a material can significantly modify its hydrophobicity as water droplets can be suspended on the peaks of the surface topography, bridging across the gaps. This is because the length scales are such to make surface tension the dominant force, rather than gravity. The capillary length for water is 2.7 mm, so the contact angles of water droplets on surfaces with length scales of this magnitude and less will be dominated by surface tension. As the heights of peaks in the surface topography are reduced, water droplet contact angles can also be reduced (McHale *et al.*, 2007).

Kinney *et al.* (2012) reported that mixing hydrophobic biochar with an otherwise hydrophilic soil at rates of up 7% by weight reduced the soil's wettability. However, the differences were not statistically significant. Similarly, Smetanová *et al.* (2012) found that mixing a hydrophobic biochar with a hydrophilic soil at rates of 5 and 10% by weight did not substantially alter the wettability of the soil. Furthermore, the overland flow responses of biochar-amended soils were dominated by the infiltration properties of the soils rather than their wettability (Smetanová *et al.*, 2012). However, it should also be noted that fungal colonisation of biochar-amended soils can render them hydrophobic, regardless of whether the biochar itself is hydrophobic (Abel *et al.*, 2013). Although the evidence suggests that biochar hydrophobicity has little influence on soil water repellency, it may have significant implications for its use as a soil amendment for other reasons. Hydrophobic particles are ejected further by raindrop impact than hydrophilic particles (Ahn *et al.*, 2013), so hydrophobic biochar is more likely to be preferentially eroded from the soil by splashing. Indeed, Rumpel *et al.* (2009) found that splashing accounts for a substantial proportion of biochar erosion. Gray *et al.* (2014) reported that water uptake by biochars produced at low HTTs was lower than that of biochars produced at high HTTs, suggesting that surface hydrophobicity could have implications for the ability of biochar to increase soil WHC.

3.8.4 Overland flow

Data on the influence of biochar amendments on overland flow from soils are scarce. To date, no published studies have investigated the influence of different biochar application rates on the hydrological response of soils under simulated rainfall, and none has measured the effects of biochar application on both drainage and overland flow. Beck *et al.* (2011) found that adding biochar at a rate of 7% by weight resulted in a 4.4% increase of water retention in a greenroof soil under simulated rainfall. However, for half of the replicates the initial soil moisture content was not controlled or measured. Furthermore, as their study did not differentiate between overland flow and subsurface flow (drainage), the findings of Beck *et al.* (2011) have limited applicability to *in-situ* soils. Smetanová *et al.* (2013) reported that applying biochar produced at 500-600°C (from unspecified wood) to a sandy loam at a rate of 10% by volume decreased overland flow by up to ~40%, but drainage was not measured.

3.8.5 Crop residue removal

A key consideration in assessing the sustainability of biochar production is that where crop residues are removed from agricultural land for the purposes of biochar production, the risk of soil erosion will be increased. Crop residues left in-situ reduce raindrop impact, lessen aggregate slaking and dispersion and protect the soil from water and wind erosion (Stavi & Lal, 2013). If too high a proportion of crop residues are removed for biochar production, any potential benefits of biochar application might be cancelled out by the loss of organic-matter-rich topsoil by erosion in the first place. For example, McAloon *et al.* (2000) estimated that only about 30% of stover could be removed from cornfields after harvest as the remainder would need to be left *in situ* to provide adequate soil cover to control soil erosion. However, the maximum removable residue percentages vary according to the crop, soil, field slope and length, local wind and rainfall conditions, and management practices (Nelson, 2002), meaning that such an estimate is probably redundant. It is likely that the proportion of agricultural residues that can be safely removed for biochar production will have to be determined on a case-by-case basis.

3.8.6 Soil erosion

Data on the effect of biochar amendments on soil erosion are scarce. Smetanová *et al.* (2012) found that applying biochar by mixing at rates of 5 and 10% by volume to a sandy loam soil had no significant effect of sediment yields during rainfall simulation. Jien & Wang (2013) found that applying biochar by mixing with an acidic, silty clay soil at a rate of 25 g kg^{-1} reduced soil erosion rates by around 50%, while an application rate of 50 g kg^{-1} reduced erosional losses by nearly two-thirds. These reductions in erosion were attributed to an increase in microbial activity arising from biochar additions, leading to formation of macroaggregates (Jien & Wang, 2013). However, as the biochar additions had a significant liming effect (Jien & Wang, 2013) another possible explanation is that there was improved aggregate stability through increased bivalent cation availability (Brady & Weil, 2008). The effect of biochar application on erosion of medium-textured soils has not yet been investigated. No published data are available on the influence of biochar application on splash erosion.

3.8.7 Erosion of biochar

Major *et al.* (2010) reported that after two years, 20 - 53% of the biochar applied to a 0.1m depth in a sandy clay loam using 2 disk-harrow passes could not be accounted for by downward migration, leaching or respiration. It was therefore presumed that the biochar was lost from the soil by overland flow processes (Major *et al.*, 2010). Guggenberger *et al.* (2008) found that a larger proportion of black carbon produced by vegetation fire was present in streamwater than in the soils of a tundra-catchment.

Rumpel *et al.* (2006) investigated soil losses from water erosion on steep slopes (~25°) under slash and burn agriculture with shallow tillage, sampling from plots under rice cultivation, fallow and secondary forest. They found that whilst black carbon represented on average 15% of the carbon in the bulk soil, at the watershed level black carbon represented 30% of carbon in eroded sediments, indicating that black carbon is eroded more easily than other soil carbon (Rumpel *et al.*, 2006). The light nature of black carbon enables the largest particles to float, and the colloidal nature of finer particles allows them to remain in suspension for long periods (Rumpel *et al.*, 2006) meaning that biochar particles will be more susceptible to erosion than other soil particles. However, eroded sediment was sampled during the rainy season but the bulk soil was not sampled until after the rainy season, when the black carbon content of the soil had already been depleted by erosion. Had the bulk soil been sampled just before the rainy season, the black carbon content of the soil would have been higher, so the gap between the black carbon content of the bulk soil and that of the eroded sediments would have been smaller. Also, whilst Rumpel *et al.* do not mention whether the soils in the study were hydrophobic; their investigation was conducted during the rainy season in an area where slashing and burning is carried out just before the rainy season. Burned soil is often markedly more hydrophobic and susceptible to erosion compared with unburned terrain (Shakesby *et al.*, 2013) and it is highly possible that there were hydrophobic sites within the catchment, which could have further enhanced overland flow and accelerated erosion (Doerr *et al.*, 2000). Further research is needed to determine the whether biochar is preferentially eroded from soils on shallower, unburned slopes.

3.8.8 Aggregation and aggregate stability

Brodowski *et al.* (2006) suggested that biochar acts as a binding agent for organic matter in aggregate formation. Few studies have investigated the possibility of biochar providing surfaces for organo-mineral associations leading to increased soil aggregation, but Pronk *et al.* (2012) found that applying a commercial barbecue charcoal (ground to 63-200 μm) to an artificial soil had no effect on the formation of organo-mineral associations and a negative effect on macro-aggregation. Busscher *et al.* (2010) found that biochar amendments (produced from pecan (*Carya illinoinensis*) shell at 700°C and ground to < 2mm) applied to a loamy sand at rates of 5, 10 and 20 g kg^{-1} had mixed effects on aggregation - using application rates of 5 and 20 g kg^{-1} resulted in reduced aggregation, while a rate of 10 g kg increased aggregation. However, a further study using the same soil and biochar found that biochar applied at a rate of 10 g kg^{-1} resulted in an insignificant reduction in aggregation (Busscher *et al.*, 2011).

Root growth can increase aggregate stability through physical entanglement of aggregates by roots and through increased production of root exudates (Monroe & Kladivko, 1987). Root penetration is limited by soil strength (Brady & Weil, 2008), which Chan *et al.* (2007) found to decrease with increasing applications of biochar. Biochar application may therefore improve root development which would in turn increase aggregate stability. Furthermore, the porous structure of biochar is thought to provide a secure habitat for microbiota such as hyphae of arbuscular mycorrhizal fungi (see section 3.7), which improve soil aggregation in the rhizosphere as they grow into small pores and bind soil particles together (Voroney, 2007).
Biochar has been reported to have a liming effect (Lehmann *et al.*, 2003; Van Zwieten *et al.*, 2010). Increases in pH-dependent charges associated with biochar application could therefore have implications for aggregate stability, as bivalent cations would be more able to act as bridges between organic colloids and clays (Shainberg & Levy, 1996; Brady & Weil, 2008). The ash content of biochar may also have implications for aggregate stability.

Although sodium increases the tendency of aggregates to slake, other soluble salts can help prevent dispersion of soil colloids (Goldberg *et al.*, 1988; Brady & Weil, 2008). In the long-term however, such effects may not be particularly important, as salts and cations are progressively leached from the soil (Lehmann *et al.*, 2011).

Several published studies have investigated how biochar applications influence aggregate stability by mixing biochar with sieved and repacked soils. Peng *et al.* (2011) reported that applying rice straw biochars (produced at 350, 400 and 500°C) to an Ultisol at a rate of 10 g kg^{-1} had no effect on aggregate stability. However, applying biochar (produced from *Leucaena leucocephala* wood at 700°C, then ground to < 2 mm) to an Ultisol at rates of 25 and 50 g kg^{-1} resulted in significant increases in aggregate stability (Jien & Wang, 2013). Using biochars produced from straw, wood chip and waste sludge to amend a clayey soil, Sun & Lu (2014) measured aggregate stability using fast wetting, slow wetting and wet-stirring (Le Bissonnais, 1996a). They found that in most cases biochar application rates of 20 g kg^{-1} reduced aggregate stability of a clayey soil, while higher application rates of 40 and 60 g kg^{-1} resulted in increased aggregate stability (Sun & Lu, 2014). Soinne *et al.* (2014) produced biochar from coniferous wood chips at 550-600°C and ground to < 0.2 mm and mixed it with two clayey soils to a depth of 20 cm, at rates corresponding to 15 and 30 t ha^{-1}, which resulted in increased aggregate stability. Ibrahim *et al.* (2013) reported that application of *Conocarpus* biochar at rates up to 20 g kg^{-1} increased the aggregate stability of a sandy loam, but Liu *et al.* (2012) found that biochar application up to 16 g kg^{-1} had no effect on the aggregate stability of another sandy loam. Few data are available on the effect of biochar applications on silt loam soils. Herath *et al.* (2013) found that applying corn stover biochars (produced at 350 and 550°C) to silt loam soils at rates between 10 and 15 g kg^{-1} resulted in significant increases in aggregate stability. Liu *et al.* (2012) found that applying biochar at a rate of 4 g kg^{-1} had no effect on aggregate stability in two different silt loam soils. An application rate of 8 g kg^{-1} significantly increased the aggregate stability of one of the soils, with a further significant increase in aggregate stability when the biochar application rate was doubled to 16 g kg^{-1} (Liu *et al.*, 2012). However, these higher application rates had no effect on the aggregate stability of the other soil (Liu *et al.*, 2012). Data on the effect of biochar applications on aggregate stability under field conditions are scarce. Hardie *et al.* (2014) applied biochar (produced from acacia green waste at 550°C, particle size not reported) at a rate of 47 t ha^{-1} to a sandy loam orchard soil and found it had no effect on aggregate stability after 31 months.

3.9 Soil strength and penetration resistance

Few data are available on the effect of biochar amendments on soil strength. Chan *et al.* (2007) observed reductions in the tensile strength of an Alfisol with increasing biochar application rate. Masulili *et al.* (2010) found that applying biochar (produced from rice husks at 600°C then ground to < 0.5 mm) at a rate corresponding to 15 t ha^{-1} reduced the penetration resistance of an acid sulphate soil by around 25%. Similarly, Busscher *et al.* (2010) found that the penetration resistance of a sandy loam was reduced with increasing biochar application rate. Conversely, a later study by Busscher *et al.* (2011) using the same soil and biochar found that applying biochar at a rate of 10 g kg^{-1} to loamy sand increased penetration resistance. All of the above investigations of penetration resistance were carried out on soils in pot or column incubations. No studies to date have investigated the effect of biochar application on the penetration resistance of structural crusts formed by rainfall. Structural breakdown of aggregates during rainfall can lead sealing of the soil surface as fine particles are washed into pores, clogging them and thus restricting the permeability of the soil surface (Gabriels *et al.*, 1998). A seal can then set to a hard structured mass (crust) as it dries (Gabriels *et al.*, 1998).

Surface crusts can protect the soil, but because they reduce surface hydraulic conductivity, they can also trigger overland flow and erosion (Valentin & Bresson, 1992). This has deleterious consequences for moisture recharge and thus increases the risk of crop water stress during critical plant growth periods. Decreases in soil strength can also reduce costs associated with soil preparation such as tillage. Strong soil crusts can also mechanically impede seedling emergence, sometimes to the extent that the crop has to be resown (Brady & Weil, 2008). Further research is needed to investigate the effect of biochar application on soil sealing and crusting.

3.10 Application methods

The studies discussed in this literature review all used uniform topsoil mixing methods to apply biochar, either through mixing by hand or by using mechanical ploughing or disking to incorporate biochar to a certain depth. Conversely, biochar could be applied to the soil by alternative methods such as deep-banding, drilling, top-dressing or ecological delivery via animal feed

(Blackwell *et al.*, 2009). It should therefore be noted that the effects of biochar application highlighted in this review could be altered to some extent by use of different application methods.

3.11 Summary

Biochar has great potential both as a means of greenhouse gas mitigation and as a soil amendment, but there remain considerable uncertainties as to the effects of biochar application on soil properties.

Biochar could potentially sequester significant amounts of carbon for several thousands of years, but there is little data available as to how rapidly biochar might be oxidised in temperate climates. More precise quantification of the long-term stability of biochar requires long-term observation. Biochar application can suppress nitrous oxide and methane emissions from the soil, but further research is needed to understand the mechanisms by which these emissions suppressions occur.

Whereas many other means of carbon sequestration are energy-intensive, biochar production can be a self-sustaining or even energy-generating process. Pyrolysis can provide a range of saleable services and commodities contributing to its economic viability. Industrial-scale biochar sequestration in conjunction with bioenergy production is unlikely to become commercially attractive until carbon trading prices are more than double their current level. The economics of biochar production at the household, farm and community level must be evaluated by a very different set of criteria to that used for industrial-scale biochar production; research is needed to determine and enhance the viability of small-scale biochar production. Pyrolysis presents a useful option for waste management, particularly for potentially hazardous biological wastes. However, the suitability of sewage / wastewater sludges to be used as feedstock for biochar production must be determined on a case-by-case basis.

The cation exchange-capacity (CEC) of freshly produced biochar is relatively low, but it has been demonstrated that aged biochar has high CEC due to oxidation. More research will be necessary to ascertain the periods of time are necessary for oxidation to increase biochar CEC, particularly in temperate climates. The nutrient content of biochar varies considerably according to the initial elemental composition of feedstock material and the pyrolysis conditions used. The elemental content of biochar does not necessarily reflect the availability or the rate of release of those nutrients to plants, and the effect of biochar application on nutrient availability is not necessarily directly related to the nutrient content of the biochar itself. Biochar application can limit N availability. Further research is required to identify best practices for combined fertilizer and biochar soil amendments.

Biochar can provide a secure habitat for some soil microbiota and can adsorb allelochemicals, protecting microorganisms from their toxic effects. Furthermore, biochar can be a substrate that promotes microbial activity. Earthworm avoidance studies have had mixed results depending on the HTT used to produce the biochar, the application rate used, and the soil type and moisture content.

Numerous studies have demonstrated that biochar application can increase soil water-holding capacity (WHC), but research indicates that there are minimum thresholds which biochar applications must exceed in order to have a substantive effect on soil moisture retention. The moisture retention of biochar will increase according to the abundance of certain pore sizes; further research is necessary to identify which feedstocks and production practices will produce biochars which positively influence soil moisture retention. No published data are available on the effect of biochar amendments on osmotic suction; research is needed to investigate the effects of biochar application on the total energy-cost of water uptake by plants (including both matric and osmotic suction).

Application of biochar can be expected to reduce bulk density by increasing the organic matter content of the soil and increasing total porosity. However, if the biochar has a low mechanical strength and disintegrates, clogging pore spaces, the soil bulk density could potentially increase. Further research is essential to investigate the mechanical strength of biochar is affected by feedstock material and pyrolysis conditions.

Freshly produced biochar can be hydrophobic, but hydrophobicity is not necessarily limited only to fresh biochar. Biochar hydrophobicity can be eliminated at certain pyrolysis temperatures, depending on the feedstock. Further research is needed to determine the pyrolysis temperatures necessary to eliminate hydrophobicity on a range of feedstocks.

If too high a proportion of crop residues are removed for biochar production, loss of topsoil may cancel out any potential benefits of biochar application.

Biochar can be preferentially eroded from burned soils on steep slopes, but further research is needed to determine whether biochar is also preferentially eroded on unburned soils on shallower slopes.

Previous studies have observed both increases and decreases in soil aggregation following biochar addition. The effect of biochar on SOM, soil strength and soil biota will have important consequences for aggregate stability, but limited data are available on the effect of biochar on aggregate stability under field conditions. Most studies of the impact of biochar on aggregate stability have been based on incubation experiments. Several studies have observed increased aggregate stability in clayey soils following biochar application, though in some cases there have been reductions in aggregate stability where relatively low application rates are used. Studies of aggregate stability in biochar-amended sandy soils have observed mixed effects. Data on the effect of biochar on aggregate stability in medium-textured soils are scarce. Relatively low application rates (< 16 g kg^{-1}) have been shown to increase aggregate stability, but the effect of higher application rates has not been investigated. Moreover, to date, there has been little investigation of how biochar application methods might influence the effect of biochar amendments on soil properties.

Addressing the research gaps identified above will (i) enable a more thorough evaluation of the potential of biochar production as a means of carbon sequestration, (ii) inform biochar producers as to how certain properties of biochar can be maximised or avoided, and (iii) enable soil managers to make more informed decisions about applying biochar to their soils.

Some of the key research gaps related to potential effects of biochar as a soil amendment are addressed through laboratory experiments in the following chapters. The objectives of the remainder of this thesis are thus to investigate how the preparation of biochar amendments (i.e. use of different pyrolysis temperatures, feedstocks and particle sizes) can influence their effect on soil hydrology and related properties, and how different biochar application rates influence soil hydrology, erosion and crust formation during rainfall. These objectives were achieved by addressing the following key research questions:

i. How do feedstock (biomass type and particle size) and HTT influence biochar hydrophobicity, CEC and yield?
ii. How do feedstock biomass type and HTT influence biochar CEC?
iii. How feedstock biomass type and HTT influence biochar yield?
iv. How does HTT influence the effect of biochar amendments on soil bulk density, WHC and suction?
v. How does particle size influence the effect of biochar amendments on soil bulk density, WHC and suction?
vi. How do different biochar application rates influence moisture retention, drainage and overland flow of a soil under simulated rainfall?
vii. How do different biochar application rates influence aggregate stability, splash and slopewash erosion and seal formation of a soil during simulated rainfall?

4 THE EFFECTS OF FEEDSTOCK AND PYROLYSIS TEMPERATURE ON BIOCHAR PROPERTIES

4.1 Introduction

Bicohar is often described as being hydrophobic (Amonette & Joseph, 2009; Lehmann *et al.*, 2009; Major *et al.*, 2009; Reza *et al.*, 2012; Briggs *et al.*, 2012; Baronti *et al.*, 2014). Hydrophobic particles are ejected further by raindrop impact than hydrophilic particles (Ahn *et al.*, 2013), so hydrophobic biochar is more likely to be preferentially eroded from the soil by splashing. Also, it has been demonstrated that the surface hydrophobicity of biochar particles is more important than their porosity in determining their uptake of water (Gray *et al.*, 2014).

Anecdotal evidence indicates that the surface hydrophobicity of 'fresh' biochar might be reduced by the reabsorption and readsorption of condensed volatiles on the surface of biochar particles (R. Bryant, pers. comm., 3rd March 2011). This suggests that biochar particle size could influence hydrophobicity, as larger particles would have a larger surface area to volume ratio, limiting the mass transfer of volatiles out of the particles in the first instance (Antal & Grønli, 2003). Biochar particle size diminishes with increasing pyrolysis temperature however, and the tensile strength of biochar decreases as pyrolysis temperature increases, making particles more susceptible to attrition if sieved (Downie *et al.*, 2009; Kim *et al.* 2012). As such, biochars produced at higher temperatures could have smaller particle sizes than biochar produced at lower temperatures, even if both were ground to pass through the same sized sieve aperture.

Biochar hydrophobicity varies according to the feedstock used, and can be reduced by increasing the highest treatment temperature (HTT) used in pyrolysing biomass to produce biochar (Kinney *et al.*, 2012). However, higher HTTs produce lower biochar yields (Demirbas, 2004) and it has been claimed that increasing HTT to eliminate biochar hydrophobicity will have a deleterious effect on the cation exchange-capacity (CEC) of biochar, often considered one its prime qualities as a soil amendment. The initial hydrophobic and CEC properties of biochars are likely to be altered within months of biochar being applied to the soil (Cheng *et al.*, 2006). As biochar ages in the soil, hydrolysis and oxidation of biochar surfaces can deplete aliphatic compounds and increase concentrations of acidic functional groups, resulting in increased CEC and reduced hydrophobicity (Cheng *et al.*, 2006). Leaching by water and / or various plant-derived alcohols and acids can also reduce biochar hydrophobicity (Briggs *et al.*, 2012).

No studies to date have simultaneously investigated the influence of feedstock type and HTT on biochar yield, hydrophobicity and CEC. The purpose of this investigation was to gain an improved understanding of how different feedstocks and HTTs would affect biochar yield and influence the hydrophobicity and CEC of the biochars prior to their application to soil.

4.2 Methods

4.2.1 Biochar production

Biochar samples were produced from willow (*Salix viminalis*) and Miscanthus (*M. x giganteus*) feedstocks supplied by IBERS, Aberystwyth, and Sitka spruce (*Picea sitchensis*) supplied by SelectFor Ltd., Aberystwyth. These feedstocks are henceforth referred to as Salix, Miscanthus, and Picea respectively. They were selected to represent commonly available deciduous, graminoid and coniferous feedstocks respectively. *Salix* (willow) and *Miscanthus* are prevalent energy crops, while *Picea* (Sitka spruce) is a widespread forestry species. These different feedstock types have diverse biochemical composition, with varying cellulose, lignin and mineral ash content; these can influence biochar yield and surface properties (Kinney *et al.*, 2012).

Prior to pyrolysis, all feedstock materials were chipped and sieved to obtain the 2 - 5 mm fraction. Particle size was controlled because it can have a significant effect on yield; smaller feedstock particle sizes result in lower biochar yields (Demirbas, 2004). For *Salix*, the 5 - 10 and 10 - 20 mm fractions were also obtained to investigate whether feedstock particle influences biochar hydrophobicity. Feedstocks were then oven-dried to constant weight at 40°C to ensure that (i) any observed differences in percentage yield were not influenced by moisture loss and (ii) differences in cation exchange-capacity (CEC) were not influenced by evolution of steam within samples removing tars and maximising porosity, increasing the surface area (Smernik, 2009). Although a more complete drying of the wood could have been achieved using an oven temperature of 80 - 120 °C, a lower drying temperature was chosen to avoid biomass degradation which begins at 50°C with changes in the amorphous region in cellulose (Mehrotra *et al.*, 2010).

Feedstocks were pyrolysed in an electrically heated Vectstar VTF 7 tube furnace with an alumina worktube continuously purged with nitrogen (N_2) gas. The N_2 was supplied from an oxygen-free, pressurised gas cylinder. A dual-stage 0 to 4 bar gas regulator was used in combination with a needle valve and a Cole-Parmer rotameter to control the N_2 flow rate (Figure 4.1). A gas-tight seal at the ends of the worktube was achieved using stainless-steel end-plates with O-ring seals compressed onto the machined-flat tube ends using butterfly screws clamped to the reactor tube with a worm-drive clamp. The end-plates had openings with nipple connectors, allowing entry of a k-type thermocouple and N_2 via rubber tubing at the upstream end of the furnace and exhaust via rubber tubing at the downstream end (Figure 4.1). To ensure an oxygen-free atmosphere, the furnace and tubing were purged with N_2 at 0.5 l min^{-1} for 5 minutes prior to commencement of heating with a flow rate of 0.05 l min^{-1} maintained thereafter (throughout the heating program and cooling to below 40°C). Exhaust gases were passed through an ice trap condenser then vented through a fume hood (Figure 4.1). Feedstocks were inserted into the furnace in alumina boats. Condensed tars within the furnace or alumina boats were cleaned between production runs by using an air pump to purge the worktube with air whilst it was heated to 650 °C, causing the tars to be combusted.

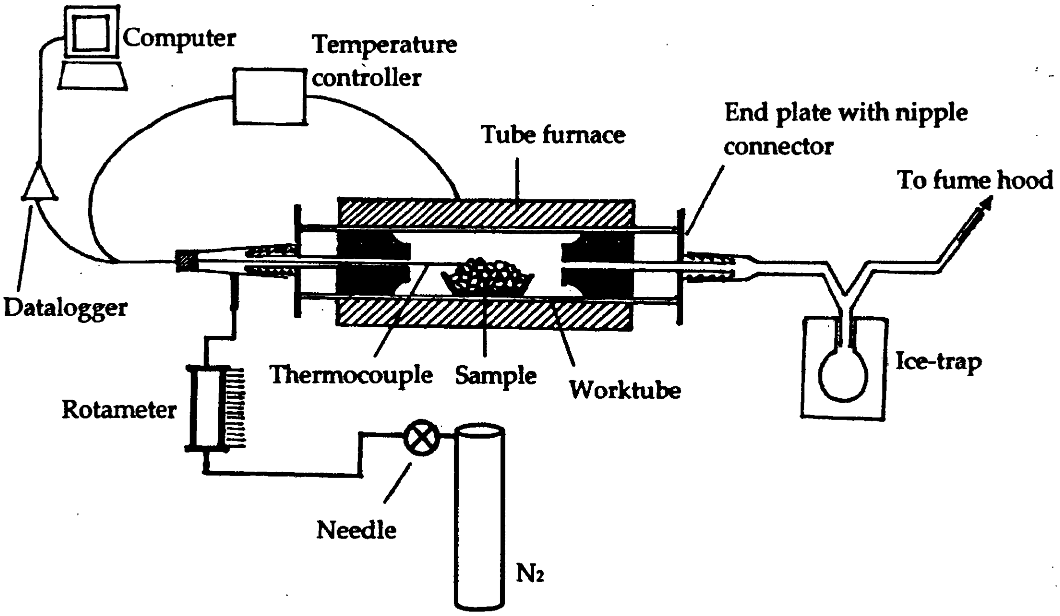


Figure 4.1: Schematic diagram of pyrolysis apparatus (adapted from Woolf, 2011)

The temperature of the tube furnace was controlled using a Fuji PXZ4 temperature controller and logged using a Pico TC-08 thermocouple datalogger with a logging program created in Visual Basic 6.0 (Microsoft, USA). Pilot studies showed that the thermal mass of the ceramic worktube consistently caused time lags of several minutes between the heating rates programmed through the temperature controller and those observed in the heating rate recorded by the thermocouple within the furnace. Further tests showed that time-lags were too long to be effectively dealt with by the controller's inbuilt algorithms for preventing temperature overshoot or undershoot. Undershooting was instead eliminated by programming temperature setpoints, which were higher than the desired temperatures by amounts equal to the undershoots observed during test runs. This method enabled highly reproducible heating curves to within ± 1 °C of the desired highest treatment temperature (HTT: the highest temperature reached during pyrolysis).

For each feedstock type, biochar samples were produced at HTTs of 350, 500, 650 and 800 °C. These HTTs were intended to represent the range of temperatures at which biochar might be produced. Project funding and time constraints rendered the investigation of varying heating rate on biochar properties impractical, so a heating rate of 10 °C min^{-1} was used for all samples. However, the furnace was first heated to 45°C and held at this temperature for 5 minutes to ensure the same starting temperature. Once the furnace had reached a temperature 50°C below the target HTT, the heating rate was slowed to minimize overshoot. The HTT was maintained for 2 hours before the furnace was allowed to cool. The resultant biochar was removed once the furnace temperature had cooled to below 40°C and stored in a sealed container.

As biochar samples were present in the furnace for the entire heating and cooling process, biochars produced using a HTT of 500°C were in fact held at temperatures > 350°C for substantially longer than two hours, biochars produced at 650°C were held at temperatures > 500°C for substantially longer than two hours and so on. Using different heating rates could have reduced this effect somewhat, but such an approach was avoided because pyrolysis is initiated at higher temperatures as heating rates is increased (Gupta & Lilley, 2003), and different heating rates affect biochar yields (Williams & Besler, 1996).

4.2.2 Biochar yield

Biochar yields were measured for each biomass type and HTT using feedstock of a 2 - 5 mm particle size. Three yield measurements were made for each treatment i.e. from three separate pyrolysis runs, except for *Salix* biochar produced using an HTT of 650°C, for which only one measurement was made. Feedstock was weighed immediately before pyrolysis and the resultant biochar was weighed immediately after removal from the furnace. Weight measurements were made using a Sartorius 5-figure balance.

4.2.3 Hydrophobicity

Several methods are used within soil science to measure hydrophobicity, so pilot studies were used to select an effective way of measuring biochar hydrophobicity. The most commonly used approach in is the water drop penetration time (WDPT) test, which measures the persistence of a soil's water repellency. The WDPT test was rejected as a possible methodology following pilot studies which showed that using ground biochar, observing the exact penetration time was difficult because droplets often became completely obscured from view by fine biochar particles drawn onto their surfaces. The WDPT test was then piloted on unground biochar particles, but it was concluded that this would be an inefficient approach due to the extreme hydrophobicity (WDPT > 3600 seconds) of some biochar particles. These problems have also been encountered by other researchers (C. Masiello, pers. comm., September 2010). In order to avoid these problems, biochar hydrophobicity was instead investigated using a Krüss Easydrop goniometer to measure water droplet contact angles. On a hydrophobic surface, water will minimize its contact with the surface, so droplets will tend to bead on the surface, having a high contact angle (Yuan & Lee, 2013). Conversely, on a hydrophilic surface, water droplets will tend to spread (Yuan & Lee, 2013). Thus, the contact angle where a water droplet, air and the surface being investigated intersect gives a measure of hydrophobicity (Figure 4.2).

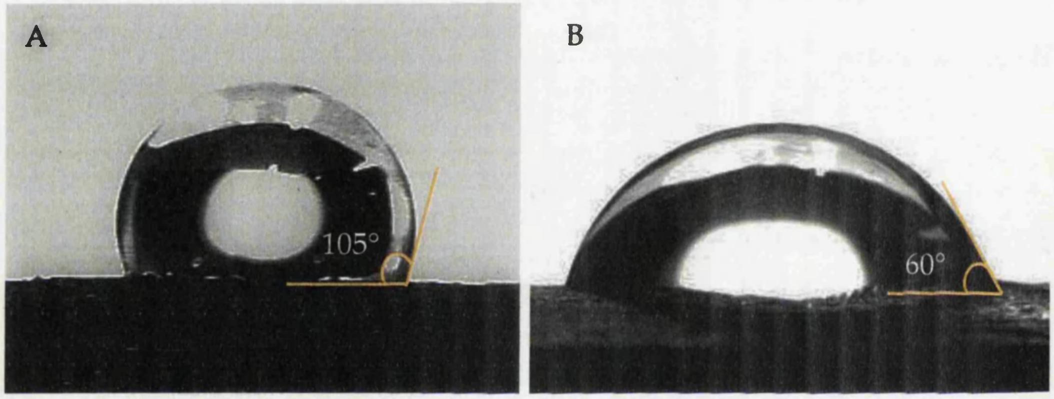


Figure 4.2: Contact angle measurements. The biochar particles were both produced from Salix feedstock. 'A' was produced at 350°C and 'B' was produced at 650°C.

Preliminary tests showed that ground biochar particles covering the surface of the water droplet obscured the contact-angle, so unground biochar particles were used instead. A droplet of deonized water (6 μl) was dropped onto a piece of biochar held in place using Play-Doh (a modelling compound produced from flour, water, salt, boric acid and mineral oil by Hasbro Inc., Rhode Island, USA) from a height of 10 mm, using an automated syringe (Figure 4.3). After 20 seconds, an image of the water droplet sitting on the biochar (illuminated from behind) was recorded by a high-resolution camera (Figure 4.3). The apparent contact angles where the water, air and biochar intersected on each side of the droplet were then measured (Figure 4.2). Pilot studies showed that that the accuracy of contact-angle measurements produced by drop-shape analysis software (DSA1 Version 1.9, Krüss, Germany) was unsatisfactory, so measurements were instead made manually using *ImageJ* software (Version 1.45c, National Institutes of Health, USA). When droplets infiltrated biochar or spread over the surface, the contact angle was recorded as zero.

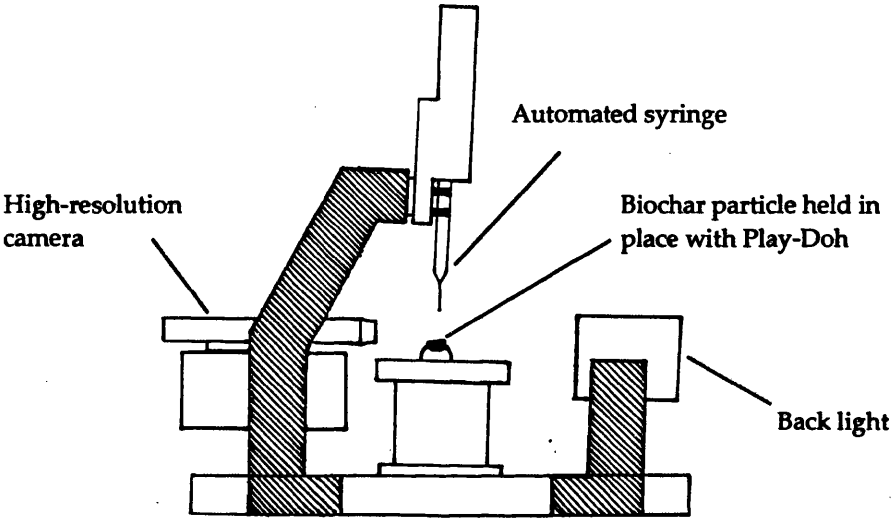


Figure 4.3: Goniometer

This procedure was carried out 50 times, giving a total of 100 contact angle measurements, one on each side of each water droplet, for each of the following:

(i) Biochar produced from each feedstock material at each HTT using only the 2 - 5 mm fraction, immediately following the sample removal from the furnace after cooling to <40°C. This size fraction was selected because it represented the largest fraction by mass, ensuring sufficient sample availability.

(ii) Biochar produced at 350°C from each particle-size fraction of *Salix* immediately following the sample removal from the furnace after cooling to < 40°C. The feedstock and HTT used were selected on the basis of evidence from pilot studies which indicated that they were most likely to produce hydrophobic biochar.

(iii) Biochar produced at 350°C from the 10 - 20 mm fraction of Salix feedstock at 2 hours, 7 days and 21 days from when the biochar was removed from the furnace after cooling < 40°C. These time periods were selected on the basis of anecdotal evidence which suggested that immediately following production, biochar surfaces were coated by condensed volatiles, but after three weeks the tars were no longer visible (R. Bryant, pers. comm., 3rd March 2011). This design thus provided a means of investigating whether biochar hydrophobicity might be influenced by reabsorption of condensed volatiles over time.

For each treatment, hydrophobicity was tested using biochar from a single batch.

4.2.4 Stereomicroscopy

Images of biochar particles were produced to assess visually the effect of feedstock type and pyrolysis temperature on the surface roughness of biochar particles. Images were obtained using a Leica MZ FL III fluorescence stereomicroscope in combination with a QImaging MicroPublisher 3.3 camera operated using QCapture Pro software (Version 6.0, QImaging, Canada).

4.2.5 Cation exchange-capacity

Cation exchange-capacity (CEC) was determined four times for each feedstock material at each HTT except 800°C, for which CEC was determined three times for each feedstock material. CEC was measured using sub-samples drawn from a composite sample produced from multiple pyrolysis runs. The method adopted used ammonium acetate to remove ash and buffer pH (Hendershot *et al.*, 2008). 1.00 to 2.00 g of biochar was weighed out into a jar. 40 ml of 1 M analytical grade ammonium acetate (NH_4OAc) were added to the tube, which was then sealed and shaken for 5 minutes on a reciprocal shaker (115 rpm). The tube was then removed from the shaker, agitated to rinse down biochar adhering to the sides and lid of the jar and left to stand overnight. The jar was then shaken again for 15 minutes, before the contents were transferred to a Buchner funnel with Whatman no. 42 ashless filter paper over a 500 ml filtering flask. The jar and lid were rinsed into the funnel with 1 M NH_4OAc from a wash bottle. The biochar was then washed with four 30 ml portions of 1 M NH_4OAc, each portion draining completely before the next was added. Any residual NH_4OAc was washed from the biochar with three 40 ml portions of isopropanol, with each portion again being allowed to drain completely before the next was added. The Buchner funnel was then placed onto a new flask and the biochar leached with four 50 ml portions of 1 M KCl, each portion being allowed to drain fully before the next was added. The leachate was then transferred to a 250 ml volumetric flask. Double distilled water was used to rinse the filtering flask into the volumetric flask and top up the volumetric flask to volume. Finally, the resultant solution was mixed thoroughly and a portion saved for analysis of NH_4 content using a SEAL Analytical AA3 automated segmented flow analyser.

The 2 - 5 mm size fraction was used to produce the biochar samples because it represented the largest fraction by mass, ensuring sufficient sample availability. The biochar samples were not ground prior to CEC analysis. Biochar particle size diminishes with increasing pyrolysis temperature and specific surface area can increase by up to two orders of magnitude (Kim *et al.* 2012; Brown *et al.* 2006), which may contribute to any differences in CEC between biochars produced at different temperatures. Grinding the biochar down to a standard particle size would have been inappropriate because it would have eliminated such an effect. Furthermore, the tensile strength of biochar decreases as pyrolysis temperature increases, making particles more susceptible to attrition if sieved (Downie *et al.*, 2009). As such, biochars produced at higher temperatures could have smaller particle sizes than biochar produced at lower temperatures, even if both were ground to pass through the same sized sieve aperture. Attempting to standardize the particle size of biochars produced at different HTTs is therefore problematic.

4.2.6 Statistical analyses

Normality of the hydrophobicity data was checked using the Kolmogorov-Smirnov test (Kolmogorov, 1933; Smirnov, 1948). This quantifies the maximum distance between the empirical distribution function of the sample and the cumulative distribution function, the normal distrubtion. Given data points J_1 to J_n, the empirical distribution function, E_N, is defined thus:

$$E_N = \frac{n(k)}{N}$$

Where $n(k)$ is the number of data points less than J_k, and the J_k are ordered from least to greatest value. This is a step function increasing by $1/N$ at the value of each ordered data point. The Kolmogorov-Smirnov test statistic is given by:

$$K = \max_{1\leq k\leq N}\left(C(J_k) - \frac{k-1}{N}, \frac{k}{N} - C(J_k)\right)$$

Where C is the theoretical cumulative distribution function. The K statistic is then compared to a critical value obtained from a probability table to determine whether or not the dataset is normally distributed.

The datasets collected in this investigation were either small or not normally distributed, so non-parametric methods were used for all statistical analyses.

Overall differences between biochars produced from different feedstocks or at different temperatures were analysed using the Kruskal-Wallis one-way analysis of variance by ranks (Kruskal & Wallis, 1952). This statistic is obtained by ranking the data from all groups together, from 1 to n, ignoring group membership; tied values are assigned the mean of the ranks that they would have received had they not been tied. The sum of ranks and mean of ranks is then calculated both for each group then for all groups combined and the statistic '*H*' is calculated thus:

$$H = \frac{1}{Q^2}\left\{\sum_{m=1}^{j}\frac{S_m^2}{n_m} - \frac{N(N+1)^2}{4}\right\}$$

Where j is the number of groups, S_m is the sum of ranks for the m^{th} group, n_m is the sample size of the m^{th} group, N is the total number of observations in all groups combined and Q^2 is given by:

$$Q^2 = \frac{1}{N-1}\sum_{m=1}^{j}\sum_{d=1}^{n_m} r_{dm}^2 - \frac{N(N+1)^2}{4}$$

Where r_{dm} is the rank for the d^{th} observation in the m^{th} group. The *p* value is then approximated by comparing *H* with the x^2 distribution according to the number of degrees of freedom, determined by *j* - *1*.

Mann-Whitney *U*-tests were used for *post hoc* pairwise comparisons (Mann & Whitney, 1947). As with the Kruskal-Wallis test, the data from both groups is numerically ranked from 1 to *n*, ignoring group membership, with equal values being assigned the mean of the ranks that they would have received had they not been equal. The sum of the ranks for group 1 is then determined, with *U* calculated thus:

$$U = n_1 n_2 + \frac{n_1(n_1 + 1)}{2} - S_1$$

Where n_1 is the sample size for group 1, and S_1 is the sum of ranks for group 1. The *U* statistic is then compared to the probability tables provided by Mann & Whitney (1947) to determine the *p* value according to the sample sizes of the two groups being compared. To control the familywise Error rate, significance values from *U*-tests were subjected to Bonferroni adjustment, meaning that the *p* values obtained using *U*- tests were multiplied by the total number of inter-group comparisons made for a family of tests using a given dataset (Dunn, 1961)

Jonckheere-Terpstra tests were used to assess trends with *a priori* ordering (Jonckheere, 1954). For example, the alternative hypothesis could be: group 1 median ≤ group 2 median ≤ group 3 ≤ group 4 median, where each group represents a higher temperature or dosage than the preceding group. For each group 1 value in turn, the number of values in groups 2, 3 and 4 that are greater than the group 1 value in question are counted (a tied value is counted as 0.5). This process is repeated to compare group 2 to groups 3 and

4, and group 3 to group 4; the total count is M. A count is also made of the number of values in groups 2, 3 and 4 that are smaller than the group 1 value in question (again, a tied value is counted as 0.5). Again, this process is repeated to compare group 2 to groups 3 and 4, and group 3 to group 4; the total count is Q. The Jonckheere-Terpstra statistic, S, is then calculated thus:

$$S = M - Q$$

The S statistic is then compared to the probability tables provided by Jonckheere (1954) to determine the p value according to the number of groups, and the group sample sizes.

All statistical analyses were completed using SPSS (v. 19, IBM, USA), except for the Jonckheere-Terpstra tests, which were manually calculated from first principles using Microsoft Excel (2010) because SPSS was found to produce erroneous output for this test. A 95% confidence level was adopted for all tests; differences were considered to be statistically significant where $p \leq 0.05$.

4.3 Results

4.3.1 Biochar yield

For all feedstocks, the average biochar yield decreased with each increase in HTT (Table 4.1). Using a HTT of 350°C, there were no significant differences between the biochar yields produced by different feedstocks (Table 4.2). At HTTs of 500°C and 650°C, there were statistically significant differences between the biochar yields produced using different feedstocks (Table 4.2). For all feedstocks, the largest reductions in biochar yield occurred between HTTs of 350 and 500°C. For *Salix* and *Miscanthus* feedstocks, median yield decreased from ~40% to ~30%, while for *Picea* feedstock, median yield decreased from 47% to 37%. Further increases in HTT had less effect on the average biochar yield of *Salix* and *Miscanthus* feedstocks; yields at 800°C were only ~3.5% lower than at 500°C (Figure 4.4). Using *Picea* feedstock, median yield was diminished from 37% to 31% between 500 and 650°C, with a further 2% reduction in yield between 650 and 800°C. Using a HTT of 800°C, the biochar yields for all feedstocks were ~25-30% and there were no statistically significant differences between them (Table 4.2). The range of yields produced from *Salix* and *Miscanthus* feedstocks was relatively small at all HTTs (Figure 4.4). However, for *Picea* feedstock, there appeared to be an overall trend for the range of biochar yields produced to decrease with increasing HTT (Figure 4.4).

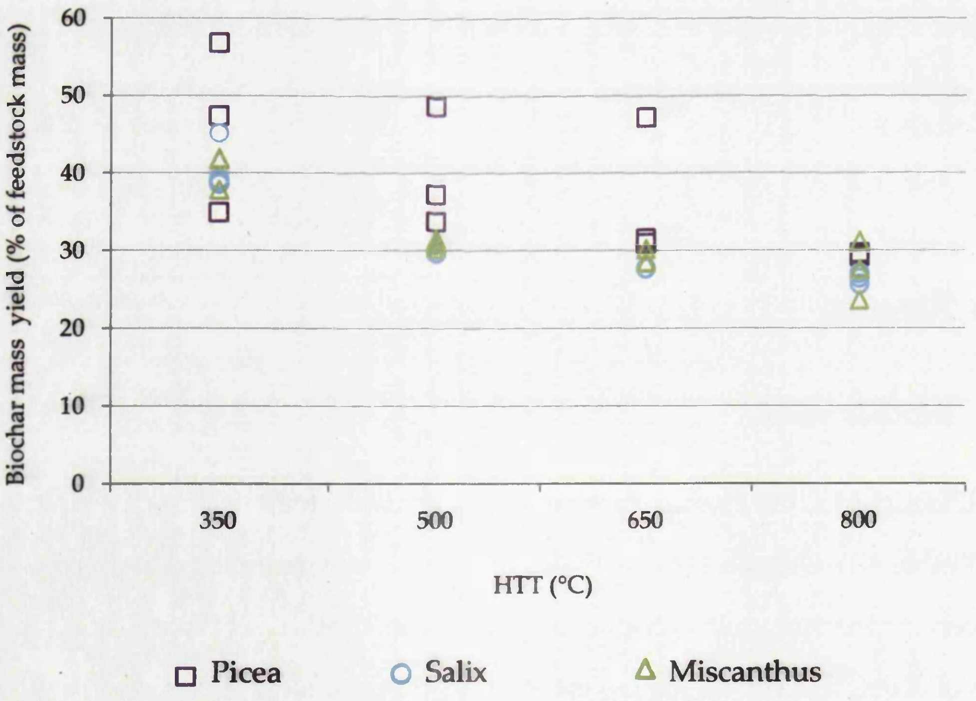


Figure 4.4: The effect of highest treatment temperature on the yield of biochar produced from different feedstock types

Table 4.1: Tests for differences between biochar yields at different temperatures and for trends of decreasing yield with increasing pyrolysis temperature

Feedstock	Kruskal-Wallis			Jonckheere-Terpstra	
	H	df	*p*	*S*	*p*
Salix	8.35	3	0.001	36	< 0.001
Miscanthus	8.13	3	0.015	44	< 0.001
Picea	7.82	3	0.021	42	< 0.001

Table 4.2: Tests for differences between biochar yields produced from different feedstocks at different highest treatment temperatures

HTT	Kruskal-Wallis		
	H	df	*p*
350°C	0.69	2	0.757
500°C	7.20	2	0.004
650°C	5.14	2	0.043
800°C	3.20	2	0.254

4.3.2 Hydrophobicity

4.3.2.1 The effect of HTT

Biochar hydrophobicity was significantly affected by HTT for all feedstocks. Statistically significant reductions in hydrophobicity occurred with each increase in HTT for all three feedstocks, with the exception of the difference between biochars produced at 650°C and 800°C from *Miscanthus* feedstock (Table 4.3). For *Miscanthus* and *Picea* biochars, the largest absolute decreases in hydrophobicity occurred when increasing the HTT from 350°C to 500°C, which led to a 40% reduction in mean contact angle for both feedstocks; from 96° to 57° for *Miscanthus* and from 83° to 47° for Spruce (Figure 4.5). However, this temperature increase had the least effect for *Salix* feedstock, resulting in a hydrophobicity reduction of just 14%. Increasing HTT from 500°C to 650°C halved the hydrophobicity of *Miscanthus* and *Picea* biochars but decreased the hydrophobicity of *Salix* biochar by only 27%. Increasing HTT from 650°C to 800°C reduced the hydrophobicity of *Salix* biochar by a further third, and of *Picea* biochar by a further half, but did not significantly affect the hydrophobicity of *Miscanthus* biochar (Table 4.3). Overall, the mean contact angles observed on *Salix, Miscanthus* and *Picea* biochars pyrolysed using a HTT of 800°C were respectively 58%, 70% and 80% lower than those on biochars produced at 350°C.

Biochar hydrophobicity was significantly affected by feedstock type at all HTTs (Table 4.4). *Salix* biochars were over a third more hydrophobic than *Miscanthus* or *Picea* biochars at all HTTs except 350°C (Table 4.4). When produced using HTTs of 350°C and 800°C, *Miscanthus* biochars were respectively 14% and 32% more hydrophobic than *Picea* biochars, but there were no significant differences between the two when HTTs of 500°C and 650°C were used (Table 4.4).

For all feedstocks, contact angle variability increased with increasing HTT (Figure 4.5).

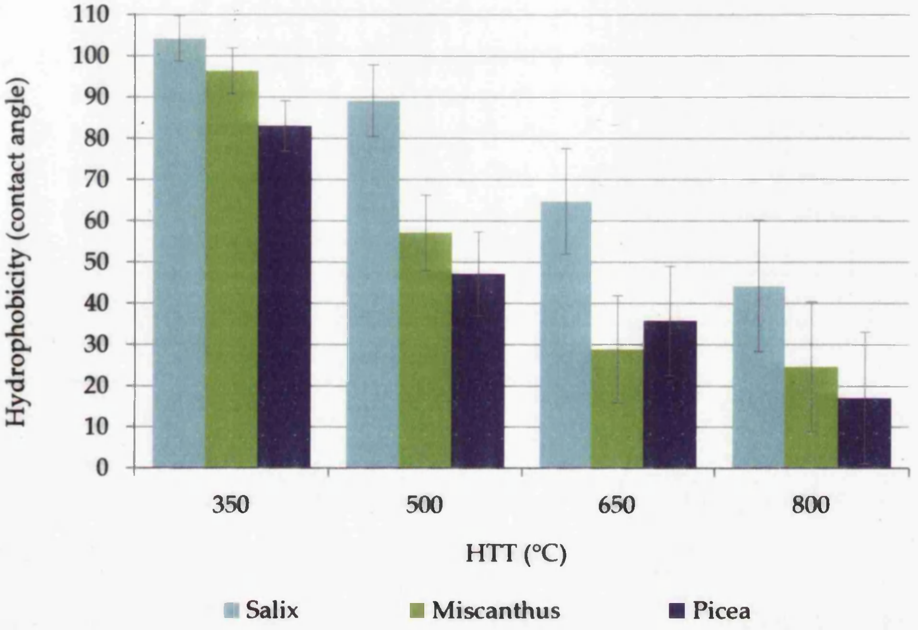


Figure 4.5: The effect of feedstock and HTT on biochar hydrophobicity (Error bars represent 95% confidence intervals (CIs), n = 100)

Table 4.3: Tests for differences between hydrophobicity of biochars produced using different HTTs (for U-tests, p is 1-tailed and Bonferroni-adjusted)

Feedstock	Kruskal-Wallis		Mann-Whitney	
HTTs compared (°C)	*H*	(df)	*U*	*p*
Salix	208.47	(3)		< 0.001
350 vs. 500			2334.5	< 0.001
500 vs. 650			2403.0	< 0.001
650 vs. 800			3022.5	< 0.001
Miscanthus	279.26	(3)		< 0.001
350 vs. 500			151.0	< 0.001
500 vs. 650			1729.0	< 0.001
650 vs. 800			4527.0	0.238
Picea	223.94	(3)		< 0.001
350 vs. 500			838.0	< 0.001
500 vs. 650			3900.0	0.010
650 vs. 800			317.50	< 0.001

Table 4.4: Tests for differences between hydrophobicity of biochars produced from different feedstocks (for U-tests, p is 2-tailed and Bonferroni-adjusted)

HTT	Kruskal-Wallis		Mann-Whitney	
Feedstocks compared	*H*	(df)	*U*	*p*
350°C	106.27	(2)		< 0.001
Salix vs. *Miscanthus*			3016.0	< 0.001
Salix vs. *Picea*			1284.5	< 0.001
Miscanthus vs. *Picea*			1913.5	< 0.001
500°C	153.40	(2)		< 0.001
Salix vs. *Miscanthus*			641.0	< 0.001
Salix vs. *Picea*			638.0	< 0.001
Miscanthus vs. *Picea*			4187.0	0.140
650°C	75.10	(2)		< 0.001
Salix vs. *Miscanthus*			1677.0	< 0.001
Salix vs. *Picea*			2360.0	< 0.001
Miscanthus vs. *Picea*			4263.0	0.201
800°C	44.88	(2)		< 0.001
Salix vs. *Miscanthus*			3157.0	< 0.001
Salix vs. *Picea*			2400.0	< 0.001
Miscanthus vs. *Picea*			4128.5	0.086

4.3.2.2 The effect of feedstock particle size

The particle size of feedstock had a statistically significant effect on the hydrophobicity of *Salix* biochar ($H(2) = 10.62, p = 0.005$). The hydrophobicity of *Salix* biochars produced from 2 - 5 and 5 - 10 mm feedstock was almost identical; both had mean water droplet contact angles of 104 ±14° (± denotes standard deviation). In contrast, the mean water droplet contact angle on biochar produced from 10-20 mm *Salix* feedstock was lower (100 ±14°); the differences between this particle size and the smaller two were statistically significant (Table 4.5).

Table 4.5: Tests for differences between hydrophobicity of biochars produced from different particle size fractions of Salix feedstock (n = 100, p is 2-tailed and Bonferroni-adjusted)

Feedstock particle sizes (mm)	Mann-Whitney	
	U	*p*
2 - 5 vs. 5 - 10	4921.0	0.500
2 - 5 vs. 10 - 20	3850.0	0.008
5 - 10 vs. 10 - 20	3843.5	0.008

4.3.2.3 The effect of time since production

As Figure 4.6 illustrates, the hydrophobicity of *Salix* biochar did not change significantly between the day it was produced and 7 days and 21 days later ($p = 0.062$) .

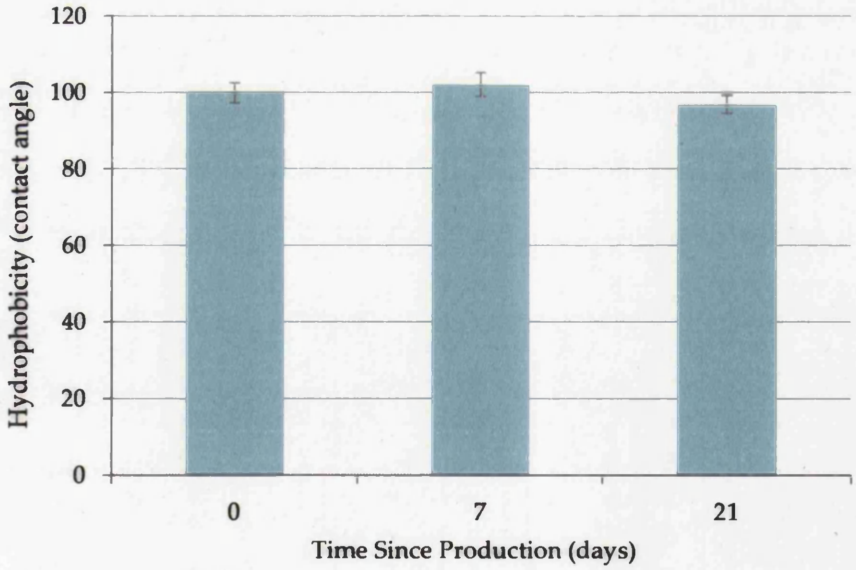


Figure 4.6: The effect of time since production on the hydrophobicity of Salix biochar produced at 350°C (Error bars represent 95% CIs, n = 100)

4.3.3 Cation exchange-capacity

CEC was significantly affected by HTT for *Salix* and *Miscanthus* feedstocks, but not for *Picea* feedstock (Table 4.6). The largest changes in CEC occurred between HTTs of 350 and 500°C, the mean more than doubling for each feedstock. This was a statistically significant change in CEC in the case of *Salix* and *Miscanthus* feedstocks (Table 4.6). For all subsequent increases in HTT, biochar CEC was invariant (Figure 4.7).

Biochar CEC was significantly affected by feedstock material at all HTTs (Table 4.7). The mean CECs of biochars produced from *Salix* were consistently double that of biochars produced from *Picea* (Figure 4.7), though the differences between them were only statistically significant at HTTs of 500 and 650°C (Table 4.7). The mean CECs of biochars produced from *Miscanthus* feedstock were consistently ~3 times higher than those produced from *Picea* biomass (Figure 4.7); the differences were statistically significant at each HTT except 800°C (Table 4.7). The mean CEC of *Miscanthus* biochar was higher than that of *Salix* biochar at all HTTs except for 650°C (Figure 4.7), but the differences between them were only statistically significant at 350°C (Table 4.7).

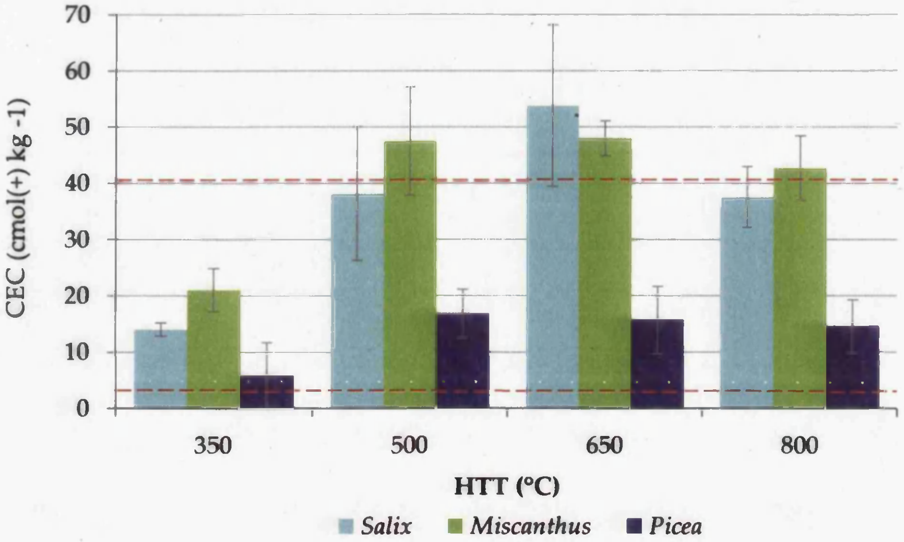


Figure 4.7: The effect of feedstock and HTT on biochar CEC (Error bars represent 95% CIs. Red dashed lines represent typical range of soil CEC values (Brady & Weil, 2008). For biochars produced at 350 - 650°C, n = 4, for biochars produced at 800°C, n = 3.)

Table 4.6: Tests for differences between CECs of biochars produced using different HTTs (for U-tests, p is 1-tailed and Bonferroni-adjusted)

Feedstock	Kruskal-Wallis		Mann-Whitney	
HTTs compared (°C)	*H*	(df)	*U*	*p*
Salix	9.84	(3)		0.004
350 vs. 500			0.00	0.042
500 vs. 650			3.00	0.300
650 vs. 800			2.00	0.342
Miscanthus	9.18	(3)		0.009
350 vs. 500			0.00	0.042
500 vs. 650			7.00	1.000
650 vs. 800			2.00	0.342
Picea	4.78	(3)		0.189

Table 4.7: Tests for differences between CECs of biochars produced using different HTTs (for U-tests, p is 1-tailed and Bonferroni-adjusted)

HTT	Kruskal-Wallis		Mann-Whitney	
Feedstocks compared	*H*	(df)	*U*	*p*
350°C	8.35	(2)		0.002
Salix vs. *Miscanthus*			0.0	0.042
Salix vs. *Picea*			3.0	1.000
Miscanthus vs. *Picea*			0.0	0.042
500°C	7.73	(2)		0.007
Salix vs. *Miscanthus*			5.0	0.729
Salix vs. *Picea*			0.0	0.042
Miscanthus vs. *Picea*			0.0	0.042
650°C	7.73	(2)		0.007
Salix vs. *Miscanthus*			5.0	0.729
Salix vs. *Picea*			0.0	0.042
Miscanthus vs. *Picea*			0.0	0.042
800°C	5.96	(2)		0.025
Salix vs. *Miscanthus*			2.0	0.600
Salix vs. *Picea*			0.0	0.150
Miscanthus vs. *Picea*			0.0	0.150

4.4 Discussion

4.4.1 Biochar yield

The decreases in yield observed with increasing HTT are in agreement with, *inter alia*, the findings of Demirbas (2004), Hossain *et al.* (2011) and Mašek *et al.* (2013). At pyrolysis temperatures below 250°C, mass is lost by formation of water from cellulose and evolution of CO_2 and CO (Antal & Grønli, 2003). Decomposition of hemicellulose begins at 220°C and is largely completed by

315°C (Yang *et al.*, 2007). As the lowest HTT used in this investigation was 350°C, hemicellulose content is unlikely to have contributed to differences between weight losses of feedstocks at different HTTs. Biochar yields are greater at lower pyrolysis temperatures because there are lower losses of CH_4, H_2 and CO (Novak *et al.*, 2009). Pyrolysis (and weight loss) of cellulose occurs between 315°C and 400°C (Yang *et al.*, 2007) and cellulose-derived levoglucosan tars can be volatilized at 300-600°C (Amonette & Joseph, 2009), meaning biochar yields significantly decline between HTTs of 300°C and 600°C. Increasing the HTT beyond 600°C results in the removal of more of the O, H, N and S in the original feedstock (Amonette & Joseph, 2009). Lignin starts to decompose at around 160°C and steadily continues to do so up to 900°C (Yang *et al.*, 2007). Lignin preferentially forms char during pyrolysis, so using feedstocks with high lignin contents tends to deliver higher biochar yields (Antal & Grønli, 2003; Demirbas, 2004). Lignin weight loss during pyrolysis is typically less than half that of cellulose because it is less easily dehydrated and produces more residual biochar (Brown, 2009). The literature indicates that *Picea* is likely to have had the highest lignin content of the feedstocks used in this investigation (Table 4.8), which could explain why it delivered the highest mean biochar yields at all pyrolysis temperatures and why reductions in yield with increases in HTT were larger than for *Miscanthus* and *Salix* feedstocks. The similarities between the yields obtained from *Miscanthus* x giganteus and *Salix* viminalis feedstocks suggest that their lignin contents were similar.

Table 4.8: Lignin and cellulose content of feedstocks

Biomass	Composition (%)		References
	Lignin	Cellulose	
Miscanthus x giganteus	12-28	42 - 52	Ververis *et al.*, 2004; Brosse *et al.*, 2012
Picea sitchensis	28	44 - 46	Ramsden & Blake, 1997; Nuopponen *et al.*, 2006
Salix viminalis	25 - 27	38 - 41	Waliszewska *et al.*, 2006

4.4.2 Hydrophobicity

4.4.2.1 The effect of feedstock particle size

The relatively lower hydrophobicity of biochar produced using the 10-20 mm particle size compared to the smaller particle sizes may be due to the effect of larger feedstock particle size on pyrolysis reactions. Larger particle sizes can limit heat transfer into particles and the mass transfer of volatiles out of the biochar (Antal & Grønli, 2003; Downie *et al.*, 2009). This could ultimately result in a lesser volume of hydrophobic tars condensing on the surface of biochar, with unescaped volatiles instead condensing within the particle. Further research is needed to determine whether this is the case. The heating rate for small particles is higher than for larger particles (Zanzi, 2001). Different heating rates can result in different concentrations of functional groups (Ammonette and Joseph, 2009), which could have contributed to differences in hydrophobicity.

Although the differences between the hydrophobicity of different biochar particle size fractions were statistically significant, the differences were small and unlikely to have any substantial influence on the use of biochar as a soil amendment. Moreover, it is likely that biochars of 10-20 mm would be ground to maximise their specific surface area prior to being applied to soil, which, if the explanation given above for the greater hydrophobicity of this particle size fraction is correct, could eliminate the effect of larger feedstock particle sizes in reducing biochar hydrophobicity anyway (because the internal surfaces where volatiles condensed would be exposed by grinding). Also, as Downie *et al.* (2009) suggest, the influence of larger particle sizes might be overcome by using longer retention times.

4.4.2.2 The effect of time since production

That biochar hydrophobicity did not decrease with time since production demonstrates that the hydrophobicity of these biochars was not reduced by reabsorption of condensed volatiles. It is more likely that hydrophobicity is instead eliminated by oxidation of biochar surfaces and leaching (Cheng *et al.*, 2006; Briggs *et al.*, 2012). However, further research is needed to determine whether the presence and subsequent reabsorption of condensed volatiles on biochars produced without N_2 purge gas contributes to variations in biochar hydrophobicity.

4.4.2.3 The effect of HTT

In surface science, Young's Law stipulates that a water / solid contact angle of 90° delineates the boundary between hydrophobic and hydrophilic solids (Young, 1805). If a water droplet on a surface has a contact angle of <90°, the surface is considered hydrophilic. If the contact angle is >90°, the surface is considered hydrophobic. It is often assumed in soil science that the same contact angle threshold is indicative of whether or not a soil is hydrophobic (Shirtcliffe *et al.*, 2006). Applying this principle to biochar, it can be concluded that *Picea* biochar was hydrophilic even when using a HTT of 350°C and *Miscanthus* biochar became hydrophilic when using a HTT ≥500°C. These findings support the theory proposed by Kinney *et al.* (2012) that biochar hydrophobicity is related to alkyl functionalities which are largely destroyed by pyrolysis up to 500°C. Indeed, the most dramatic decreases in the hydrophobicity of biochars produced from *Miscanthus* and *Picea* feedstocks occurred between HTTs of 350 and 500°C. The largest reduction in the hydrophobicity of *Salix* biochar nonetheless occurred between HTTs of 500 and 650°C, indicating that factors other than the destruction of alkyl functionalities at 500°C can contribute to changes in biochar hydrophobicity.

Although the mean droplet contact angle on *Salix* biochar was below 90° using a HTT of 500°C, the 95% upper confidence interval only dropped below 90° between HTTs of 500 and 650°C (Figure 4.5). Moreover, Shirtcliffe *et al.* (2006) demonstrated theoretically and experimentally that water cannot enter many soils unless the contact angle is less than approximately 50°. This finding may also apply to biochar, though it should be noted Shirtcliffe *et al.* (2006) examined multi-particle surfaces, whereas this investigation used single (but porous) particles. Using a 50° contact angle threshold to define biochars as hydrophilic or hydrophobic, *Picea* and *Miscanthus* biochars can only be classified as hydrophilic with 95% confidence at a HTT of 650°C, though *Picea* biochar became more wettable using a HTT of 800°C (Figure 4.5). Although the mean water droplet contact angle on *Salix* biochar was below 50° using a HTT of 800°C (Figure 4.5), there is less than 95%

confidence that the true mean contact angle was in fact below 50°. Using HTTs of 800°C, contact angles of 0° were only recorded for 20% of droplets on *Salix* biochar, and 37% of droplets for both *Picea* and *Miscanthus* biochars, so there was clearly a residual resistance to wetting of the biochar surfaces even at the highest pyrolysis temperature.

If alkyl functionalities were solely responsible for biochar hydrophobicity, the wettability of biochars produced at HTTs >500°C would be the same, because alkyl groups are destroyed at HTTs between 400 and 500°C. However, differences in the wettability of biochars produced from different feedstocks persisted at HTTs beyond 500°C. A plausible explanation for continued reductions in hydrophobicity at HTTs beyond 500°C would be increasing surface charge, but this cannot have been the case as the surface charge characteristics of the biochars were not significantly altered by increases in HTT beyond 500°C (

Table 4.6). It therefore seems likely that other factors influence biochar hydrophobicity besides surface chemistry.

Surface chemistry alone can only achieve maximum contact angles of around 120° on flat surfaces (McHale *et al.*, 2007). Greater contact angles can only occur where there is a sufficiently 'rough' surface at the sub-mm scale (McHale *et al.*, 2007). For *Salix* biochar produced using a HTT of 350°C, 15% of the contact angles recorded were greater than 120°, while for *Miscanthus* and *Picea* biochars produced at the same temperature, 6% and 7% of the contact angles recorded were greater than 120°. This demonstrates that the surface topography of biochar particles contributes to their hydrophobicity.

As pyrolysis temperature is increased from 300 to 1000°C, biochar particles shrink as a result of pyrolysis reactions (rearrangement of chemical bonds and the coalescence of graphite nuclei within the particle) and loss of water mass (Emmerich & Luengo, 1996; Di Blasi, 1996; Freitas *et al.*, 1997; Hagge & Bryden, 2002; Antal & Grønli, 2003; Downie *et al.*, 2009). Shrinkage of particles is three-dimensional (Pulido-Novicio *et al.*, 2001), so the height of peaks in the surface topographies of biochar particles will be reduced in proportion to the overall reduction in particle size, meaning that biochar surfaces become smoother and therefore less hydrophobic as HTT increases (Figures 4.8 - 4.10). This effect would be more complex for woody feedstock particles where some of the surface is covered in bark, as the bark will often have a higher lignin content than the rest of the wood (Harkin & Rowe, 1971), potentially resulting in different amounts of shrinkage at the surface compared to the rest of the char.

Contact angle variability increased with increasing HTT for all feedstocks, demonstrating that changes in the hydrophobicity of biochar surfaces are not uniform. Instead biochar hydrophobicity becomes more heterogeneous with increasing HTT, indicating changes in the surface chemistry and topography of biochar particles are gradual rather than subject to sudden, uniform changes at certain threshold temperatures. As such, specific sites on biochar particles will be more or less hydrophobic than other sites.

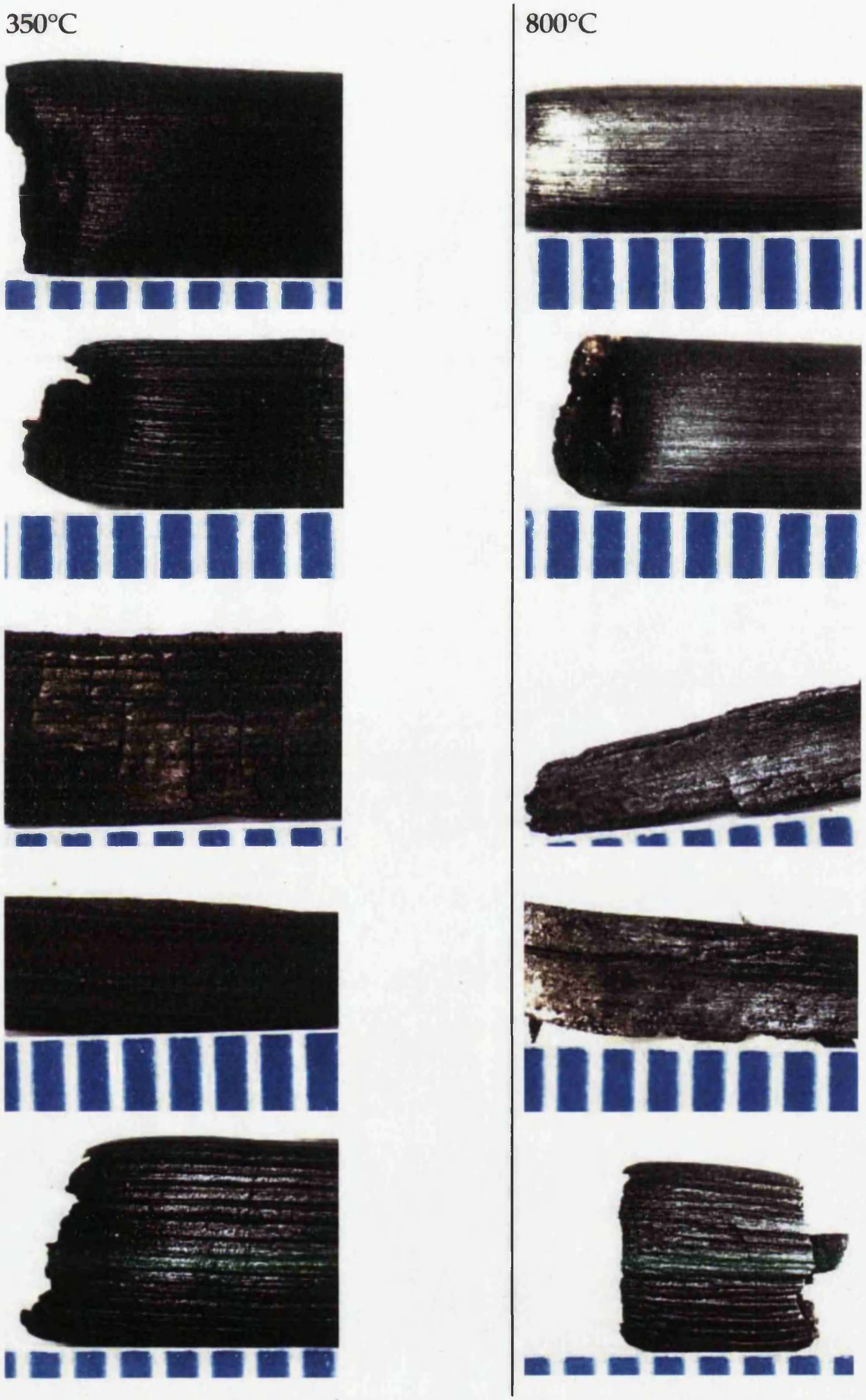


Figure 4.8: Stereomicroscope images of Miscanthus biochars (For scale, blue marks are at 1 mm intervals)

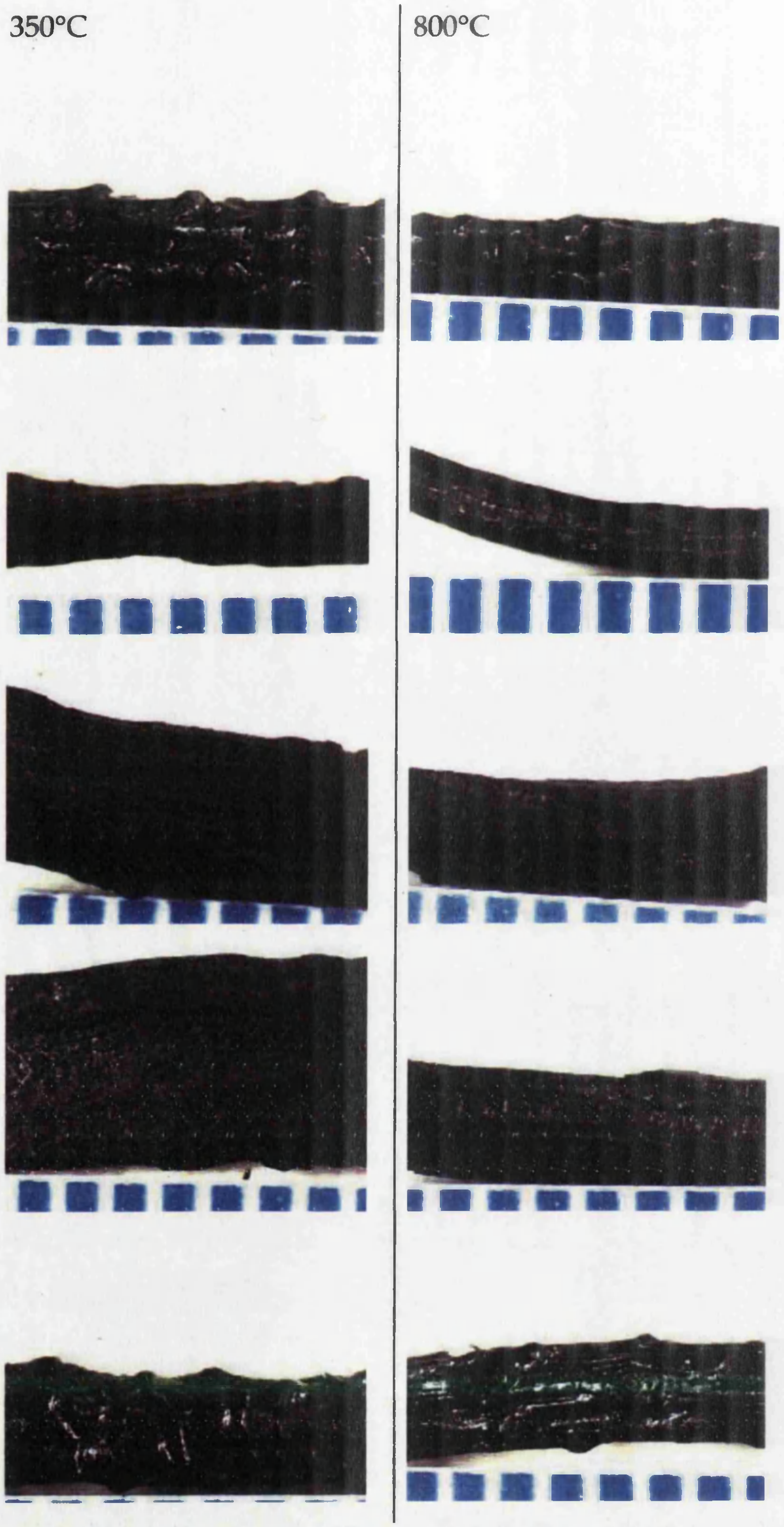


Figure 4.9: Stereomicroscope images of Picea biochars (For scale, blue marks are at 1 mm intervals)

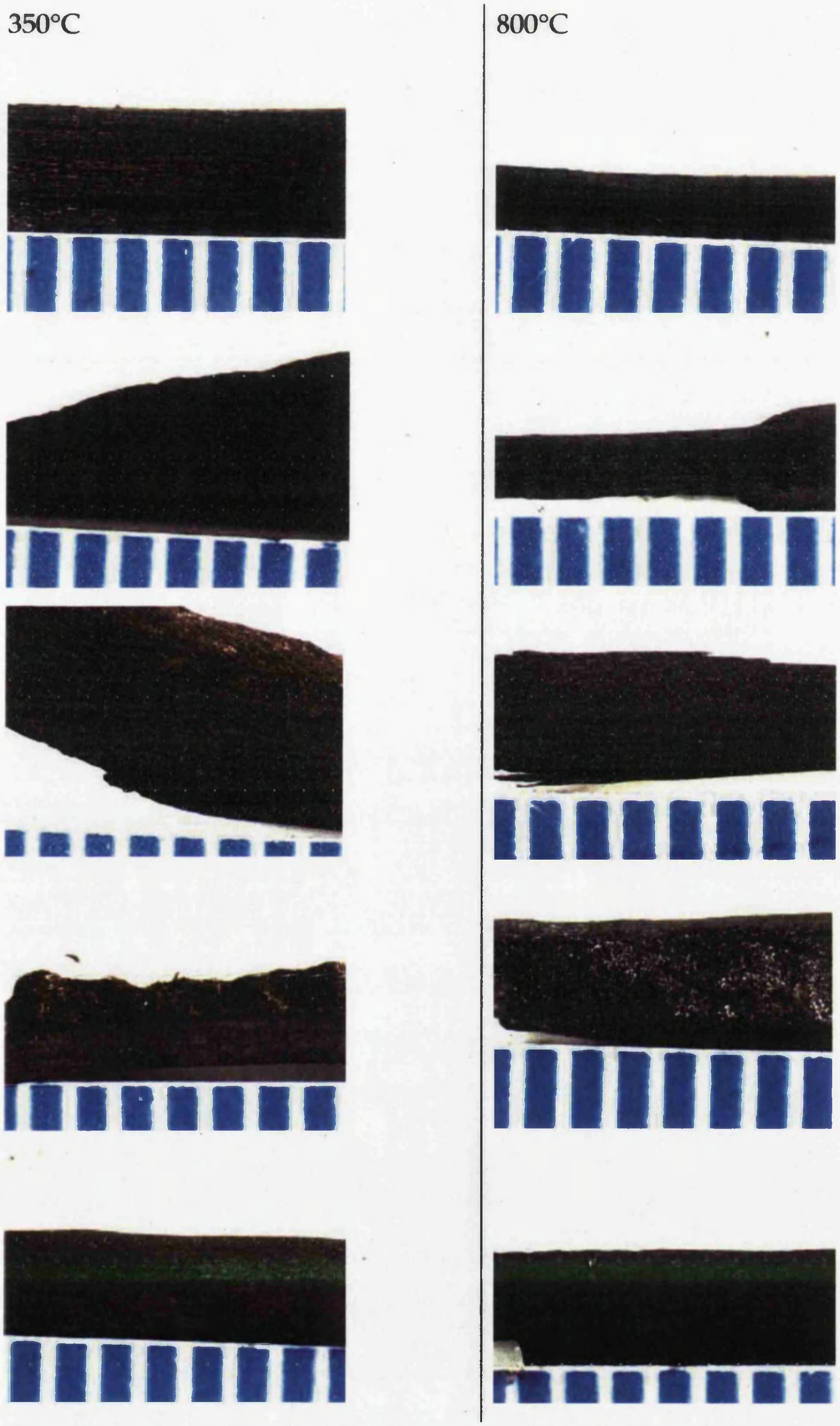


Figure 4.10: Stereomicroscope images of Picea biochars (for scale, blue marks are at 1 mm intervals)

4.4.2.4 The effect of feedstock type

Kinney *et al.* (2012) found that biochar hydrophobicity was correlated to alkyl functionalities. At temperatures below 500°C, differences in hydrophobicity between biochars produced from different feedstocks will therefore result in part from differences in the concentrations of alkyl functionalities inherited from the original biomass. Alkyl is representative of plant structures such as lipids and cutans which are present in different concentrations in different biomass (Krull *et al.*, 2009). However, at HTTs above 500°C, the conversion of alkyls to aryls is almost complete (Krull *et al.*, 2009), meaning that contrasts in the chemical characteristics of feedstocks will become less important in influencing biochar hydrophobicity. The differences in hydrophobicity of biochars produced from different feedstocks at HTTs above 500°C thus provide further evidence of the importance of biochar surface topography.

Some of the differences in hydrophobicity between the two wood-derived biochars may have arisen from their different densities. The average density of *Salix viminalis* is 0.59 g cm^{-3} (Vargas *et al.*, 2012). This is much higher than the average density of *Picea sitchensis*, which is 0.35 g cm^{-3} (Moore, 2011). Generally speaking, the lower the density of a wood, the easier it is to cut, resulting in smoother surfaces (Simpson & TenWolde, 1999). Denser woods are more likely to split or splinter when cut. It is therefore possible that the lower hydrophobicity of *Picea* biochar compared to *Salix* biochar was partly attributable to their different densities resulting in different degrees of surface smoothness when the feedstocks were chipped. Also, *Picea* has a fine, even texture and a consistently straight grain, whereas *Salix* usually has a more medium (rougher) texture; this may have also contributed to differences in the surface topographies of *Salix* biochar and *Picea* biochar.

Miscanthus feedstock yielded more hydrophobic biochar than *Picea* feedstock at most HTTs, this difference presumably arose in part from the uniformly ribbed structure of *Miscanthus* stems (Figure 4.8) augmenting hydrophobicity to a greater extent than the texture of *Picea* feedstocks.

The extent to which particles shrink as they are pyrolysed differs according to the proportions of lignin, cellulose and hemicellulose, and other organic and inorganic materials in the feedstock (Hagge & Bryden, 2002). Fengel & Grosser (1975) tabulated data from more than 350 papers investigating the composition of 153 wood species. On average, stem wood in temperate-zone hardwoods contains 40-50% cellulose and 20-25% lignin, while temperate-zone softwoods contain 40-45% cellulose and 25-35% lignin (Fengel & Grosser, 1975). Cellulose is thermally degraded between 315°C and 400°C whereas lignin starts to decompose at around 160°C and steadily continues to do so up to 900°C (Yang *et al.*, 2007). Different proportions of these components in the different feedstocks used in this study (Table 4.8) would have influenced the extent to which the physical structure and therefore, surface topography of biochar particles was modified at different pyrolysis temperatures.

The proportion of inorganic components (ash content) also has implications for physical structure however and can cause dramatic changes in the physical and structural composition of biochar where ash fusion or sintering occurs (Downie *et al.*, 2009). As Table 4.9 demonstrates, the *Miscanthus* feedstock used in this study would probably have had substantially higher ash content than the *Salix* or *Picea* feedstocks. *Miscanthus* feedstock particles would therefore to have been more susceptible to changes in its structural composition due to ash fusion or sintering during pyrolysis. This may have contributed to differences in surface roughness and therefore, differences in hydrophobicity between the feedstocks.

Table 4.9: Reported ash contents of Picea, Salix and Miscanthus stems

Reference	Ash content (% dry weight)		
	Picea	*Salix*	*Miscanthus*
van Ree (1995)	-	-	1.50
Wilén *et al.* (1996)	-	1.18	2.30
	-	-	3.31
Miles *et al.* (1996)	-	0.95	2.30
	-	1.10	4.15
Illerup & Rathmann (1996)	-	2.10	1.50
Moilanen *et al.* (1997)	-	1.20	3.30
Hallgren *et al.* (1999)	-	1.90	1.50
Guanxing *et al.* (1999)	-	-	2.80
Yu *et al.* (1999)	-	2.50	-
Antal *et al.* (2000)	0.30	-	-
Romey *et al.* (2001)	-	1.60	-
Sørum *et al.* (2001)	0.20	-	-
Wekelin *et al.* (2005)	0.40	-	-
Obernberger *et al.* (2006)	-	2.00	4.00
Rhén *et al.* (2007)	0.36	-	-
Tutus *et al.* (2010)	0.32	-	-
Butler *et al.* (2013)	0.26	1.16	3.43
Wang & Dibdiakova (2014)	0.19	-	-
Mean (± standard deviation)	0.29 (± 0.08)	1.57 (± 0.54)	2.74 (± 0.98)

4.4.3 Cation exchange-capacity

Apart from the increase in HTT from 350 to 500°C, increases in HTT did not affect biochar CEC. However, feedstock type had a significant effect on CEC at all HTTs. This corresponds to the finding of Zhao *et al.* (2013) that CEC is predominantly controlled by feedstock rather than temperature. That the average CECs of *Miscanthus* biochars were generally higher than the average CECs of *Picea* and *Salix* biochars supports the conclusions of Mukherjee *et al.* (2011), who also found that graminoid biochars had a higher CEC than woody biochars derived from coniferous and deciduous feedstocks.

The CECs of biochars produced at 500, 650 and 800°C were higher than those produced at 350°C. This supports the findings of Lehmann (2007a) and may indicate that that there were larger numbers of oxygen-bearing functional groups on the biochars produced at higher temperatures as observed by Nishimiya *et al.* (1998). Differences in specific surface area may also have contributed to differences between the CECs of biochars produced at different temperatures and from different feedstock. Specific surface area was not measured in this study due to time and budget limitations, but *Picea* feedstock is likely to have a smoother surface than *Salix* feedstock (see section 4.4.2.4), so the *Picea* biochars probably would have had a lower specific surface area per unit weight than the *Salix* biochars. The shortest axes of *Miscanthus* feedstock particles were generally substantially smaller than those of *Picea* or *Salix* feedstocks i.e. *Miscanthus* feedstock particles had a more platy shape, while *Picea* and *Salix* feedstock particles had a more cylindrical shape. *Miscanthus* biochars are therefore likely to have had a higher specific surface area than *Picea* and *Salix* biochars. Differences in biochar specific surface area resulting from feedstock type or HTT (due to particle shrinkage) could have resulted in different degrees of oxidation following production enabled by differences in intrasurface accessibility (Zimmerman, 2010). The biochars in this study were stored under ambient conditions for several months prior to CEC determination. The outer surfaces of biochar particles can undergo abiotic oxidation within a few months of their production, even under ambient atmosphere and temperature (Cheng *et al.*, 2006; Cheng *et al.*, 2008). Oxidation of aromatic C on biochar surfaces forms carboxylic groups, which increases CEC (Glaser *et al.*, 2002). Logically, the biochars with larger specific surface area could have been subject to more abiotic oxidation than those with smaller specific surface area. Consequently, even if carboxylic groups were progressively eliminated with increasing pyrolysis temperature (Antal & Grønli, 2003), biochars produced at higher temperatures could undergo more oxidation resulting in them having a higher density of carboxylic groups and, therefore, a higher CEC. Biochar shape can to some extent be controlled; grinding raw feedstock tends to produce large, fibrous particles, whereas grinding biochar tends to produce shorter, more rounded particles (Abdullah & Wu, 2009).

Although the CEC determination method used in this study should have removed most of the ash content (mineral residue) of biochars by washing with ammonium acetate, it is possible that ash content may have influenced CEC determination. There are no statistically robust comparisons of plant-derived ash and biochar CECs in the literature, but the CEC of plant ash can be high (Smith, 1969; Fritze *et al.*, 1995) and may have been a further influence on biochar CEC. Ash content of biochar increases with increasing temperature (Bagreev, 2001, Novak *et al.*, 2009; Yuan *et al.*, 2011) which (assuming ash CEC is high) might to some extent counter the effect of progressive elimination of acidic functionalities on the surface of the biochar itself as HTT increases. Ash content of biochar is also strongly influenced by feedstock material; graminoid biomass will produce biochar with much higher ash content than woody biomass (Obernberger *et al.*, 2006; Hammes *et al.*, 2006) and deciduous wood generally has more ash content than coniferous wood (Wenzl, 1970; Obernberger *et al.*, 2006). Ash content may have accordingly contributed to the differences in CEC between different feedstock types. The literature indicates that Picea is likely to have had the lowest ash content of the feedstocks used in this study, while Miscanthus is likely to have had the highest (Table 4.9). This corresponds to the typical ordering of CEC values observed in biochars produced from those feedstocks (Figure 4.7).

The biochar CECs reported in this study are indicative only of the effect that they might have on soil CEC when first applied. The CEC of newly produced biochar is relatively low under any production scenario (Lehmann, 2007a). As Figure 4.7 illustrates, the range of biochar CECs found in this study were broadly similar to normal CEC values of soils, which typically range from ~3 to ~40 cmol(+) kg^{-1} (Brady & Weil, 2008). The CECs of fresh biochar observed in the present study were very low compared to those typical of soil humus, which range from ~150 to ~250 cmol(+) kg^{-1} (Brady & Weil, 2008). Nevertheless, had the biochars been ground, their CECs would probably have been substantially higher due to larger specific surface area. Over the lifespan of biochar, changes to its chemical properties following its application to soil may be more important than properties arising from its production. Oxidation of biochar once it is mixed with soil can leads to substantial increases in its CEC over time (Cheng *et al.*, 2008). Differences between CECs of biochars recorded in this study are negligible compared to the CECs recorded for aged biochar, which can be orders of magnitude greater (Liang *et al.*, 2006).

If ash content does make a significant contribution to biochar CEC, this will diminish over time as it is leached out. As Joseph *et al.* (2009) suggest, a more useful way of classifying biochar CEC might be based on assessment of how it changes once applied to soil. It may also be more worthwhile to focus on the effect that biochar has on overall soil nutrient adsorption rather than on the CEC of the biochar itself. The CEC of biochar itself does not necessarily equate to its potential contribution to soil CEC. Much of the internal surface area of biochar particles may not be in contact with plant roots or the soil solution (except under saturated conditions), so even if its CEC is high, it is not necessarily functionally important. Whilst the contribution of biochar to soil CEC could be amplified by adsorption of organic C rich in functional groups, biochar pores may be blocked by adsorbed substances, rendering adsorption sites in inner pores inaccessible (Hammes & Schmidt, 2009). Furthermore, it should be remembered that the physical adsorption capacity of biochar may be an important factor influencing soil nutrient dynamics, regardless of any effect of HTT on chemical adsorption capacity (Ding *et al.*, 2010).

4.5 Limitations

The apparent effect of biochar hydrophobicity being lower when larger feedstock particles are used may in practice be eliminated by grinding of biochar following production. Further investigation is needed to determine whether this is the case.

The finding that biochar hydrophobicity is not affected by time since production may not apply to all biochar production systems. This study used a purge gas in biochar production, meaning that a proportion of evaporated volatiles were removed from the furnace and condensed elsewhere. Where no purge gas is used, a greater proportion of evaporated volatiles will condense on biochar surfaces. This could potentially result in (i) freshly produced biochar being more hydrophobic than when produced using purge gas and (ii) a reduction in biochar surface hydrophobicity over time since production resulting from the absorption of condensed volatiles. Additional research is necessary to determine whether the biochar hydrophobicity is affected by the use of purge gas and whether the hydrophobicity of biochar produced without purge gas is influenced by time since production.

This study offers a theoretical explanation of the potential for differences in biochar surface topography to contribute to differences in hydrophobicity. Quantitative analyses of differences in biochar surface topography related to pyrolysis temperature and feedstock are needed to enable experimental demonstration of the relationship between biochar surface roughness and biochar hydrophobicity.

A combination of differences in the specific surface areas of biochars and differences in the period of storage prior to CEC determination could have resulted in different degrees of oxidation of biochar surfaces during storage, which in turn could have influenced biochar CEC through the formation of carboxylic groups. The hydrophobicity and CEC data presented in this study provide an understanding of the properties of fresh biochar, but are of limited value in determining the likely long-term effects of biochars on soil properties. As biochar surfaces are progressively oxidised in the soil environment, formation of functional groups is likely to render them progressively less hydrophobic, while increasing their CEC (Cheng *et al.*, 2008). Biochar CEC may also be influenced by progressive leaching of ash. Changes in biochar properties following application to the soil may thus be more important than the initial surface properties arising from the production technique used.

4.6 Summary

For all feedstocks, biochar yield decreased with increasing HTT. The largest reductions in median yield occurred between HTTs of 350 and 500°C due to weight loss associated with pyrolysis of cellulose (Yang *et al.*, 2007). Further reductions in median yield were smaller for all feedstocks. *Picea* feedstock tended to produce the largest yields, presumably because it had the highest lignin content.

Biochar hydrophobicity was affected by feedstock particle size, but the differences were small and unlikely to influence substantially the overall hydrologic properties of biochar as a soil amendment. The hydrophobicity of stored biochar did not decrease with time since production, demonstrating that hydrophobicity was not reduced by reabsorption of condensed volatiles. For all feedstocks, biochar hydrophobicity was significantly reduced with each increase in HTT (except for *Miscanthus* feedstock between HTTs of 650 and 800°C). Biochar hydrophobicity was not solely attributable to surface chemistry. Contact angles > 120° were recorded on all biochars produced at 350°C, demonstrating that surface topography also contributed to biochar hydrophobicity. Reductions in hydrophobicity with increasing HTT were related to the surface topography of biochar becoming smoother as particles shrank, not just to changes in surface chemistry. The hydrophobicity of different feedstocks responded differently to increases in HTT because of variations in their chemical composition. Contrasts in the chemical composition of feedstocks will also result in different concentrations of alkyl functionalities on biochar surfaces causing differences in hydrophobicity. Furthermore, at different HTTs, certain precursor materials shrink more than others and may become smoother and therefore less hydrophobic. The hydrophobicity of biochar surfaces becomes increasingly heterogeneous as HTT is increased.

Increasing HTT did not have a deleterious effect on biochar CEC. Biochar CEC is predominantly controlled by feedstock rather than HTT. Differences in CEC may have arisen from differences in concentrations of carboxyl groups on the surfaces of biochar particles. Differences in specific surface area resulting in different degrees of oxidation during storage, and differences in ash content between biochars produced from different feedstocks and at different HTTs may also have contributed. If ash content does make a significant contribution to biochar CEC, it is likely to become decreasingly important once biochar is applied to soil and ash is leached out of the biochar.

5 THE EFFECTS OF PYROLYSIS TEMPERATURE ON BIOCHAR SOIL AMENDMENTS

5.1 Introduction

Biochar amendments have been reported to improve soil bulk density (Joseph *et al.*, 2009) and water-holding capacities (Laird *et al.*, 2010b). Laird *et al.* (2010b) found that biochar amendments increased the amount of water retained in fine-loamy sand at -1 and -5 bars of matric potential. Gray *et al.* (2014) reported that biochars produced at low temperatures took up water less effectively than high temperature biochars due to differences in hydrophobicity. Similarly, Lei & Zhang (2013) reported that biochars increased soil water retention most effectively when a high HTT was used.

There are few other data available on the effect that different HTTs have on the influence that biochars have on soil bulk density, water-holding capacity and matric suction. Caused by the attraction of water to solid surfaces resulting from adhesive forces and capillarity, matric suction influences the retention and movement of soil water (Brady & Weil, 2008). Furthermore, there does not appear to be any discussion in the literature of the effect that biochar amendments have on soil osmotic suction, which, combined with matric suction, affects the amount of energy plants must exert to take up water. Osmotic suction is caused by inorganic and organic solutes in the soil solution. As water molecules cluster around solute ions or molecules, the freedom of movement of the water is reduced; osmotic suction therefore increases as solute concentrations increase (Brady & Weil, 2008). Improved understanding of how HTT affects the influence of biochars on soil hydrology may enable identification of certain pyrolysis temperatures that should produce biochars that are more or less effective than others in amending particular soil properties.

In order to address the research gaps, outlined above, the experiments presented in this chapter were primarily carried out to investigate the following research questions:

(i) Whether or not all biochar amendments affect bulk density, water-holding capacity and matric, osmotic and total suction, regardless of the pyrolysis temperature used to produce them

(ii) Whether biochars produced at different HTTs affect these soil properties in different ways and / or to different extents

During the course of experimental work to address the above questions, different effects on fungal growth between treatments were observed and recorded. Improved understanding of how pyrolysis temperature influences the effects of biochar amendments on soil hydrology and biology may enable identification of certain temperatures that are more or less beneficial than others in terms of producing biochars capable of amending particular soil properties in particular ways.

5.2 Methods

5.2.1 Biochar production

The experiments presented in this chapter required large amounts of biochar, which could not be produced within the time and cost constraints of the project using the method presented in Chapter 4. Biochar samples were instead produced at the UK Biochar Research Centre (UKBRC), University of Edinburgh, from softwood pellets in an electrically-heated rotary kiln (Figure 5.1). This kiln was not in commission at the time the experiments presented in Chapter 4 were begun, hence why the experiments presented in Chapter 4 used biochar produced by a different pyrolysis process.

Softwood pellets were delivered from the conical hopper to the kiln heat-tube by a feed screw; the kiln was rated at up to 50 kg h^{-1} dry feed throughput. The tube was heated in three independently controllable zones by radiant electrical elements. Kiln temperature was measured for each zone and at intermediate points between the zones. Material passed along the length of the tube through a rolling motion with forward movement induced by the following feed and a slight downward incline of 3°. Solids were separated from gas and vapour by gravity in a water-jacketed discharge chamber surrounding the downstream end of the heat tube. Solids were conveyed to a product discharge drum by a water-cooled screw. Gases and vapours passed into an afterburner chamber where they were combusted to destroy toxic products (W. Lowe, pers. comm., 2nd July 2012). Biochars were produced using four different HTTs: 400°C, 500°C, 600°C and 700°C (henceforth referred to as 400°C biochar, 500°C biochar *etc.*).

Figure 5.1: Electrically-heated rotary kiln at UKBRC (credit: UKBRC, 2011)

5.2.2 Preparation of soil-biochar mixtures

Each biochar type described above was ground and sieved to obtain a particle size fraction of 0.4 - 1 mm, selected on the assumption that it would be likely to significantly influence bulk density and moisture retention, maximising the possibility of observing differences between biochars produced at different temperatures. It was thought that smaller particles could clog pores whereas larger particles might have too low a specific surface area to significantly influence the soil properties. As the data presented in Chapter 6 demonstrate, the 0.4 - 1 mm particle size fraction did indeed have the strongest influence on soil properties of the particle size fractions investigated in the present study. These data are presented separately for clarity and readability.

The soil used in these experiments was proprietary sandy loam supplied by Boughton (Kettering, Northamptonshire) that was sieved to < 2 mm and air-dried. Particle size-analysis using laser diffraction (Malvern Mastersizer 2000, Malvern Instruments Ltd., UK) showed that the soil comprised 50% sand, 46% silt and 4% clay (n = 20). A sandy loam soil was selected for this investigation because increases in WHC associated with biochar application have often been observed in sandy soils (e.g. Gaskin *et al.*, 2007; Novak *et al.*, 2009; Case *et al.*, 2012; Basso *et al.*, 2013), but are less likely in soils with higher clay content (Tryon, 1948; Dugan *et al.*, 2010). Using a sandy loam soil thus ensured a reasonable likelihood of differences in soil moisture retention being observed due to biochar application.

Biochars were applied to the soil at rates of 50 g kg^{-1} (based on post-production weight) and thoroughly mixed, to mimic biochar being ploughed or disked into topsoil. It should be acknowledged however that alternative methods of application could be used, for example deep-banding, drilling, top-dressing or ecological delivery via animal feed (Blackwell *et al.*, 2009). The findings of previous studies suggest that for many soils, an application rate of at least ~20 g kg^{-1} is needed for biochar to increase soil WHC (Chan *et al.*, 2007; Gaskin *et al.*, 2007; Busscher *et al.*, 2010). An application rate of 50 g kg^{-1} was therefore used to maximise the probability of biochars increasing soil moisture retention, in turn increasing the likelihood of observing differences between the effects of different biochars. A higher application rate was not used because these were considered unlikely to become commercially realistic within foreseeable timescales.

The soil-biochar mixture was poured into a measuring cylinder which was repeatedly tapped on the laboratory bench from a height of < 2 cm, until a 140 ml volume of soil was obtained, with no reduction in volume observed with further tapping. Once the soils were added to 150 ml pots used for the WHC and suction experiments, this volume of soil would leave sufficient head space for water to be added and, in the case of the suction experiments, a filter paper to be suspended over the soil surface using an O-ring. This sample of soil-biochar mixture would then be used to measure bulk density, water-holding capacity or matric suction. Soil without added biochar was used as a control.

5.2.3 Bulk Density Determination

Bulk density of biochars was determined gravimetrically on a dry basis using 25-ml biochar. The biochar poured into a measuring cylinder which was repeatedly tapped on the laboratory bench from a height of < 2 cm, until a 140 ml volume of soil was obtained, with no reduction in volume observed with further tapping. This volume of biochar was then weighed. 5 replicates were carried out for each HTT. Bulk density of soil-biochar mixtures was measured gravimetrically on a dry basis by the same method, using a volume of 140 cm^3 soil (see section 5.2.2). 25 replicates were carried out for each soil or soil-biochar mixture.

5.2.4 Measurement of Water-holding capacity

The water-holding capacities of the soils were measured gravimetrically, using 150 ml clear polypropylene pots (H 68 mm, OD 60mm) with twenty equidistantly spaced 0.5 mm holes in the bottom of the pot covered by 55 mm diameter Whatmann no. 42 filter paper which was slightly wetted to aid adhesion to the bottom of the pot (Figure 5.2). Each pot (including filter paper and lid) was weighed, then 140 ml of soil were added (determined on a tapped basis) and the weight of the pot and its contents was recorded. The lids were then removed and deionized water was slowly added until the pot was saturated. Saturation was ensured by visually checking that the soil was uniformly wetted at all depths and all around the pot, along with the commencement of drainage from the bottom of the pot and water pooling at the surface. The lids were then replaced and the samples left to drain in a constant temperature room at 21°C to eliminate evaporation.

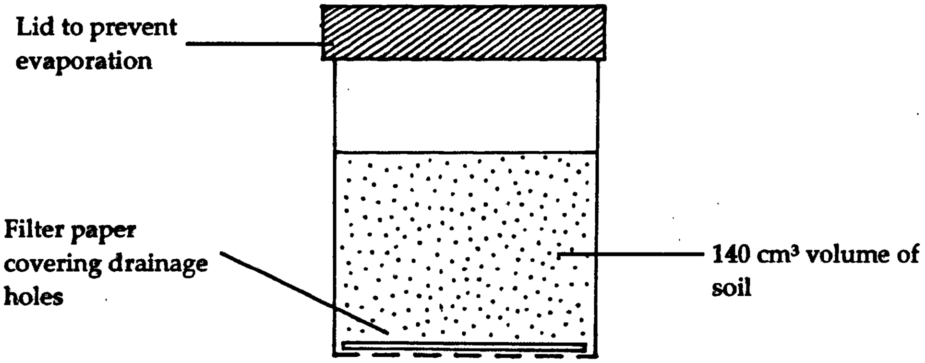


Figure 5.2: Pot measurement of WHC (not to scale)

After 24 hours, the base of each pot was gently dabbed with paper towel to remove water than had drained from the soil but remained on the surface of the pot, then the pots were reweighed. The water-holding capacity of each sample, expressed volumetrically, was calculated as the amount of water retained (grams converted to cm^3) per volume of dry soil (control) or soil-biochar mixture (140 cm^3). Five replicates were carried out for each treatment.

5.2.5 Measurement of suction

Soil suctions were inferred for each soil-biochar mixture using the filter paper method (ASTM, 2010). A 70 ml volume of soil or soil-biochar mixture was put into a 150 ml propylene pot (H 68 mm, OD 60mm) and half of the total amount of water needed to create a total water content of 0.17 cm^3 cm^{-3} was slowly added using a syringe. Using tweezers, a 42.5 mm diameter Whatman no.42 filter paper was placed over the surface of the soil, inserted between two protective Whatman no.42 55 mm diameter filter papers (Figure 5.3). The remaining 70 ml volume of soil or soil-biochar mixture was added to the pot and gently tapped to constant volume, and the remaining water evenly dripped around the surface. A PVC ring support was then positioned on the soil surface, on to which a 42.5 mm filter paper (Whatman no. 42) was placed (Figure 5.3). The pot lid was screwed on immediately, and sealed with PVC tape to ensure that the pot remained airtight. The pot was then placed in an insulated chest resting on a polystyrene block and left to allow moisture equilibration between the soil or soil-biochar mixture and the filter papers.

After 14 days the pot was removed from the insulated container. The top filter paper was then quickly extracted using tweezers, sealed in a pre-weighed weighing tin and immediately weighed using a Sartorius 4-figure balance. The top half of the soil was then removed from the pot to allow the middle filter paper to be extracted and weighed in the same way. With their lids half open, the tins were placed in an oven to dry at 105°C. After 24 hours, the lids were closed and the tins were removed from the oven and placed on a large aluminium block to expedite cooling. Once cooled, the tins were weighed (again using a Sartorius 4-figure balance). This process was completed five times for each treatment.

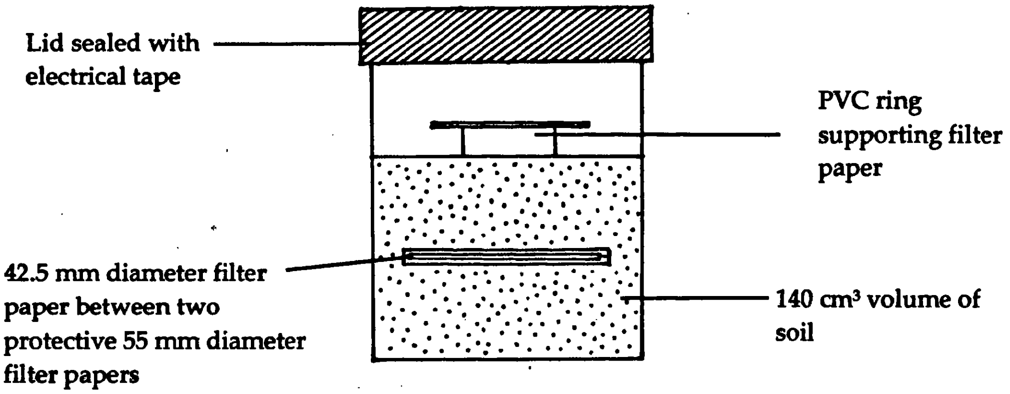


Figure 5.3: Measurement of soil suction using the filter paper method (not to scale)

The working principle of this method is simply that either through vapour flow or liquid flow, the filter papers will come to moisture equilibrium with the soil, such that the suction value of the filter papers and the soil will be the same (Bulut & Wray, 2005). In a sealed container at equilibrium in isothermal conditions, suction in water vapour will be equal to the suction of the soil pore water (Bulut & Wray, 2005). As the evaporation of water molecules is limited by both osmotic and matric suction, the moisture content of the filter paper above the soil surface relates to a total suction value. Osmotic suction does not influence the mass movement of water within soils, so the moisture content of the filter paper from the centre of the soil relates to a matric suction value. From the weight measurements of filter papers it was possible to calculate their water content prior to drying. This moisture content was used to infer total and matric suction values using the ASTM D5298-10 calibration curves for Whatman no. 42 filter papers (ASTM, 2010). Calibration curves have been developed for other filter papers (most notably Scheicher & Schuell no. 589) and their quality is relatively uniform, but Whatman no. 42 filter papers were selected for this investigation as they have been found to have the most consistent suction characteristics (Leong *et al.*, 2002).

Pilot studies identified a water content of 0.17 cm^3 cm^{-3} (~35% of the water-holding capacity of the soil without biochar additions) as an ideal water content to investigate differences between the effects of biochars on soil suction. Using higher water contents, the filter papers tended to become saturated and disintegrate when removed from the soil, while at lower water contents, the filter papers did not become sufficiently wetted for differences in matric suction to be observed, probably due to rapid evaporation of moisture from the filter papers as they were transferred from the soil pots to weighing tins. A moistened filter paper can lose 5% or more of its mass by evaporation during 5 to 10 seconds of exposure in a room with a relative humidity of 30% to 50% (ASTM, 2010).

5.2.6 Fungal growth

When the filter papers were removed from pots following 14 days incubation, the surfaces of the soils were visually checked for the presence of fungal growth. Where fungal growth was observed without magnification, samples were set aside for viewing with a stereomicroscope.

5.2.7 Statistical Analyses

For each factor investigated, the effect of each biochar amendment was individually compared to the control soil (to which no biochar was added) using a Bonferroni-adjusted Mann-Whitney U-test (Mann & Whitney, 1947; Dunn, 1961). Overall differences between biochars were analysed using the Kruskal-Wallis test (Kruskal & Wallis, 1952). Mann-Whitney U-tests were used for *post hoc* pairwise comparisons in which significance values were subjected to Bonferroni adjustment to eliminate family-wise Error (Mann & Whitney, 1947; Dunn, 1961). All statistical analyses were completed using SPSS (v. 19, IBM, USA). A 95% confidence level was adopted for all tests; differences were considered to be statistically significant where $p \leq 0.05$.

5.3 Results

5.3.1 Bulk density

5.3.1.1 Bulk density of biochar amendments

Figure 5.4 illustrates the effect of HTT on biochar bulk density. There were significant differences between the bulk densities of biochars produced at different HTTs ($H(3) = 17.07$, $p < 0.001$). Biochar bulk density was significantly increased (by 16%) as HTT was increased from 400°C to 500°C (Table 5.1). Increasing HTT to 600°C reduced biochar bulk density to be significantly less than that of the 400°C biochar, but there was no further effect on biochar bulk density when HTT was increased to 700°C (Table 5.1)

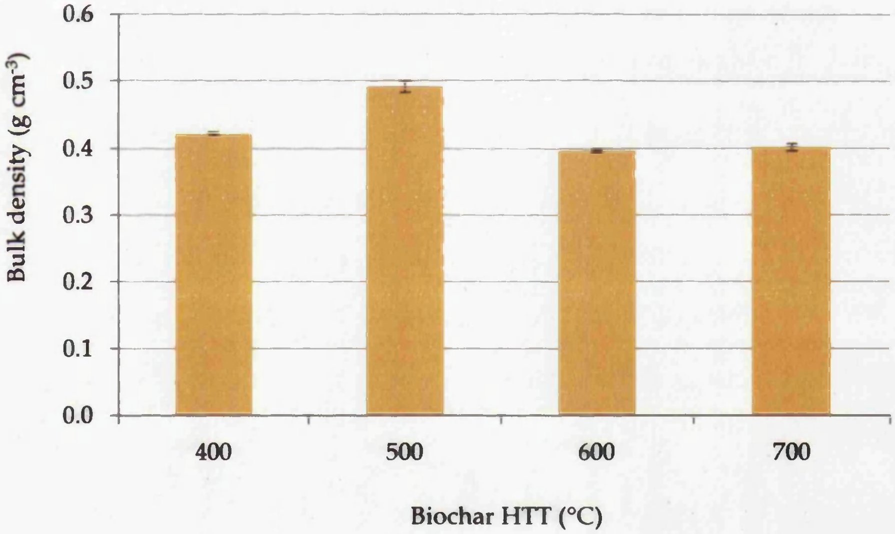


Figure 5.4: The effect of different HTTs on biochar bulk density (Error bars represent 95% CIs, n = 5)

Table 5.1: Tests for differences between bulk densities of biochars produced at different HTTs (p is 2-tailed and Bonferroni-adjusted)

HTTs of biochar additions compared (°C)	Mann-Whitney	
	U	*p*
400 vs. 500	0.0	0.024
600 vs .700	3.5	0.237
400 vs. 600 and 700	0.0	0.003

5.3.1.2 Bulk density of biochar-amended soils

Figure 5.5 shows the effect that biochars producing using different HTTs had on the bulk density of a sandy loam. Each type of biochar addition resulted in a statistically significant reduction in bulk density (Table 5.2). There were significant differences between biochars produced using different HTTs in terms of their effects on bulk density ($H(3) = 18.68, p < 0.001$). Biochars produced at 400 and 500°C reduced the bulk density of the sandy loam by 5 and 6% respectively, but were not statistically different from each other (Table 5.3). The bulk density of the soil was reduced the most by the biochars pyrolysed using HTTs of 600 or 700°C, which both reduced the soil's bulk density by ~8%; the effects of these two biochars were statistically similar to each other, but significantly different from biochars produced at 400 and 500°C (Table 5.3).

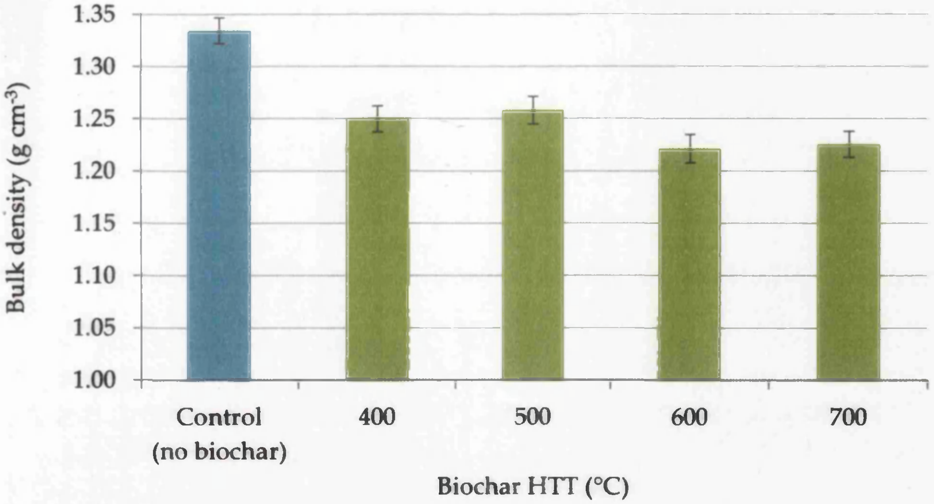


Figure 5.5: The effect of biochars produced using different HTTs on the bulk density of a sandy loam (Error bars represent 95% CIs, n = 25)

Table 5.2: Tests for differences between bulk densities of soils with biochar additions compared to soil without biochar (p is 1-tailed and Bonferroni-adjusted)

HTT of biochar addition (°C)	Mann-Whitney	
	U	*p*
400	21.0	< 0.001
500	36.0	< 0.001
600	5.0	< 0.001
700	3.0	< 0.001

Table 5.3: Tests for differences between bulk densities of soils with biochar additions produced using different HTTs (p is 2-tailed and Bonferroni-adjusted)

HTTs of biochar additions compared (°C)	Mann-Whitney	
	U	*p*
400 vs. 500	271.5	1.000
600 vs. 700	295.5	1.000
400 and 500 vs. 600 and 700	633.0	< 0.001

5.3.2 Water-holding capacity

Figure 5.6 illustrates how biochars produced using different pyrolysis temperatures affected the WHC of a sandy loam. Only biochar produced at 500°C significantly affected the soil's WHC (Table 5.4), increasing it by 11.6%. There were significant differences between the effects of different biochar additions on the soil's water-holding capacity ($H(3) = 11.71$, $p < 0.001$). The mean WHCs of soils amended with 400 and 500°C biochars were significantly higher (7% and 16% respectively) than that of soil amended with 700°C biochar (Table 5.5). However, the WHC of soil containing 400°C did not significantly differ from the WHCs of soils containing 500 or 600°C biochars, and the WHC of soil containing 600°C biochar was not significantly different for the WHCs of any of the other soils (Table 5.5).

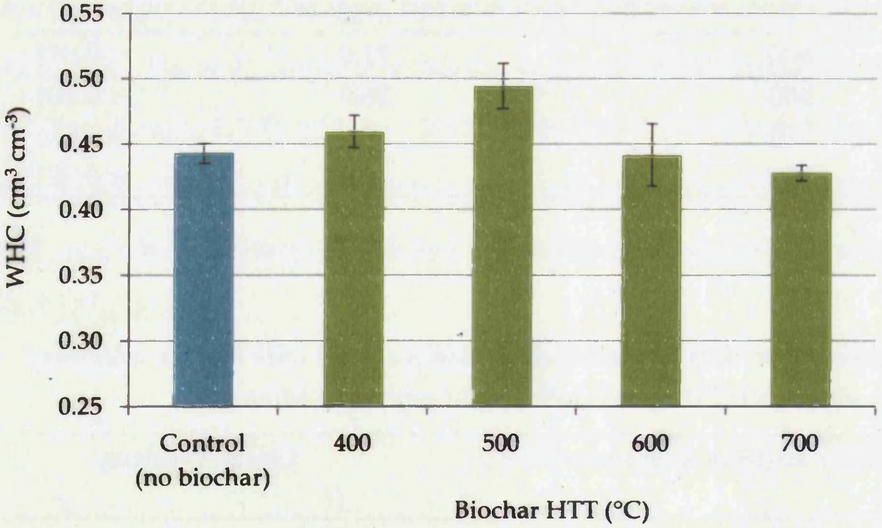


Figure 5.6: The effect of biochars produced using different HTTs on soil water-holding capacity (Error bars represent 95% CIs, n = 5)

Table 5.4: Tests for differences between WHCs of soils with biochar additions compared to soil without biochar (p is 1-tailed and Bonferroni-adjusted)

HTT of biochar addition (°C)	Mann-Whitney	
	U	*p*
400	4.0	0.192
500	0.0	0.016
600	10.0	1.000
700	3.0	0.112

Table 5.5: Tests for differences between WHCs of soils with biochar additions produced at differing HTTs (p is 2-tailed and Bonferroni-adjusted)

HTT of biochar additions in soils being compared (°C)	Mann-Whitney	
	U	*p*
400 vs. 500	2.0	0.192
400 vs. 600	8.0	1.000
400 vs. 700	0.0	0.048
500 vs. 600	2.0	0.192
500 vs. 700	0.0	0.048
600 vs. 700	11.0	1.000

5.3.3 Total suction

As Figure 5.7 illustrates, the peak temperature at which biochars were produced had a significant influence on the extent to which they affected total soil suction. Biochar produced using a HTT of 500°C was the only amendment which significantly affected total soil suction (Table 5.6), increasing it by almost 100%.

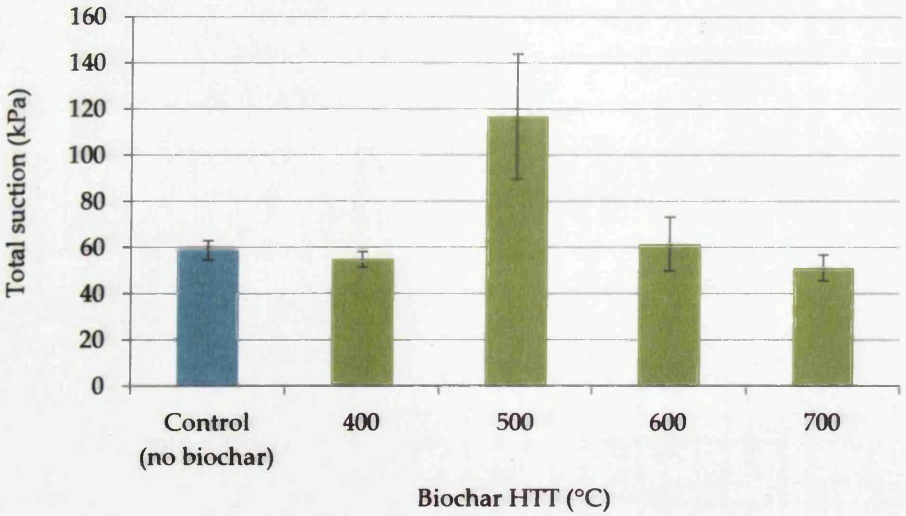


Figure 5.7: The effect of biochar amendments produced using different HTTs on total suction (Error bars represent 95% CIs, n = 5)

Table 5.6: Tests for differences in total suction of soils with biochar additions compared to soil without biochar (p is 1-tailed and Bonferroni-adjusted)

HTT of biochar addition (°C)	Mann-Whitney	
	U	*p*
400	4.0	0.192
500	0.0	0.016
600	12.0	1.000
700	3.0	0.112

5.3.4 Matric suction

Each biochar addition resulted in significantly higher soil matric suction (Table 5.7). Statistically significant differences were observed between the matric suctions of soils with different biochar additions ($H(3) = 13.4$, $p < 0.001$). Biochar produced using a HTT of 400°C had a significantly lesser effect on matric suction than any of the other biochars (Table 5.8), but nonetheless increased matric suction by over one-third. Biochar produced using a HTT of 500°C had a significantly larger effect than any of the other biochars (Table 5.8), almost tripling the matric suction of the soil (Figure 5.8). Biochar amendments produced using HTTs of 600°C and 700°C increased matric suction by 137% and 95% respectively, but there was no statistically significant difference between them (Table 5.8).

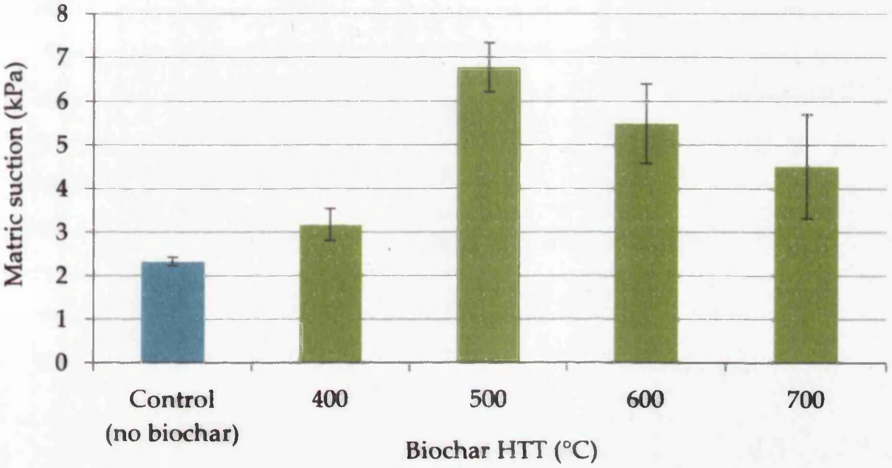


Figure 5.8: The effect of biochars amendments produced using different HTTs on matric suction (Error bars represent 95% CIs, n = 5)

Table 5.7: Tests for differences between matric suction of soils with biochar additions compared to soil without biochar (p is 1-tailed and Bonferroni-adjusted)

HTT of biochar addition (°C)	Mann-Whitney	
	U	*p*
400	0.0	0.016
500	0.0	0.016
600	0.0	0.016
700	0.0	0.016

Table 5.8: Tests for differences between matric suctions of soils with biochar additions produced at differing HTTs (p is 1-tailed and Bonferroni-adjusted)

HTT of biochar additions in soils being compared (°C)	Mann-Whitney	
	U	*p*
400 vs. 500	0.0	0.016
600 vs. 700	6.0	0.444
500 vs. 600 and 700	6.0	0.039
400 vs. 600 and 700	2.0	0.005

5.3.5 Fungal growth

Prolific fungal mycelia were observed without magnification on the surfaces of soils containing 500°C biochar following the 14 days of equilibration carried out for the suction experiments (Figure 5.10). However, none was seen on the surfaces of soils containing 400°C, 600°C or 700°C biochars.

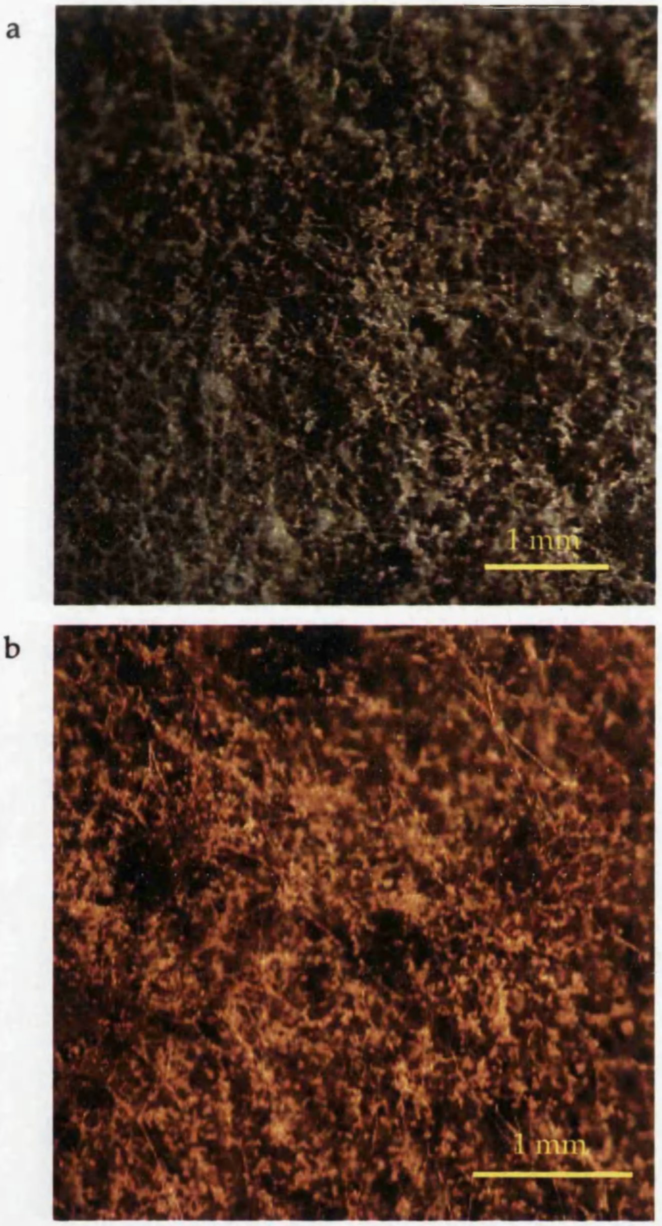


Figure 5.9: Fungal mycelia on the surface of soil amended with 500°C biochar

5.4 Discussion

The high bulk density of 500°C biochar may be related to the condensates present on the surface of the biochar particles produced at this temperature. These condensates could have filled biochar pores (Muradov *et al.*, 2012) and / or enabled tighter packing of particles by lubrication. The low bulk densities of biochars produced at 600 and 700°C can be attributed to pore widening and coalescence with increasing HTT (Angin, 2013). The variation in bulk density with increasing temperature is in contrast with the findings of Rajkovich *et al.* (2012), who concluded that biochar bulk density was not affected by HTT. Comparison of the bulk densities of the biochars themselves and the effect they had on the bulk density of a sandy loam demonstrates that differences in the bulk densities of biochars are not necessarily indicative of the effect they will have on the bulk density of a soil, because the packing arrangement of a mass of biochar particles is unrelated to the packing arrangement of a mass of soil containing disperse biochar particles. 500°C biochar had a much higher bulk density than that of 400°C biochar, but their effect on the bulk density of the soil was the same (presumably because the effect of condensates on the surface of 500°C biochar particles became less important once the biochar was interspersed between soil particles). However, biochars produced at 600 and 700°C had both the lowest bulk densities and the greatest effect of decreasing the bulk density of the soil.

The high water-holding capacity of soils amended with 500°C biochar corresponds to the work of Kinney *et al.* (2012) who found that the WHCs of biochars produced from corn stover (*Zea mays*) and apple wood (*Malus* *domestica*) were highest when a HTT of 500°C was used. However, the results of the present study contrast somewhat with those of Lei & Zhang (2013) who found that the effect of biochar on soil moisture retention was greatest when an HTT of 700°C was used. The present investigation demonstrates that the effect that biochar amendments have on soil bulk density are not necessarily indicative of the effect they will have on soil water-holding capacity. For example, the bulk density of soil containing 700°C biochar was lower than that of soil containing 500°C biochar, but the WHC and matric suction of soils with 500°C biochar were higher.

If changes in hydrophobicity with increasing pyrolysis temperature for softwood pellets were similar to those observed for *Picea sitchensis* (see Chapter 4), then there would have been a dramatic decrease in hydrophobic sites on the surface of biochar between HTTs of 400°C and 500°C, with less substantial decreases thereafter (see section 4.3.2.1), meaning that factors other than hydrophobicity became more important. Gray *et al.* (2014) reported that differences in hydrophobicity were more important than differences in porosity in determining how the WHC of columns of biochars produced at different HTTs (370 to 620°C). Contrastingly, in the present study, soil WHC was not increased by the increasing HTT of the biochar amendments, except between 400 and 500°C, which was not a statistically significant difference anyway. This suggests that once biochar is applied to the soil, the importance of biochar hydrophobicity in determining water uptake is diminished. A possible explanation for this is that saturation of the soil surrounding biochar particles eventually causes reorientation of amphiphilic molecules on the surface of biochar particles (Doerr *et al.*, 2000), rendering them wettable. If this is indeed the case, different application methods could result in greater differences between biochars produced at different HTTs than were observed in the present study, where biochar was thoroughly mixed with the soil. Applying biochar by top-dressing, deep-banding or drilling would not result in thorough mixing of biochar with the soil, they would instead result in horizontal or vertical layering of biochar above or within the soil profile. Hydrophobic biochar would therefore not be rendered wettable by saturation of surrounding soil, except at biochar layer margins. This would result in hydrophilic biochars produced at higher HTTs increasing WHC to a much greater extent than hydrophobic biochars produced at lower HTTs.

All the biochar amendments resulted in significant increases in matric suction. This can be attributed to the porosity of biochars increasing the soil surface area, as matric suction arises from the adhesive force of water being attracted to solid surfaces (Brady & Weil, 2008). Higher WHC and matric suction in soils amended with 500°C biochar compared to soils amended with 400°C biochar may be related to an increase in biochar porosity between HTTs of 400 and 500°C (Lua *et al.*, 2004; Lehmann, 2007a; Chen *et al.*, 2008; Angin, 2013). Biochar particles produced at 600 and 700°C were less dense than biochar particles produced at 500°C. Interestingly, although soil amended with 600°C biochar had a significantly lower bulk density than soils amended with 400 or 500°C biochars, measurements of WHC and matric suction in soils with 600°C biochar were not significantly different from those recorded for soils with 400 or 500°C biochars. However, despite having lower bulk density, soil amended with 700°C had lower WHC and matric suction than soil amended with 500°C biochar. There are several possible explanations for this. Relative to 500°C biochar, 700°C biochar may have directly or indirectly increased the average pore size of the soil (due to the biochar having larger pores or somehow limiting tight packing of soil particles), resulting in increased hydraulic conductivity (and consequently lower WHC) and reduced matric suction. An alternative explanation is that less of the pore space within 700°C biochar was interconnected or accessible to water, because some of the pore spaces were sealed-off by intermediate melts at HTTs >500°C (Lua *et al.*, 2004; Angin, 2013). A further possibility is that some pores of < 2 nm diameter may have widened and / or coalesced at HTTs beyond 500°C (Zhang *et al.*, 2004; Fu *et al.*, 2011), increasing the chance of internal pore volume being sealed off by clay-sized mineral particles clogging outer pores. However, pores with diameters in the range of 2 - 50 nm may be too small to significantly influence the hydrological properties of biochar anyway (Nomo, 2004; Sohi *et al.*, 2010; Kinney *et al.*, 2012).

Differences in surface charge arising from different HTTs may also have contributed to the effects of biochars had on soil moisture retention. Water molecules are polar and can be attracted to negatively charged surfaces by the hydrogen (positive) end of the molecules (Brady & Weil, 2008). The results presented in Chapter 4 suggest that biochar particles produced at 500°C could have had more negative charges on their surfaces than biochar particles produced at 400°C, which could have contributed to the former increasing soil WHC to a greater extent than the latter. If the effect of HTT on the surface charge of *Picea* biochars (see section 4.3.3) applies to softwood pellet biochars, then surface charges of biochars produced from softwood pellets at 500, 600 and 700°C would have been similar. Surface charge would therefore not have contributed to any differences in the effects of these biochars on soil WHC.

Biochars produced at 600 or 700°C had less effect on WHC and matric suction than biochar produced at 500°C, which has implications for their effects on nutrient leaching. In sandy soils, biochar particles may act similarly to clay, holding large volumes of immobile water near the soil surface even at high matric potentials. While this could increase the amount of water available to plants, it would also increase the amount of dissolved nutrients retained near the soil surface, accessible to plants (Major *et al.*, 2009). The findings of this investigation, however, suggest that not all biochar porosity is necessarily functional once biochar is applied to the soil.

A further factor that would have contributed at least in part to the effects that different biochars had on matric suction was the growth of fungi visible at the surface of soils amended with 500°C biochar after 14 days incubation. Although this is to some extent a cofounding factor in interpreting the data pertaining to the effect of different HTT biochars on matric suction, the matric suction data correspond well to the WHC measurements, suggesting that the influence of fungal growth on matric suction was minimal compared to the effect of the biochar itself. In experiments investigating the effect of biochars (produced at 500°C) of different particle size on matric suction (see Chapter 6), substantially less fungal growth was observed on the surfaces of soils amended with 2 - 3 and 4 - 5 mm biochars compared to those amended with < 0.2 and 4 - 5 mm diameter biochars, presumably because there was less substrate surface area available. However, there were no significant differences between the effects of biochars of different particle size on matric suction, again indicating that the effect of fungal growth on matric suction was minimal.

Although all biochar amendments significantly increased matric suction, only 500°C biochar significantly increased total suction. This suggests that the effect of biochar amendments increasing matric suction and, therefore, increasing the amount of energy plants must expend to take up water, can be counteracted by the effect of biochar amendments 'displacing' the native soil, reducing solute concentrations and, therefore, reducing osmotic suction. Alternatively, it is possible that biochars sorbed solutes from the soil solution (Thomas *et al.*, 2013). For soils with low osmotic potential, the effect of biochar on matric potential will have a greater influence on plants' ability to take up water. The present results indicate that biochars produced at 400, 600 and 700°C can significantly increase soil WHC without significantly affecting the amount of energy plants must expend to access water. However, it must be acknowledged that further research is necessary to verify whether this is indeed the case over the entire soil moisture release curve.

The increase in total suction resulting from 500°C biochar amendments indicates that this biochar introduced substantially more solutes to the soil than other biochars did. At pyrolysis temperatures between 300 and 600°C, tar and liquid forming processes become increasingly important, while at temperatures over 600°C, tar and liquid formation is minimal, with gas formation dominating instead (Amonette & Joseph, 2009). As such, the biochar produced at 500°C is likely to have held a greater volume of tars and / or other liquids than the biochars produced at 400, 600 and 700°C. Visual observations confirmed that this was indeed the case. It is likely that the liquids associated with 500°C biochar were responsible for increasing osmotic suction and therefore total suction.

The inferred effect of the 500°C biochar on osmotic suction has implications for its potential use as an agronomic amendment, as the findings of this investigation suggest it could increase plant moisture stress, at least immediately after application. Further research is needed to evaluate the lengths of time over which this effect would persist, as it is likely that it will decline significantly as the solutes are leached from the soil. Higher osmotic suction will reduce moisture availability because more water is held in the soil at the permanent wilting coefficient than would be retained by matric suction alone (Brady & Weil, 2008). Plants are most susceptible to elevated osmotic suction in early stages of growth; high solute concentrations may delay or even prevent seed germination or kill young seedlings (Brady & Weil, 2002). For established plants, although increased osmotic suction can result in reduced growth and yield as the amount of energy they must expend to accumulate solutes in order to obtain water by osmosis is increased (Taylor, 1952; Kirkham, 2005), it rarely results in wilting or reduced water intake (Brady & Weil, 2008). In trials co-ordinated by Carbon Gold Ltd. (Bristol), several growers observed poor seedling emergence in biochar-amended soils and composts, but established plants outperformed those in soils or composts without biochar additions (B. Raskin, pers. comm., June 2012). These effects could have resulted in part from biochar additions increasing the osmotic suction of soils which would have been particularly important in the early stages of plant growth, but less important once plants had become established (at which point the effects of biochar amendments on other soil properties became more important), or once the solutes associated with biochar amendments had been leached from the soil.

The dense hyphal branching seen on the surface of soils amended with 500°C biochar (Figure 5.10) suggests that 500°C biochar amendments introduced a nutritionally rich substrate for the fungi; the extent of hyphal branching is directly related to the concentration of nutrients in the substrate (O'Toole, 2006). Biochar is highly recalcitrant, and recalcitrance tends to increase with increasing HTT (Zhao *et al.*, 2013) so it is unlikely that differences in fungal growth observed over 14 days between soils amended with biochars produced at different HTTs resulted from differences between the biochar solids themselves (Thies & Rillig, 2009). In the short-term at least, residual bio-oils on biochar particles are likely to be the only substrates available to support fungal growth and metabolism (Thies & Rillig, 2009). From visual observations of the biochars used in this study, it was evident that biochar produced at 500°C was much richer in condensates than the others. This corresponds to the finding that 500°C biochar amendments resulted in substantial increases in osmotic suction, meaning that this biochar amendment carried high concentrations of solutes.

Under pyrolysis conditions, lignin decomposition begins at 280°C and continues up to 500°C, a product of which is condensable vapours and liquid aerosols that are recovered as pyroligneous acid and insoluble tar condensates (Mohan *et al.*, 2006). Pyroligneous acid condensate is typically high in acetic acid, formic acid, methanol and aldehydes (Steiner *et al.*, 2008). With high concentrations of pyroligneous acid, some aldehydes and acids can serve as biocides (Steiner *et al.*, 2008). However, at lower concentrations the alcohols, acids and aldehydes contained in pyroligneous acid can serve as carbon and energy substrates for soil microorganisms (Tye & Willetts, 1976; Steiner *et al.*, 2008). An alternative explanation is that 500°C biochar amendments introduced solutes that had a toxic effect on grazers of fungi (Thies & Rillig, 2009). Biochar pH tends to increase with increasing temperature (Novak *et al.*, 2009; Hossain *et al.*, 2011; Yuan *et al.*, 2011) and is thus unlikely to have contributed to the unique effect of 500°C biochar on fungal growth compared to biochars produced using other HTTs.

Fungal hyphae exude polysaccharides and other organic compounds, forming sticky webs that bind soil particles together (Brady & Weil, 2008). There was evidence of fungal hyphae enmeshing soil particles together at the surface of soils amended with 500°C biochar (Figure 5.10b). This biochar could therefore be a useful amendment for promoting soil aggregation in sandy soils. Fungal growth could also lead to increased soil hydrophobicity. Indeed, Abel *et al.* (2013) observed increased local hydrophobicity in soil amended with hydrochar due to fungal colonisation of the char (hydrochar is similar to biochar, but produced in a pressurised aqueous solution at lower temperatures). Consequently, although HTT directly affects biochar wettability through its influence on surface chemistry and topography (see Chapter 4) the influence of HTT on the extent to which biochars provide fungal substrates may also affect biochar and soil wettability.

Further research is necessary to determine the persistence of the effect of 500°C biochar on fungal growth. It is probable that the organisms colonising fresh biochar particles with post-pyrolysis condensates on their surfaces will differ considerably from those colonizing the biochar once the condensates have been metabolized (Thies & Rillig, 2009). At meso- and macro-aggregate level, fungal filaments and metabolic products act as binding agents (Thies & Rillig, 2009). Therefore, where condensates promote fungal growth, the hydrophobicity of the biochar itself could be less important in controlling the rates at which it is eroded from the soil, as fungi can help to stabilize biochar in the soil matrix and within soil aggregates. However, it should also be noted that fungal colonisation of biochar-amended soils can render them extremely hydrophobic, regardless of whether the biochar itself is hydrophobic (Abel *et al.*, 2013).

It should be remembered, however, that the biochar application rate used in this study was high (50 g kg^{-1}). Differences observed between biochars produced at different temperatures may be less significant at lower, currently more commercially realistic application rates.

5.5 Limitations

In absolute terms, the accuracy of the inferred matric suction values reported in section 5.3.4 is doubtful. Matric suction accounts for the majority of total suction in most soils (Yerima & Van Ranst, 2005). Conversely, the values reported in section 5.3.4 suggest that osmotic suction was 1 - 2 orders of magnitude greater than matric suction for all treatments. For example, in soil containing 600°C biochar, the mean inferred matric suction was 5.58 kPa, whereas the mean total suction (matric and osmotic suction combined) was 64.38 kPa. The inferred osmotic suction, calculated by subtracting matric suction from total suction, would therefore be 58.80 kPa; 10 times greater than matric suction. Osmotic suction can substantial in saline soils, but the mean electrical conductivity of the soil used in this study was 35.9 μS cm^{-1}, meaning that it contained less than 1% of the salinity necessary for it to be considered a saline soil (Brady & Weil, 2008). It is therefore probable that the matric suction values produced in the experiment were subject to an experimental error.

The most likely explanation for this is the filter papers placed in the middle of the soil (for inference of matric suction) were disproportionately wet and therefore not at moisture equilibrium with the surrounding soil. As described in section 5.2.5, the soil incubation pots were prepared as follows: half the soil was put in the pot, then half of the water added, then the filter papers, then the rest of the soil, then the second portion of water. The problem with this approach is that the filter paper in the middle of the soil would have absorbed a lot of moisture as the second portion of soil was poured in, forcing the filter paper into close contact with the very wet soil immediately beneath it. During the incubation period however, there was less force pushing the filter paper into the soil beneath because the top layer of soil was resting on the filter paper rather than falling onto it, so there was less force pushing the soil and filter paper together. The moisture content of the filter paper therefore began to approach, but did not reach, equilibrium with the surrounding soil within the 14 day incubation period. This could have been avoided had the first half of the water been added to the pot before or halfway through the first portion of soil being added.

In any case, it must be concluded that the matric suction values presented in section 5.3.4 cannot be accepted as absolute measures of matric suction. Moreover, osmotic suction cannot be calculated by subtracting the matric suction values presented in section 5.3.4 from the total suction values presented in section 5.3.3. The data are nonetheless useful for evaluating the relative differences in suction between treatments, because the same method was used for all treatments and many of the differences between treatments are statistically significant, therefore they cannot be due to chance. Accordingly, it is reasonable to assume that where relative differences in total suction values between treatments did not reflect relative differences in matric suction values between treatments, it was because differences in matric suction were counteracted by differences in osmotic suction.

Ideally, the biochars used for the experiments presented in this chapter would have been produced by the same method as described in Chapter 4, but this was not possible due to the budget and time limitations of the project however, this was not possible. It is not certain that the changes in biochar surface hydrophobicity and charge observed with increasing pyrolysis temperature using the pyrolysis process described in Chapter 4 also apply to the pyrolysis process described at the beginning of this chapter. Interpreting the results of the presented in this chapter in the light of the findings of the experiments presented in Chapter 4 is therefore problematic. Biochar hydrophobicity was not measured, so the precise effect that differences in hydrophobicity between biochars produced at different temperatures had on the moisture retention of different soil-biochar mixtures is unclear.

The present study used sieved, repacked soils. The structures, pore architectures, aggregates and inter-aggregate pore size distributions of the soils were therefore artefacts of the sieving, mixing and repacking process, and do not necessarily resemble the properties of soils amended with biochar *in-situ*, where the direct effects of biochar on moisture retention will be complicated by indirect effects through the influence of biochar on soil aggregation and aggregate stability. Moreover, in field situations, the effect of biochar on soil properties will be complicated by its effects on above- and below-ground biota.

The biochar application rates used in this study were very high and not currently commercially realistic for broadacre agriculture. Differences between the effects of biochars produced at different pyrolysis temperatures observed in the present study may not be observed when lower application rates are used. Moreover, differences between biochars may be less important in soils where biochar application has little or no effect on moisture retention because the soil has high clay or organic matter content. Furthermore, differences between the effects of biochars produced at different pyrolysis temperatures may be different where different biochar particle size fractions are used; differences in moisture retention arising from differences in biochar pore connectivity could be augmented where larger biochar particles are used, or reduced where smaller particles are used. Also, in this study, biochar was mixed with soil to mimic ploughing, but it should be acknowledged that alternative methods of application could be used, for example deep-banding, drilling, top-dressing or ecological delivery via animal feed (Blackwell *et al.*, 2009), which could result in biochar having different effects.

Finally, the differences in matric and total suction reported in this study represent only one soil moisture content. Further research is needed to determine whether and to what extent the differences observed apply across the whole moisture release curve.

5.6 Summary

Biochar amendments significantly reduced soil bulk density, but the extent to which they did so differed according to the temperature at which they were produced; the effect of biochars produced at higher temperatures in reducing bulk density was larger than the effect of those produced at lower temperatures.

All biochar amendments resulted in reduced soil bulk density, but this effect was greater for biochars produced at HTTs of 600 and 700°C than for those produced at 400 and 500°C. Only 500°C biochar significantly increased the soil's WHC, but all biochars increased matric suction (at a water content of 0.17 cm^3 cm^{-3}). For both of these properties, the mean effect of amendments increased as biochar HTT increased from 400°C to 500°C, then decreased with subsequent increases in HTT up to 700°C. These effects may be related to an increase in biochar porosity between HTTs of 400°C and 500°C and widening of soil or biochar pores, or reduction in pore interconnectivity and/or accessibility with further increases in HTT.

In terms of the energy plants would have to expend to access water, the effect of biochars produced at 400°C, 600°C and 700°C increasing matric suction appears to be counteracted by their effect osmotic suction, which can be attributed to these biochars displacing native soil, reducing solute concentrations. Biochar produced at 500°C significantly augmented total suction as it significantly increased both matric and osmotic suction. The increase in osmotic suction in soils amended with 500°C biochar is probably related to the higher production of tars and other liquids when an HTT of

500°C is used. The findings of this study suggest that 500°C biochar could - at least initially - increase plant moisture stress, particularly for seedlings.

Prolific fungal growth observed in soils amended with 500°C biochar can be attributed to condensates on the surface of the biochar which provided a carbon and energy substrate.

6 THE EFFECTS OF BIOCHAR SOIL AMENDMENT PARTICLE SIZE

6.1 Introduction

Biochar amendments have been reported to reduce bulk density (Joseph *et al.*, 2009) and increase water-holding capacity (Laird *et al.*, 2010b) in certain soils. Laird *et al.* (2010b) found that biochar amendments increased the amount of water retained in a fine-loamy soil at -1 and -5 bars of matric potential. However, there is no discussion in the literature of how biochar particle size influences the biochars have on soil bulk density, water-holding capacity and matric suction.

Lehmann *et al.* (2003) concluded that using different sized biochar particles (1 mm and 20 mm diameter) had only minor effects on nutrient uptake and biomass production of Cowpea (*Vigna unguiculata*). It was argued by Joseph *et al.* (2009) that inclusion of particle size in a biochar classification system was unnecessary, though particle size has subsequently been included in the classification system of the International Biochar Initiative (2013). It has been speculated that smaller particles may increase the influence of biochar soil amendments due to greater contact area, but Joseph *et al.* (2009) argued that the high porosity of biochar particles may make particle size irrelevant. Soil hydrology may be influenced by the smallest particle size fractions of biochar blocking pores. However, as Verheijen *et al.* (2010) noted, empirical studies of such effects are scarce and further research to evaluate the implications of differing biochar particle sizes on soil processes and functioning is needed.

Using biochars of four different particle sizes to amend a sandy loam soil, this part of the study aims to address these research gaps by testing whether biochars of different particle size affect bulk density, water-holding capacity and total, matric and osmotic suction in different ways and / or to different extents. Improved understanding of how particle size affects the influence of biochars on soil hydrology may enable identification of certain particle sizes that are more or less beneficial than others in terms of amending a particular soil property. Greater knowledge of the influence of biochar particle size on soil hydrology will also aid understanding of how the effects of biochar amendments may change as they are physically broken down in the soil.

6.2 Methods

Biochar was produced at UKBRC (see 5.2.1) from softwood pellets using a HTT of 500°C. This HTT was selected because biochar produced at this temperature was found to have the greatest influence on soil moisture retention (see Chapter 5). The biochar pellets were ground and sieved to obtain four different particle size fractions: < 0.2, 0.4 - 1, 2 - 3 and 4 - 5 mm to ensure that all the biochar particles within each fraction were at least half or double the size of any particles within other fractions, increasing the likelihood of differences being observed. Biochars were applied to the sandy loam soil described in Chapter 5 (50% sand, 46% silt, 4% clay) at a rate of 50 g kg^{-1}. A sandy loam soil was selected for this investigation because increases in WHC associated with biochar application have often been observed in sandy soils (e.g. Gaskin *et al.*, 2007; Novak *et al.*, 2009; Case *et al.*, 2012; Basso *et al.*, 2013), but are less likely in soils with higher clay content (Tryon, 1948;

Dugan *et al.*, 2010). Using a sandy loam soil thus ensured a reasonable likelihood of differences in soil moisture retention being observed due to biochar application. Biochars were applied to the soil at rates of 50 g kg^{-1} (based on post-production weight) and thoroughly mixed, to mimic biochar being ploughed or disked into topsoil. It is however acknowledged that alternative methods of application could be used, for example deep-banding, drilling, top-dressing or ecological delivery via animal feed (Blackwell *et al.*, 2009). The findings of previous studies suggest that for many soils, an application rate of at least ~20 g kg^{-1} is needed for biochar to increase soil WHC (Chan *et al.*, 2007; Gaskin *et al.*, 2007; Busscher *et al.*, 2010). An application rate of 50 g kg^{-1} was therefore used to maximise the probability of biochars increasing soil moisture retention, in turn increasing the likelihood of observing differences between the effects of different biochars. A higher application rate was not used because these were considered unlikely to become commercially realistic within foreseeable timescales.

The methods used in this chapter were the same as those specified in Chapter 5; the results are presented separately to aid clarity and readability. Bulk density was assessed by weighing 140 ml volumes of dry soil-biochar mixtures, WHC was measured gravimetrically and suction was investigated using the filter paper method. For bulk density measurements, 25 replicates were made for the control (no biochar) treatment and the 0.4 - 1 mm biochar amendment, while 10 replicates were carried out for soils with biochar amendments having particle sizes of < 0.2, 2 - 3 and 4 - 5 mm. Non-parametric statistical tests were used to analyse this data to ensure the unbalanced design did not influence findings.

6.3 Results

6.3.1 Bulk Density

Each particle size of biochar resulted in a statistically significant reduction in soil bulk density (Table 6.1). A Kruskal-Wallis test indicated that there were significant differences between the effects of different sized biochars on bulk density ($H(3) = 20.26$, $p < 0.001$). Applying biochar with a particle size of <0.2 mm to the soil had the greatest effect, reducing the mean bulk density from 1.33 to 1.23 g cm^{-3}. This was a significantly lower bulk density than those of the soils amended with biochars of larger particle sizes (Table 6.2). Applying the largest biochar particle size (4 - 5 mm) had the least effect on the soil's bulk density, resulting in a mean bulk density of 1.28 g cm^{-3}. This was ~4% lower than the bulk density of the control soil, but significantly higher than the bulk densities resulting from using any of the other particle sizes (Table 6.2). Biochars with particle sizes of 0.4 - 1 and 2 - 3 mm reduced the soil bulk density by ~5 and ~7% respectively; these effects were not significantly different from each other (Table 6.2).

Table 6.1: Tests for differences between bulk densities of soils with biochar additions compared to soil without biochar (p is 1-tailed and Bonferroni-adjusted)

Biochar particle size (mm)	Mann-Whitney	
	U	*p*
< 0.2	0.0	< 0.001
0.4 - 1	36.0	< 0.001
2 - 3	55.0	< 0.001
4 - 5	14.0	< 0.001

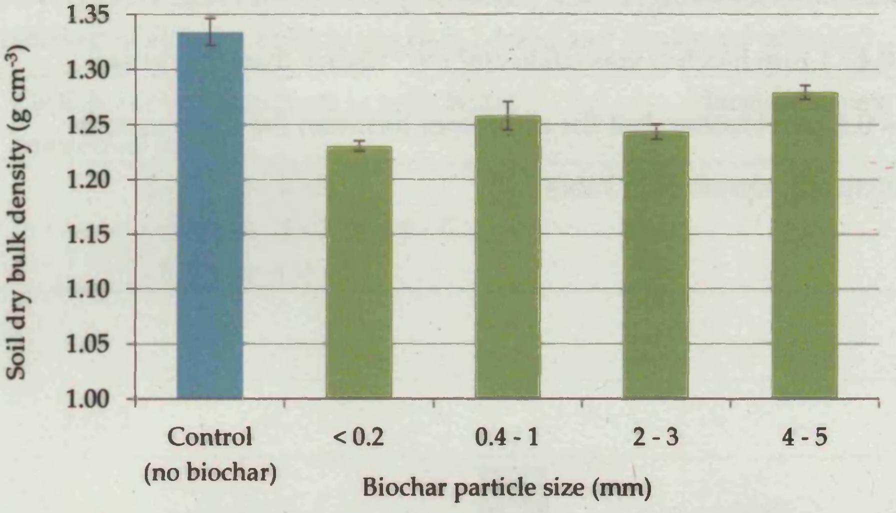


Figure 6.1: The effect of different sized biochars on the bulk density of a sandy loam (Error bars represent 95% CIs, n = 5)

Table 6.2: Tests for differences between bulk densities of soils with biochar additions of differing particle size (p is 2-tailed and Bonferroni-adjusted)

Biochar particle size (mm)	Mann-Whitney	
	U	*p*
0.4 - 1 vs. 2 - 3	83.0	0.387
< 0.2 vs. 0.4 - 1 and 2 - 3	72.0	0.012
0.4 - 1 and 2 - 3 vs. 4 - 5	69.0	0.009

6.3.2 Water-holding capacity

Biochar of 0.4 - 1 mm particle size was the only amendment to significantly influence WHC (Table 6.3), with soil amended with this biochar retaining 12% more water than the control treatment (Figure 6.2). There was no significant difference between soils containing 2 - 3 or 4 - 5 mm biochars; both had WHCs of ~0.43 cm^3 cm^{-3}. The mean WHC soil containing < 0.2 mm biochar was 6% higher relative to soil containing 2 - 5 mm biochar, and this difference was statistically significant (Table 6.4). The mean WHC of soil containing 0.4 - 1 mm biochar was 0.036 cm^3 cm^{-3} higher than that of soil containing < 0.2 mm biochar, but the difference between the the two soils was not statistically significant (Table 6.4).

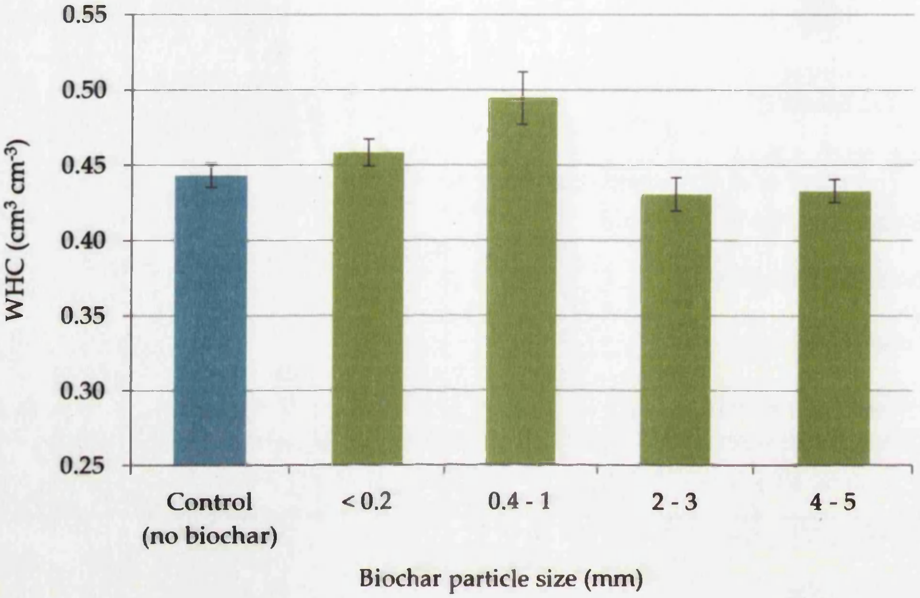


Figure 6.2: The effect of additions of biochars of differing particle size on the water-holding capacity of a sandy loam (Error bars represent 95% CIs, n = 5)

Table 6.3: Tests for differences between water-holding capacities of soils with biochar additions compared to soil without biochar (p is 1-tailed and Bonferroni-adjusted)

Biochar particle size (mm)	Mann-Whitney	
	U	*p*
< 0.2	4.0	0.192
0.4 - 1	0.0	0.016
2 - 3	6.0	0.444
4 - 5	5.0	0.300

Table 6.4: Tests for differences between water-holding capacities of soils with biochar additions of differing particle size (p is 1-tailed and Bonferroni-adjusted)

Particle sizes of biochars in soils being compared (mm)	Mann-Whitney *U*	*p*
2 - 3 vs. 4 - 5	11.0	1.000
< 0.2 vs. 2 - 3 and 4 - 5	3.0	0.015
< 0.2 vs . 0.4 - 1	3.0	0.168

6.3.3 Total suction

While biochar amendments of all particle sizes increased mean matric suction, in the case of biochars with a particle size between 2 and 5 mm, this effect was not statistically significant (Table 6.5). Biochar amendments of a particle size between < 0.2 and 0.4 - 1 mm did have a statistically significant effect (Table 6.5), increasing the mean total soil suction relative to the control treatment by 61% and 99% respectively (Figure 6.3). There were statistically significant differences between the effects of biochar amendments of different particle size on total soil suction ($H(3) = 12.44$, $p < 0.001$); < 0.2 mm and 0.4 - 1 mm biochars resulted in a significantly larger increase in total suction than was observed in soils amended with 2 - 3 mm and 4 - 5 mm biochars (Table 6.6).

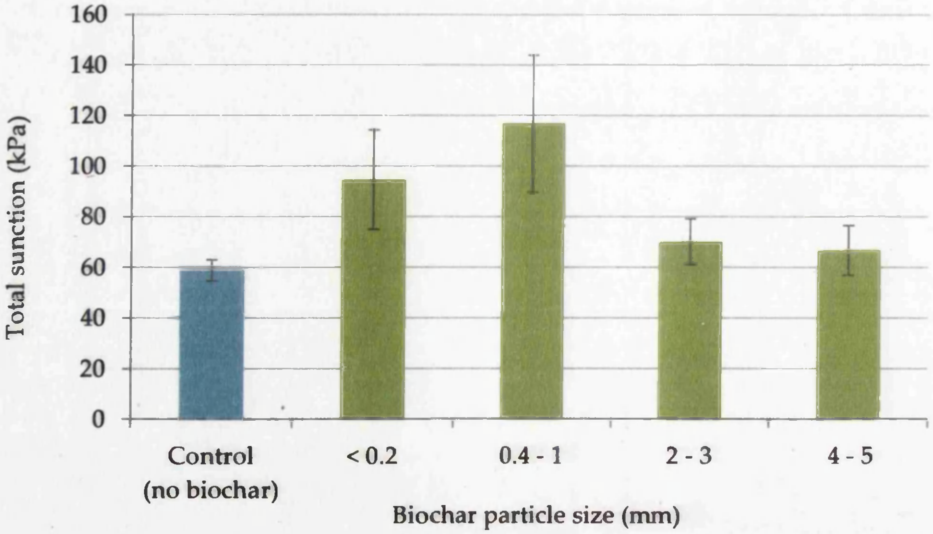


Figure 6.3: The effect of additions of biochars of differing particle size on total suction of a sandy loam (Error bars represent 95% CIs. For <0.2 mm biochar n = 4, for all other treatments n =5)

Table 6.5: Tests for differences between total suction of soils with biochar amendments compared to soil without biochar (p is 1-tailed and Bonferroni-adjusted)

Biochar particle size (mm)	Mann-Whitney	
	U	*p*
< 0.2	0.0	0.032
0.4 - 1	0.0	0.016
2 - 3	3.0	0.111
4 - 5	6.0	0.619

Table 6.6: Tests for differences between total suction of soils with biochar amendments of different particle sizes (p is 2-tailed and Bonferroni-adjusted)

Biochar particle size in soils being compared (mm)		Mann-Whitney	
		U	*p*
< 0.2	vs. 0.4 - 1	5.0	0.857
2 - 3	vs. 4 - 5	11.0	1.000
< 0.2 and 0.4 - 1	vs . 2 – 3 and 4 - 5	3.0	< 0.001

6.3.4 Matric suction

6.3.4.1 The effect of biochar particle size

Figure 6.4 illustrates the effect of different-sized biochars on the matric suction of a sandy loam. The matric suction in soil containing biochar of any particle size fraction was roughly 3 to 4 times greater than in the control treatment, and in each case this was a statistically significant effect (Table 6.7). Pairwise comparisons revealed no significant differences between the effects of different biochar sizes on matric suction (Table 6.8).

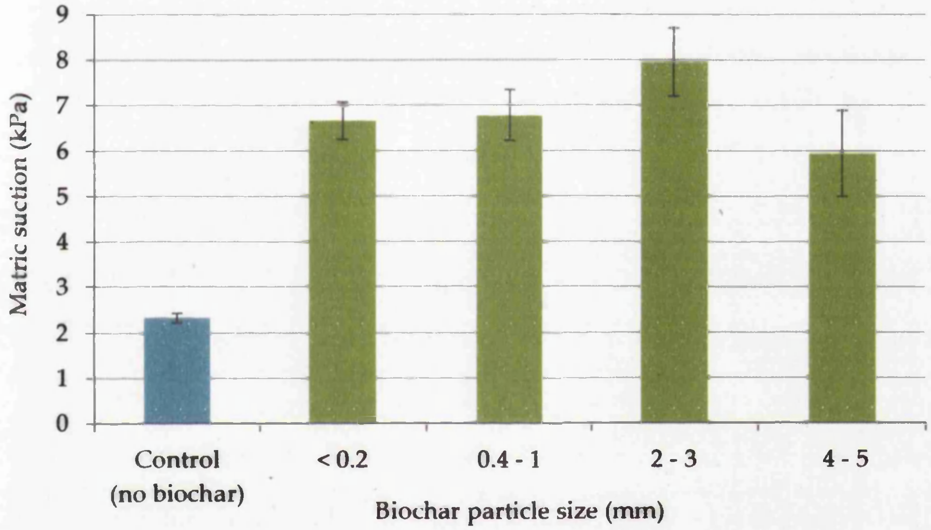


Figure 6.4: The effect of additions of biochars of differing particle size on the matric suction of a sandy loam (Error bars represent 95% CIs, n = 5)

Table 6.7: Tests for differences between matric suction of soils with biochar additions compared to soil without biochar (p is 1-tailed and Bonferroni-adjusted)

Biochar particle size (mm)	Mann-Whitney	
	U	*p*
< 0.2	0.0	0.016
0.4 - 1	0.0	0.016
2 - 3	0.0	0.016
4 - 5	0.0	0.016

Table 6.8: Tests for differences between matric suction of soils with biochar amendments of different particle sizes (p is 2-tailed and Bonferroni-adjusted)

Biochar particle size in soils being compared (mm)		Mann-Whitney	
		U	*p*
< 0.2	vs. 0.4 - 1	11.0	1.000
2 - 3	vs. 4 - 5	1.0	0.063
< 0.2 and 0.4 - 1	vs. 2 - 3	7.0	0.112
< 0.2 and 0.4 - 1	vs . 4 - 5	13.0	0.658

6.4 Discussion

The effect of biochar in reducing soil bulk density decreased as biochar particle size increased. This is probably because smaller biochar particles prevented tight packing of soil grains more effectively than larger biochar particles, which influenced the packing arrangement of a smaller volume of soil. Soil bulk density is generally lower when soil particle size is uniform (Brady & Weil, 2008). The smaller biochar particle size fractions were more uniform in size than the larger fractions. In absolute terms, the breadth of the particle size fraction for 4 - 5 mm biochars was potentially five times larger than that of < 0.2 mm biochar. Furthermore, biochar particle sizes between 0 and 1 mm were obviously much more similar to the grain sizes in the soil itself than biochar particle sizes between 4 and 5 mm. Soil-biochar mixtures containing < 0.2 and 0.4 - 1 mm biochars would therefore have had a more uniform particle size overall than soil-biochar mixtures containing 4 - 5 mm biochars. If biochar particles were sufficiently small however, they could fill the spaces between larger soil particles, resulting in a tighter packing arrangement and consequently, a higher bulk density. Differences in the effects of biochars of differing particle size are controlled by their effect on overall soil packing rather than differences in the internal porosity of the biochars themselves. Therefore, where biochars have differing particle size but are produced from a feedstock of the same type and particle size under similar pyrolysis conditions, differences between their effects on bulk density (in a sandy loam) are likely to be similar to those observed in this study.

Larger biochar particles (2 - 3 and 4 - 5 mm) reduced bulk density, but did not increase WHC. This suggests that water drained from the soil more quickly than it was able to permeate larger biochar particles. The experiments investigating these parameters were conducted in a constant temperature room and all used distilled water and biochar produced at the same temperature from the same feedstock, which was of uniform particle size. It can therefore be assumed that the surface tension and density of the water, the contact angle of the biochar with the water and its pore size distribution were constant for each biochar particle size used in this investigation. This means that the rate of movement of water into biochar pores should have been equal at first. However, the rates at which porous solids absorb liquid decrease with time and in larger biochar particles, water must travel further through a pore network before the entire particle is saturated. This means that 24 hours may have been an insufficient period of time for water to reach some the innermost porosity of 2 - 3 and 4 - 5 mm biochars, meaning that not all of their porosity was involved in water uptake during this period, hence these biochars did not significantly increase the soil WHC.

This outcome corresponds to sorption experiments carried out by Zheng *et al.* (2010), which showed that larger biochar particle sizes increased pesticide sorption equilibrium times by several days because of the greater length of time necessary for pesticides to reach their innermost regions. It is possible that if WHC had been measured after 48 h instead of after 24 h, 2 - 3 and 4 - 5 mm biochars might have had a more substantial effect on soil WHC as water would have been able to move further into the larger particles (though this might have been countered to some extent by further drainage of water from the soil). It may be the case that during wetting events in poorly drained soils, biochar particle size would have less effect on WHC because there would be more time for particles to take up water.

Biochar of < 0.2 mm particle size did not increase WHC to the same extent as 0.4 -1 mm biochar. This effect can be related to the effect that the biochars had on bulk density. Soil amended with < 0.2 mm biochar had a significantly lower bulk density than soil amended with 0.4 - 1 mm biochar, indicating greater porosity, which could increase hydraulic conductivity.

The lower moisture absorption by larger biochar particles in the WHC experiments could have arisen in part from surface hydrophobicity. Hydrophobic sites on the surface of biochar particles will have a greater impact on the hydrologic properties of larger particles than smaller particles. For large particles, a greater proportion of their porosity will be made ineffective by a certain percentage of their surface being hydrophobic than would be the case for smaller particles. As such, unless saturation conditions persist for periods sufficient to overcome the surface hydrophobicity of biochar particles, water will drain from the soil rather than be absorbed by biochar particles. It can therefore be expected that for biochars produced at higher HTTs which are less hydrophobic (see section 4.4.2.3), differences in particle size will have less effect on WHC. On the other hand, intermediate melts in biochars produced at higher HTTs can reduce pore interconnectivity (see section 5.4). This could have a more significant effect on the hydrologic properties of larger particles as a larger number of pores could be cut off by a melt than would be the case in smaller particles.

The finding that there were no significant differences between the effects of different biochar particle size fractions on matric suction suggests that the two-week incubation period allowed sufficient time for moisture to be absorbed by pores further inside larger particles, with the amount of water held by biochar being equal regardless of particle size and / or that the moisture content of the soil was sufficiently low to mean that only a certain percentage of biochar porosity was holding water, regardless of particle size. As the different size fractions were all produced under the same conditions, their pore size distribution would have been similar, meaning that there would be no differences in matric suction if they had wetted equally.

The differing effects of different sized biochar particles observed in the present study contrast somewhat with the findings of Lehmann *et al.* (2003) who used biochars of < 2 mm and ~20 mm particle size (in absolute terms, a much greater difference in size than was investigated in the present study) and observed no differences in crop growth. Nonetheless, it should be noted that Lehmann *et al.* (2003) irrigated the soils in their study daily to maintain ~60% of WHC. The findings of the present study suggest that the findings of Lehmann *et al.* (2003) might have been different had irrigation instead been applied to nearer 100% of WHC, with soils allowed to dry out more completely (over several days) before rewetting. If larger biochar particles do not necessarily wet as completely as smaller biochar particles, the moisture content of soils containing larger biochar particles would have been lower, meaning plants would have expended more energy on water uptake, resulting in lower growth.

Only biochar amendments of < 0.2 and 0.4 - 1 mm significantly increased the total suction of the soil. This can be attributed to differences in the effect that different biochar particle sizes had on osmotic suction, as there were no significant differences between the effects that different biochar particle sizes had on matric suction. Differences in osmotic suction would have arisen from biochar amendments introducing different amounts of solutes into the soil solution according to the amount of biochar surface area that was in contact with the soil solution. During pyrolysis, biochar pores can become filled with condensed volatiles (Downie *et al.*, 2009). The process of grinding larger biochar particles down to smaller size fractions could have released these condensed volatiles from pores and spread them over the surfaces of small particles, resulting in them having a greater surface area in contact with the soil solution.

Differences between the effects of biochars of different particle size on osmotic suction will become decreasingly important as biochar-introduced solutes are leached from the soil. Furthermore, biochar is brittle, so larger particles will eventually break down into smaller particles anyway. Sohi *et al.* (2009) suggested that the effect of biochar particle size may be short-lived, as once biochar is applied to the soil it 'rapidly' divides into particles of silt size or less. There will however be differences in the speed with which this occurs between different biochars; those produced at lower HTTs tend to be stronger than those produced at higher HTTs (Downie *et al.*, 2009) are thus likely to abrade into finer fractions less rapidly. Further research is needed to determine the periods over which biochar particle size can exert a significant influence on osmotic suction and the ability of plants to take up water. Regardless of the temporal nature of any biochar particle size effects, this study provides an indication of how those effects might change as biochar breaks down in the soil.

The effects of different biochar particle sizes on osmotic suction described above will not apply to all biochars. Biochar amendments do not necessarily increase osmotic suction; they can instead reduce it (see section 5.4). Further research is needed to determine whether and to what extent particle size influences the effect of biochar amendments that reduce osmotic suction. As smaller biochar particles reduce bulk density to a greater extent than larger particles, it follows that where biochars reduce osmotic suction, smaller particles may do so to a greater extent than larger particles as they are more effective displacers of the native soil.

6.5 Limitations

As with the matric suction results presented in Chapter 5, an obvious limitation for the results presented in this chapter is that the matric suction measurements presented in section 6.3.4 cannot with confidence be accepted as valid absolute values due to problems with the experimental approach (see section 5.5). The data are nonetheless useful for evaluating the relative differences in matric suction between treatments, because the same method was used for all treatments and many of the differences between treatments are statistically significant, therefore they cannot be due to chance. Accordingly, it is reasonable to assume that where relative differences in total suction values between treatments did not reflect relative differences in matric suction values between treatments, it was because differences in matric suction were counteracted by differences in osmotic suction.

The findings of the present study suggest that larger biochar particles (> 2 mm) are not as effective in increasing soil WHC as smaller biochar particles (< 1 mm). It should however be noted that the larger particles may have had more of an influence on soil WHC had saturation conditions persisted for a longer period. Biochar hydrophobicity was not measured, so it is not clear whether or not biochar surface hydrophobicity contributed to the different effects that biochars of differing particle size had on soil water-holding capacity. If hydrophobicity was indeed an influencing factor, then particle size could have less influence on the effect of biochar additions on soil WHC when biochar is produced at higher temperatures and is therefore wettable.

Biochar produced at 500°C increased osmotic suction, whereas those produced at other temperatures did not (see section 5.4). Differences in osmotic and total suction observed between biochars of different particle size produced at 500°C are not necessarily representative therefore of the differences that would be observed for biochars produced at other temperatures.

As with experiments presented in Chapter 5, the present set of experiments used sieved, repacked soils. The structures, pore architectures, aggregates and inter-aggregate pore size distributions of the soils were therefore artefacts of the sieving, mixing and repacking process, and do not necessarily resemble the properties of soils amended with biochar *in-situ*, where the direct effects of biochar on moisture retention will be complicated by indirect effects through the influence of biochar on soil aggregation and aggregate stability. Furthermore, in field situations, the effect of biochar on soil properties will be complicated by its effects on above- and below-ground biota.

It should also again be acknowledged that the biochar application rates used in this study were very high and not currently commercially realistic for broadacre agriculture. Differences between the effects of biochars produced at different pyrolysis temperatures observed in the present study may not be observed when lower application rates are used. Moreover, differences between biochars may be less important in soils where biochar application has little or no effect on moisture retention. In this study, biochar was mixed with soil to mimic ploughing, but it should be remembered that alternative methods of application could be used, for example deep-banding, drilling, top-dressing or ecological delivery via animal feed (Blackwell *et al.*, 2009), which could result in biochar having different effects.

Finally, it should once again be noted that the differences in matric and total suction reported here are representative of one soil moisture content only. Further research is needed to determine whether and to what extent the differences observed apply across the whole moisture release curve.

6.6 Summary

Biochar amendments significantly reduced the bulk density of a sandy loam, but the extent to which they did so differed according to their particle size. Biochar amendments of smaller particle size reduced bulk density more effectively than those of a larger particle size.

Biochars of < 1 mm particle size increased soil WHC, but this effect was only significant in the case of 0.4 - 1 mm biochar. Larger biochar particles (2 - 5 mm) reduced bulk density but did not increase WHC, meaning that their effect on WHC must be attributed to the biochars themselves rather than to their overall effect on the soil. That the larger biochar fractions did not affect WHC suggests that water drained from the soil more quickly than it was able to permeate larger biochar particles. Further research is needed to verify whether the patterns of difference between biochars of differing particle size observed in this investigation would apply to biochars produced using different HTTs.

Biochars of < 0.2 and 0.4 - 1 mm particle size were the only amendments that resulted in a significant increase in total suction. All biochar amendments resulted in a significant increase in matric suction (at a water content of 0.17 cm^3 cm^{-3}), regardless of their particle size. This indicates that the two-week incubation time used was sufficient for wetting of larger biochar particles to be equal to that of smaller particles. It therefore seems likely that under persistently wet conditions, moisture uptake by larger biochar particles can match that of smaller particles. However, 2 - 3 and 4 - 5 mm biochars did not significantly increase total suction as their effect of increasing matric suction was countered by a reduction in osmotic suction. This was presumably because these biochars displaced some of the original soil and did not introduce substantial amounts of solutes to the soil solution. Biochars of < 0.2 and 0.4 - 1 mm particle size did increase total suction as they resulted in an increase of both matric and osmotic suction. This can be attributed to the grinding process exposing and spreading condensed volatiles over the surfaces of the biochar particles, making a large volume of solutes available to the soil solution. It can be concluded that these smaller particle-size fractions could significantly increase the amount of energy plants would have to expend to access water. Further research is needed to determine: (i) whether these effects would apply across the entire moisture release curve; (ii) the periods of time over which increased solute concentrations would persist; and (iii) whether these differences would apply to biochars produced under different conditions.

7 EFFECTS OF BIOCHAR APPLICATION RATE ON THE HYDROLOGICAL RESPONSE OF A SOIL UNDER SIMULATED RAINFALL

7.1 Introduction

Although biochar amendments have been reported to improve soil water-holding capacities (Laird *et al.*, 2010b, Case *et al.*, 2012; Basso *et al.*, 2013), there are few studies in the literature investigating moisture retention versus run-off generation in biochar-amended soils under rainfall. Beck *et al.* (2011) found that adding biochar at a rate of 7% by weight resulted in a 4.4% increase of water retention in greenroof soil plots under simulated rainfall. However, these findings may not be trustworthy as, for half of the replicates, the initial soil moisture content was not controlled or measured. Furthermore, Beck *et al.* (2011) only measured the total discharge of water from the greenroof soil plots and therefore could not differentiate between overland flow and subsurface drainage, limiting the applicability of the results to *in-situ* soils. Smetanová *et al.* (2013) found that applying biochar produced at 500 - 600°C (from unspecified wood) to a sandy loam at a rate of 10% by volume decreased overland flow by up to ~40%, but drainage was not measured. Given the influence that feedstock material has on biochar properties (see Chapter 4), it is difficult to evaluate the implications of this research because the Smetanová *et al.* did not specify the precise feedstock used to produce the biochar. Clearly, the effects of biochar amendments on soil hydrological responses under rainfall are yet to be thoroughly explored.

Furthermore, no published studies have examined the effect of different biochar application rates on the hydrological response of a medium-textured soil under simulated rainfall.

Using three different biochar application rates, this part of the study investigated the effect of biochar amendments on the hydrological response of a silt loam under simulated rainfall, measuring both overland flow and drainage.

7.2 Methods

7.2.1 Biochar production and incubation

The pyrolysis unit used to produce the biochars used in Chapters 5 & 6 was not commissioned when the experimental process in this Chapter was begun. Biochar (supplied by Bodfari Environmental, St. Asaph) was instead produced using chippings of varying particle size produced from mixed deciduous hardwoods native to England and Wales, including Oak (*Quercus spp.*), Common Ash (*Fraxinus excelsior*), Sycamore (*Acer spp.*), Birch (*Betula spp.*) and Cherry (*Prunus spp.*). The feedstock material was pyrolysed using steel ring kilns (Figure 7.1), in which the peak pyrolysis temperature can vary according to the position within the kiln (Powell *et al.*, 2012). Following production, the biochar was stored in a heated greenhouse for 12 months because oxidation of biochar surfaces is encouraged by warm, humid conditions (Cheng *et al.*, 2006), leading to the formation of functional groups which may increase both biochar wettability (Kinney *et al.*, 2012) and the formation of organo-mineral associations between biochar and soil particles, promoting aggregate stability (Glaser *et al.*, 2000; Lin *et al.*, 2006).

Figure 7.1: Ring kilns (Credit: Bodfari Environmental)

7.2.2 **Biochar hydrophobicity**

Biochar hydrophobicity was assessed using a goniometer to measure water droplet contact angles following the methodology described in detail in section 4.2.3. One hundred contact angle measurements were made.

7.2.3 **Soil-biochar mixtures**

The soil used in this part of the study was an air-dried proprietary silt loam (9% clay, 72% silt, 19% sand) with an organic matter content of 8% which was supplied by Boughton Ltd. (Kettering). Key objectives of this experiment were to investigate the influence of different biochar application rates on aggregate stability and soil crusting following rainfall simulation, though for clarity and readability, the data on these are presented separately in Chapter 8. The sandy loam soil used for the experiments in Chapters 5 and 6 did not readily form aggregates, so a silt loam was used instead because it readily formed aggregates, was friable and because soils dominated by silt fractions are particularly susceptible to sealing and subsequent crusting (Gabriels *et al.*, 1998). Using a silt loam thus increased the likelihood of differences in soil aggregate stability, sealing and crusting being observed with different biochar application rates.

The biochar was sieved to < 2 mm as this particle size fraction was most likely to influence the water-holding capacity of the soil (see Chapter 6). The soil was sieved to < 3.35 mm, then the biochar was mixed with the soil to create triplicate samples totalling 3 kg with biochar added at rates of 0 (control), 5, 25 and 50 g kg^{-1} (dry weight). 435 ml of water (30% of the WHC of the control sample) was stirred into each sample. The samples were then stored in darkness at 21°C in lidded 4.8 litre containers. The containers were not air-tight, but the lids were removed every 6 weeks and the soils disturbed using a trowel to allow more thorough aeration and mimic bioturbation. After 250 days, the samples were air-dried to constant weight and sieved to < 5 mm.

7.2.4 Bulk density

The bulk densities of the soil-biochar mixtures were measured using the same method as described in Chapter 5. Five replicates were completed for each treatment.

7.2.5 Soil-biochar mixture hydrophobicity

The surface hydrophobicity of soil-biochar mixtures was measured using the water drop penetration time (WDPT) test. The soil-biochar mixtures were sieved to < 2 mm, placed in petri dishes of 40 mm diameter and 5 mm depth and the surfaces were levelled and smoothed using a ruler. 6 petri dishes were prepared for each soil-biochar mixture. Five equidistantly spaced droplets (~0.05 ml) of distilled water (21 °C) were applied to each dish using a pipette, and the time taken for each droplet to completely penetrate the soil surface was measured using a stopwatch. A total of 30 WDPTs were therefore recorded for each soil-biochar mixture.

7.2.6 Preparation of soil plots

A 30 mm layer of soil was spread over permeable fibreglass cloth covering a 10 mm mesh screen within a 300 x 300 mm metal plot (Bodí *et al.*, 2012). This custom-made plot had an outlet above the mesh screen (level with the top of the layer of soil) for capturing overland flow and an outlet below the mesh screen for capturing drainage (Figure 7.2).

7.2.7 Rainfall simulation

Rainfall simulation was carried out using a laboratory drip-type simulator (Figure 7.2). Three rainfall simulations were completed for each biochar application rate. Water was supplied from a 25 L tank into a 400 x 400 mm droplet box with 190 drop-formers of 0.5 mm diameter made from Teflon tubing (see Clark & Walsh, 2007). The flow of water from the tank was regulated by a switch, which was activated once the water reached a certain level in the droplet box (Bodí *et al.*, 2012). This minimised variation in the depth of water in the droplet box, thus also limiting variation in rainfall intensity. A wire mesh hanging 500 mm below the droplet box was continually oscillated by hand to break up droplets (creating a variety of droplet sizes) and randomize their landing positions.

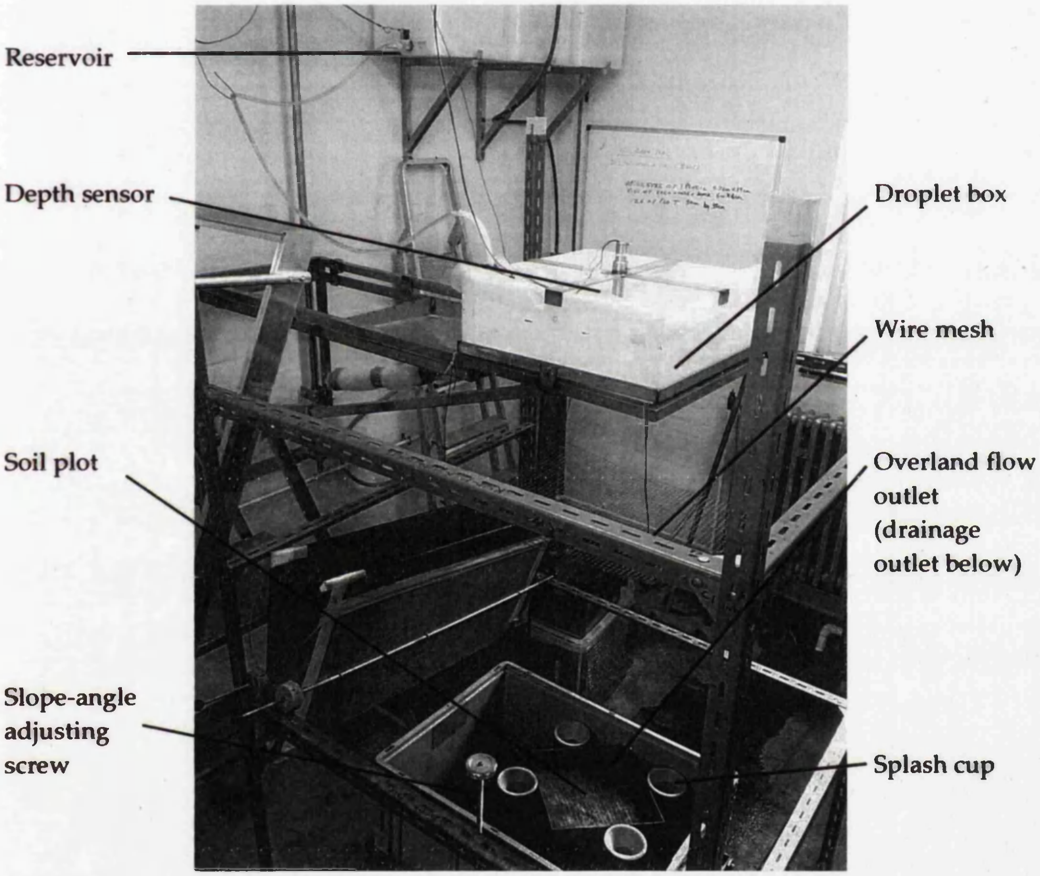


Figure 7.2: Rainfall simulator

The soil plots were placed 1.5 m below the droplet box on a slope angle of 5° and subjected to 60 minutes of simulated rainfall. The mean rainfall rate across all simulations was 79.34 ± 2.09 mm h^{-1}, which in the UK would be an extreme rainfall event (Bilham, 1935) around the 'maximum' possible point rainfall in the UK (Hand *et al.*, 2004). The highest rainfall rate ever recorded in the UK over one hour was 92 mm (Met Office, 2014). However, this rainfall rate would not be uncommon in tropical climates (Maitra *et al.*, 2009; Rahardjo *et al.*, 2012) or Mediterranean climates (Kelsch *et al.*, 2001). Rainfall rates were measured using a V-shaped tray held in place below the droplet box. For each simulation carried out, rainfall was measured for 2 minutes immediately before the simulation and 2 minutes immediately afterwards. Total rainfall for the 60 minute simulation was estimated from the mean of these two measurements, allowing subsequent calculation of overland flow coefficients and the proportions of rainwater that were held by the soils or lost by drainage. Overland flow was first measured 2 minutes after commencement of rainfall and at 4 minute intervals thereafter. Drainage (subsurface drainage) was first measured after 2 minutes and recorded every 2 minutes thereafter.

7.2.8 Statistical analyses

Kruskal-Wallis tests were used to test for overall differences between treatments (Kruskal & Wallis, 1952). Pairwise comparisons were made using Mann-Whitney U-tests (Mann & Whitney, 1947), with Bonferroni adjustments applied to control familywise Error (Dunn, 1961). Trends in the data were tested for using Jonckheere-Terpstra tests (Jonckheere, 1954). Most statistical analyses were carried out using SPSS (v.19, IBM, USA). However, Jonckheere-Terpstra tests were partly calculated manually due to an Error in SPSS and Bonferroni adjustments were also calculated manually. A 95% confidence level was adopted for all tests; differences were considered to be statistically significant where $p < 0.05$.

7.3 Results

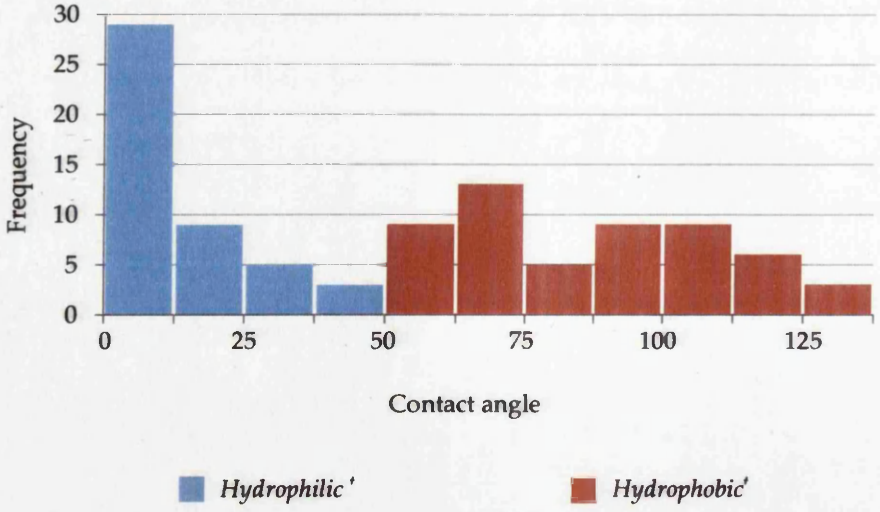
Differing biochar application rates resulted in significant differences between the hydrological responses of soils under simulated rainfall. The temporal changes in drainage and overland flow during rainfall simulations varied with the biochar contents of the soils (Figure 7.6).

7.3.1 Biochar hydrophobicity

The hydrophobicity of the biochar used in the present study was extremely varied. Around a third of the water droplets spread over the surface or infiltrated completely. However, assuming a contact angle of 50° represents a boundary between wettable and non-wettable biochar (see section 4.4.2.3), 54% of the contact angles measured were indicative of hydrophobic biochar surfaces (Figure 7.3).

7.3.2 Soil-biochar mixture hydrophobicity

Biochar application rate had no effect on the surface hydrophobicity of soil-biochar mixtures. At all application rates, 100% of water drops were able to penetrate the soil surface immediately (WDPT < 1 second).



'Assumes a contact angle of 50° delineates the boundary between hydrophobic and hydrophilic surfaces (see section 4.4.2.3).

Figure 7.3: Water droplet contact angles on biochar particles produced from mixed deciduous wood in a ring kiln

7.3.3 **Bulk density**

Figure 7.4 illustrates the effect of different biochar application rates on the bulk density of the soil. Differing biochar application rates had a significant effect on bulk density ($H(3) = 16.21$, $p < 0$ 0.001). An application rate of 5 g kg^{-1} decreased the mean bulk density of the soil, but this effect was not statistically significant (Table 7.1). An application rate of 25 g kg^{-1} significantly reduced the mean bulk density of the soil (by over 5%). Applying biochar at a rate of 50 g kg^{-1} resulted in a significantly lower bulk density than an application rate of 25 g kg^{-1} (Table 7.1), and reduced the mean bulk density by over 7% compared to soil without biochar.

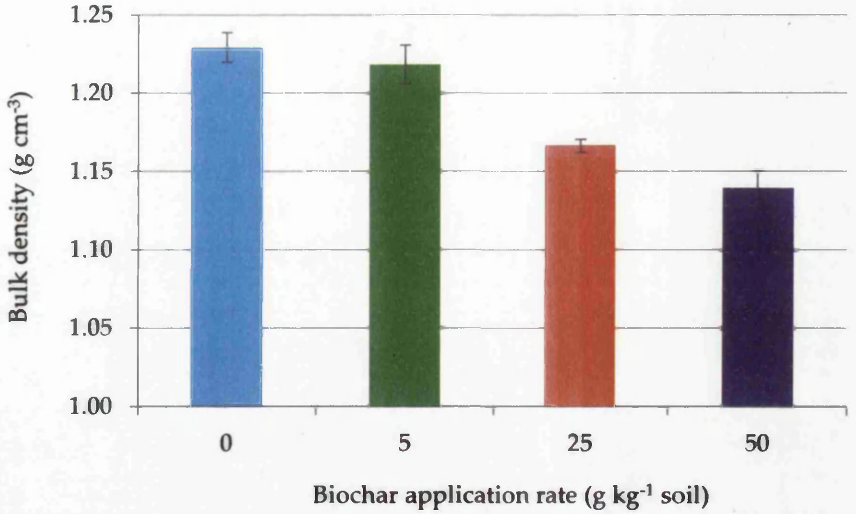


Figure 7.4: The effect of biochar application rate on the bulk density of a silt loam (Error bars represent 95% CIs, n = 5)

Table 7.1: Tests for differences between bulk densities of soils with different biochar contents (p is 1-tailed and Bonferroni-adjusted)

Biochar application rate (g kg^{-1})	Mann-Whitney	
	U	*p*
0 vs. 5	9.0	0.822
0 and 5 vs. 25	0.0	< 0.001
25 vs . 50	0.0	0.012

7.3.4 Rainwater infiltration

It is likely that the portion of rainwater that was able to infiltrate the soil was reduced as biochar application rate was increased ($S = 16$, $p = 0.147$). On average, 59% of rainwater infiltrated plots without biochar additions, while infiltration in plots with biochar contents of 50 g kg^{-1} was 54% of rainfall (Figure 7.5).

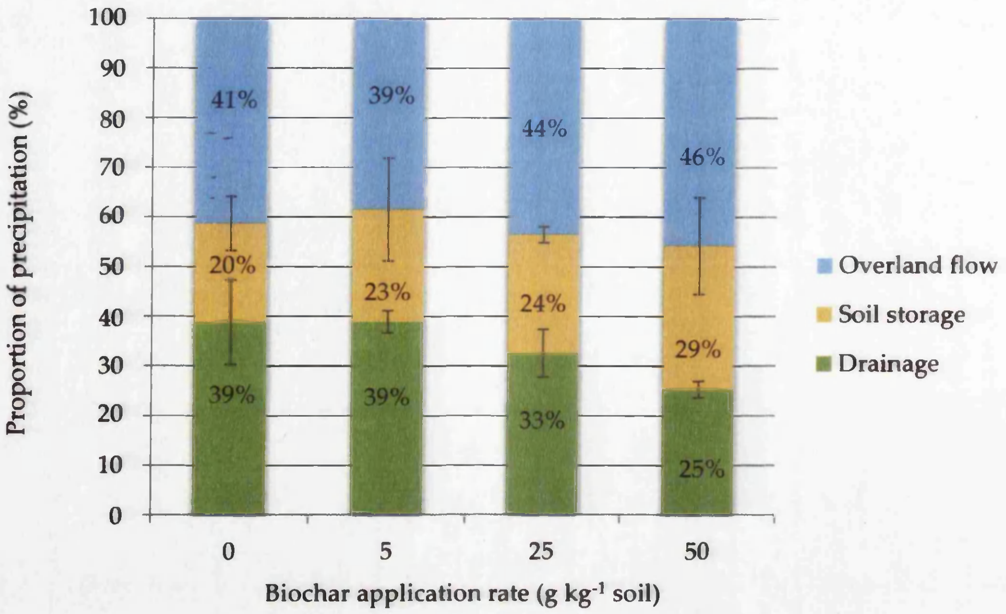


Figure 7.5: Fate of precipitation (Error bars represent 95% CIs, n =3)

7.3.4.1 Retention of rainwater in soil

There are indications that soil water retention increased with increasing biochar application rate ($S = 18, p = 0.117$). The mean proportion of rainwater retained by soil with a biochar content of 50 g kg^{-1} was 45% higher than that retained by soil without biochar (Figure 7.5). As Figure 7.6 illustrates, proportionate to the amount of rainwater infiltrating the soil in the first place, there was a significant trend for water retention to increase with increasing application rates ($S = 38, p = 0.003$).

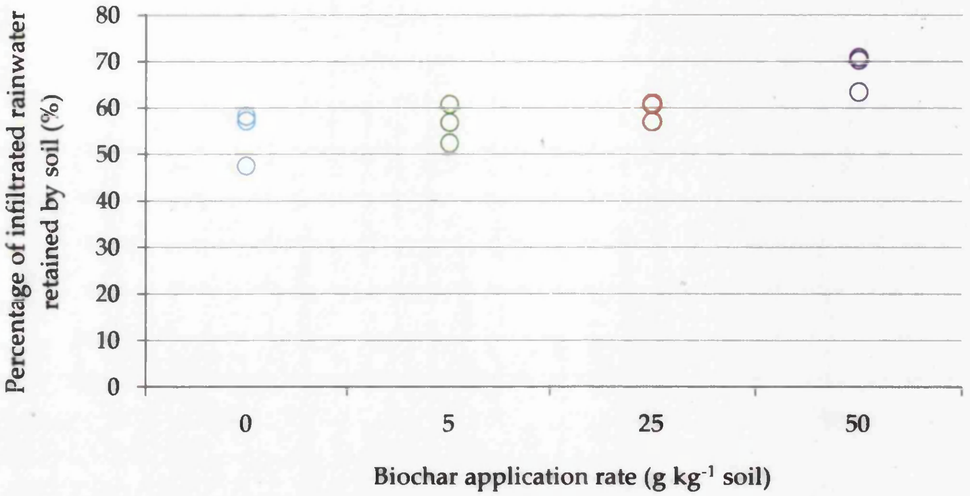


Figure 7.6: Effect of biochar application rate on retention of rainwater by soil

7.3.4.2 Drainage

Temporal changes in drainage during rainfall simulations varied with the biochar content of the soils (Figure 7.7). Commencement of drainage was slower with increasing biochar content (*S* = 13, *p* = 0.18). As Figure 7.8 illustrates, there was a statistically significant trend for the proportion of infiltrated rainfall released from the soil as drainage to decrease with increasing biochar content (*S* = 38, *p* = 0.003). For plots with biochar applied at rates of 0 or 5 g kg^{-1}, almost 40% of the total rainfall was lost from the plots by drainage. Plots with biochar content of 25 g kg^{-1} lost around a third of rainwater by drainage, whilst plots with biochar applied at a rate of 50 g kg^{-1} lost a quarter of rainwater by drainage (Figure 7.5).

Overall, the maximum drainage rate recorded over 1 minute tended to decrease with increasing biochar application rate (*S* = 39, *p* = 0 .004). In soil

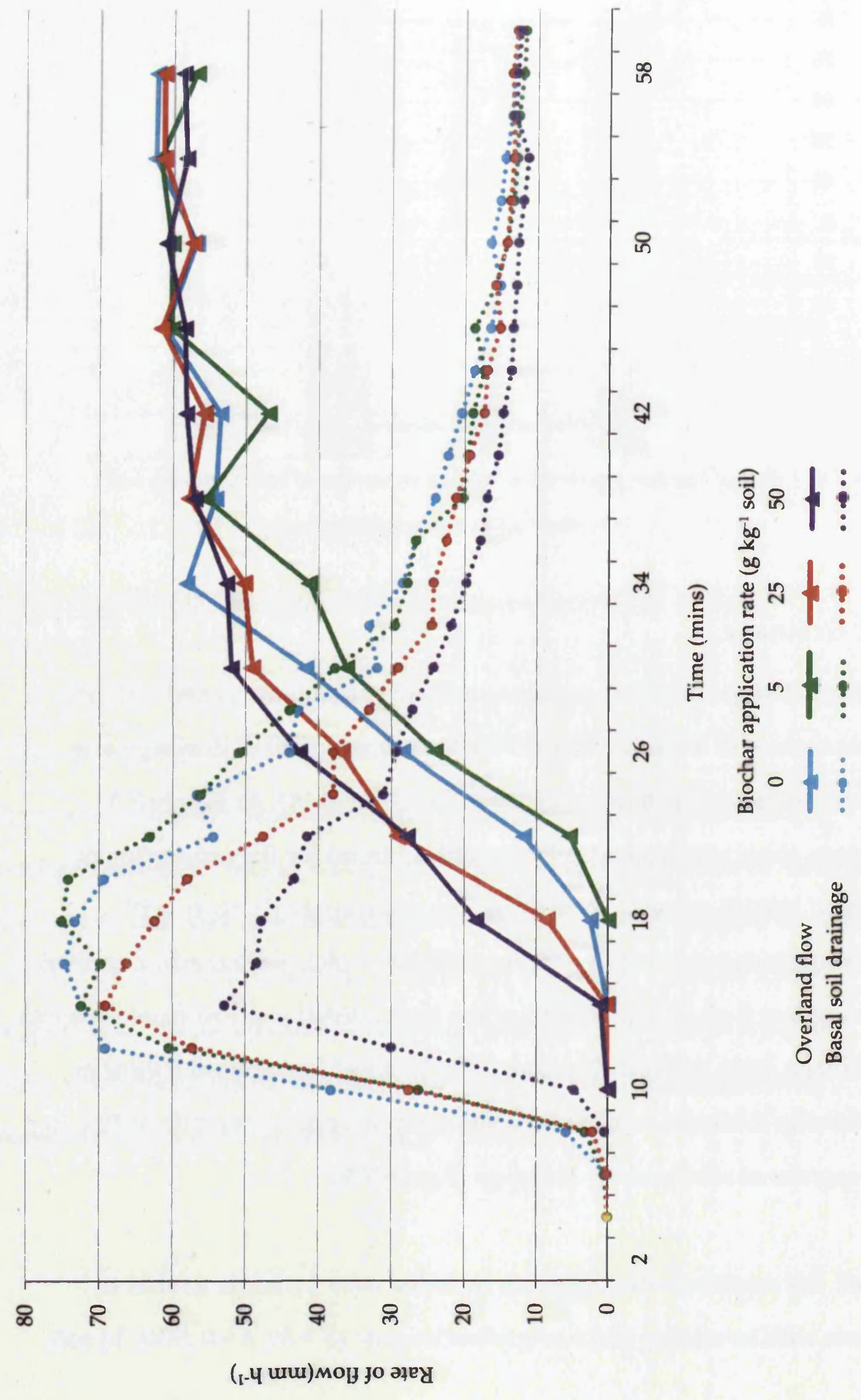


Figure 7.7: Mean hydrographs for rainfall simulations

without biochar, drainage peaked at around 75 mm h^{-1}, while in soil with a biochar content of 50 g kg^{-1}, drainage peaked at around 60 mm h^{-1} (Figure 7.9). There were no significant differences between the durations of rainfall after which peak drainage occurred in different soils ($H(3) = 0.089$, $p = 0.711$).

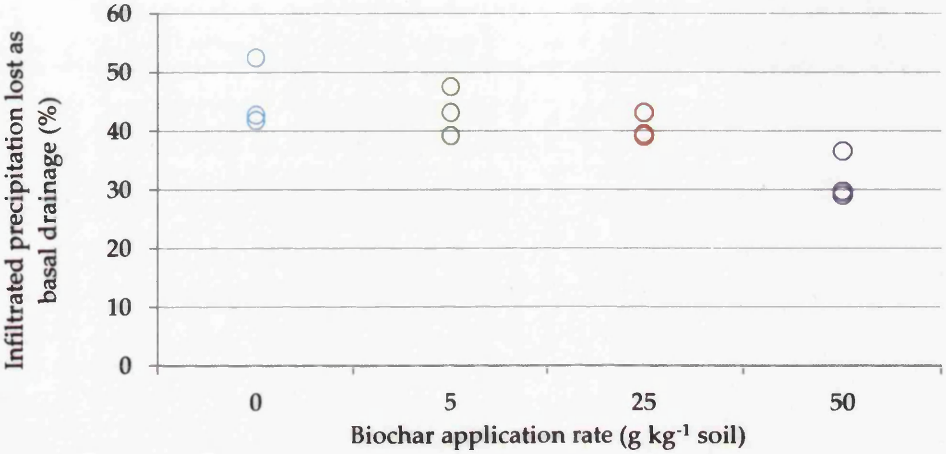


Figure 7.8: Effect of biochar application rate on proportion of infiltrated rainfall transmitted through soil as drainage

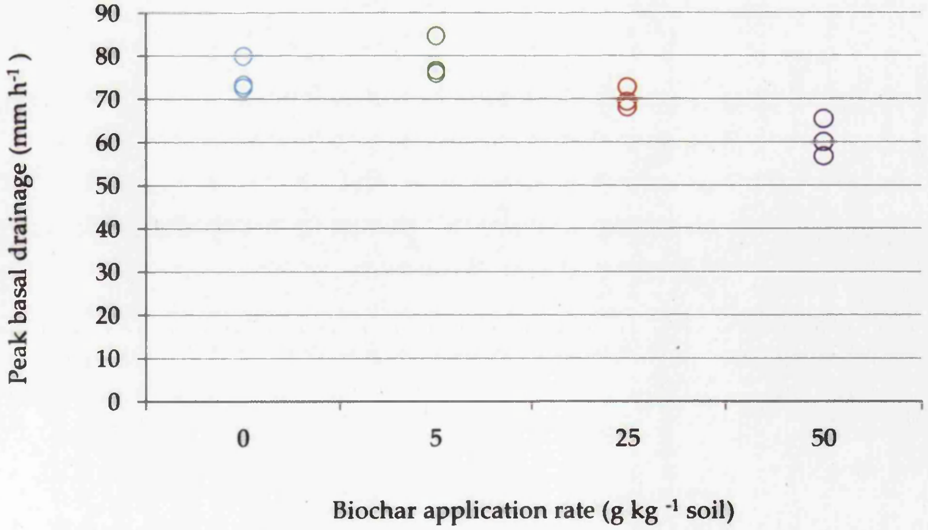


Figure 7.9: Effect of biochar application rate on peak basal drainage

7.3.5 Overland flow

Overland flow was generated more quickly as biochar content increased (S = 33, p = 0.008). For plots with biochar additions of 0 and 5 g kg^{-1}, the median time for commencement of overland flow was after 24 minutes of rainfall (Figure 7.10). For plots with 25 and 50 g kg^{-1}, the median times for commencement of overland flow were 18 and 14 minutes respectively (Figure 7.10).

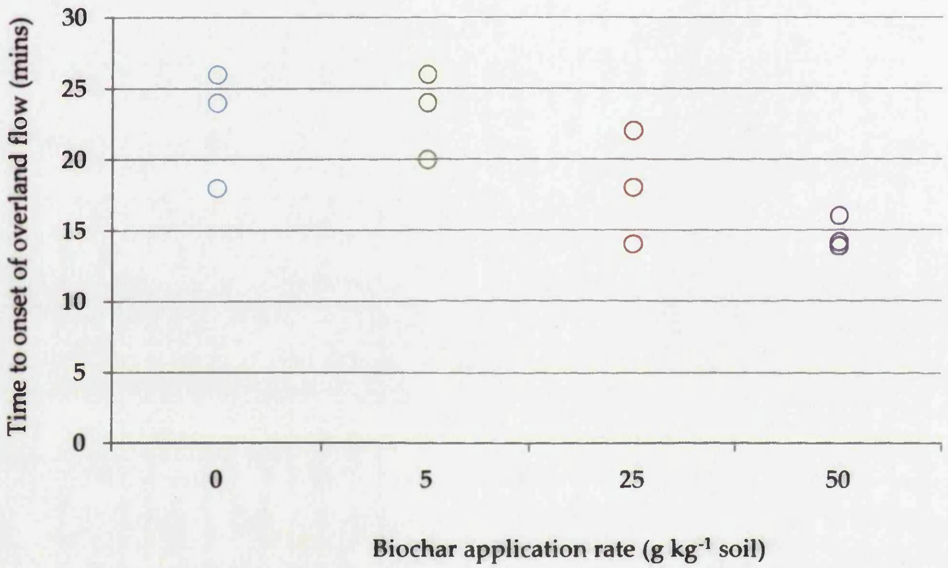


Figure 7.10: The effect of biochar application rate on time to onset of overland flow

The overland flow coefficient for plots with a biochar content of 5 g kg^{-1} was lower than that from plots without biochar. However, the overland flow coefficient for plots with biochar content of 25 g kg^{-1} was 3 percentage points higher than that from plots without biochar, and for plots with biochar content of 50 g kg^{-1} it was a further 2 percentage points higher (Figure 7.5). The data therefore suggest that overland flow volume tended to increase slightly with increasing biochar application rate (S = 16, p = 0.147). Biochar content did not significantly affect the maximum overland flow rates recorded over one minute ($H(3) = 0.524$, $p = 0.491$). However, there are indications that peak overland flow was reached more quickly as biochar content increased ($S = 30$, $p = 0.182$). There were no significant differences between the correlations of rainfall duration and overland flow volume of soils with differing biochar content.

7.4 Discussion

The variability in the wetting characteristics of the biochar used in this study is unsurprising given that the biochar was produced in a traditional kiln, from mixed deciduous wood feedstock. The peak temperature at which particles in traditional kilns are pyrolysed can vary substantially (from ~430°C to ~750°C) according to their position in the kiln (Powell *et al.*, 2012.). Biochar wettability is significantly influenced by both pyrolysis temperature and feedstock type (see Chapter 3). The biochar was stored for 12 months in a heated greenhouse and was thus subjected to warm and humid conditions, which would have enhanced oxidation of its surface (Cheng *et al.*, 2006), leading to formation of functional groups which increase surface wettability. Although a large proportion of the biochar particles were nonetheless hydrophobic, biochar application had no effect on soil wettability at application rates up to 50 g kg^{-1}. This confirms the findings of Kinney *et al.* (2012) and Smetanová *et al.* (2012) that hydrophobic biochars do not significantly affect soil wettability even at high application rates. It should however be noted that the present study and those of Kinney *et al.* (2012) and Smetanová *et al.* (2012) all mixed biochar with the soil, mimicking ploughing biochar into soil. Hydrophobic biochars may have a greater effect on soil wettability when they are instead spread over the soil surface by top-dressing.

The increasing proportion of water retained by the soil with increasing biochar application rate can be attributed to reductions in bulk density (i.e. increased porosity) and decreases in hydraulic conductivity. This finding is in agreement with studies of a number of soils in which biochar application increased water retention during rainfall (Beck *et al.*, 2011) and slowed downward movement of rainwater through the soil profile (Major *et al.*, 2006) with saturated hydraulic conductivity decreasing as application rate was increased (Brockhoff *et al.*, 2010; Githinji, 2013). Increased water retention at higher biochar application rates meant that drainage tended to commence more slowly as the biochar content of soil increased. Although overland flow was generated significantly more quickly as biochar content increased, biochar content did not affect the duration of rainfall necessary to reach peak drainage (the rate of which significantly decreased with increasing biochar content). Differences in the proportion of rainwater that was lost from the soil as drainage are therefore attributable to differences in hydraulic conductivity rather than temporal differences in the onset of surface sealing.

Although soils with biochar contents of 25 and 50 g kg^{-1} retained more rainwater than those with biochar contents of 0 and 5 g kg^{-1}, they generated overland flow more quickly. Biochar application did not result in any increased resistance to wetting, so the quicker overland flow generation observed in soil with biochar contents of 25 and 50 g kg^{-1} cannot be attributed to an increase in soil water repellency. Rather, increased rapidity of overland flow generation can be attributed to the lower aggregate stability of these soils. Aggregates at the surface of these soils would have broken down more quickly than in soils with low or zero biochar content (see section 8.3.2). This led to formation of a surface seal, reducing water infiltration, and increasing the likelihood of hortonian overland flow (see section 8.4.3). These seals dried to form crusts (Figure 7.11). It should however be noted that onset of overland flow might have been quicker in soils with high biochar content regardless of the speed of seal formation. Differences in overland flow generation may not have been caused by differences in surface infiltration capacity alone; differences in sub-surface hydraulic conductivity may have also contributed.

Overland flow was generated more rapidly in soils with high biochar contents, so the overland flow coefficients for these soils were higher than those for soils with low or zero biochar content. It can therefore be concluded that although biochar amendments may improve soil water retention by limiting drainage, they can actually reduce the amount of water that is able to infiltrate the soil in the first place. As high biochar application rates of 25 to 50 g kg^{-1} may be less effective at improving water storage than laboratory measurements of WHC might suggest. Of course, such an effect would only apply during rainfall events of sufficient intensity and / or duration to cause surface sealing or exceed the soil's hydraulic conductivity. Low application rates did not affect aggregate stability (see Chapter 8) and may therefore be capable of improving rainwater retention in soils without increasing overland flow. While Figure 7.5 indicates that such an effect may be possible, it must be acknowledged that the differences in overland flow coefficient between soils with biochar contents of 0 and 5 g kg^{-1} were not statistically significant.

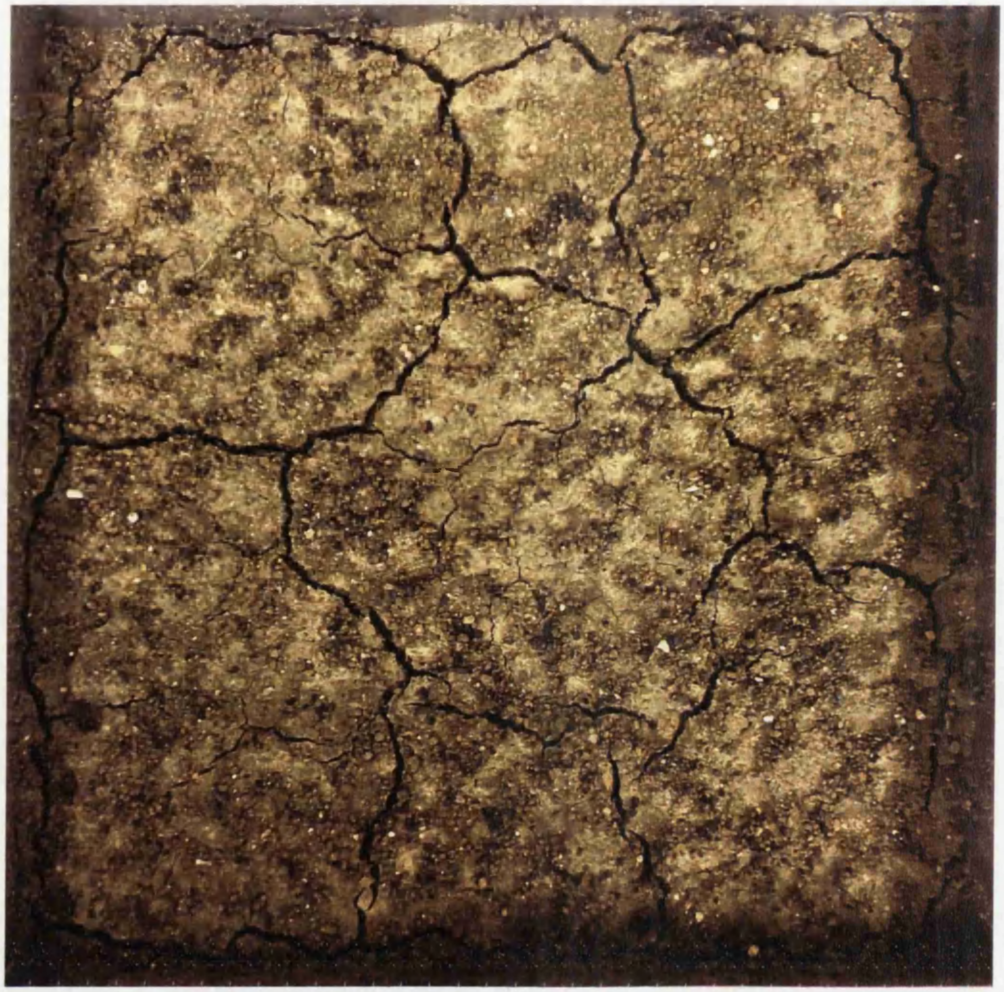


Figure 7.11: A surface crust formed by drying of a surface seal in a 300 x 300 mm soil plot with a biochar content of 25 g kg^{-1}

As Figures 7.5 – 7.10 illustrate, although application rates of 25 and 50 g kg^{-1} seemed to alter the hydrological behaviour of the soil, an application rate of 5 g kg^{-1} seemed to have little or no effect. Further research (with greater replication) is needed to confirm whether this is indeed the case and whether certain application rates represent thresholds at which the hydrological behaviour of the soil is significantly altered.

7.5 Limitations

The results of this experiment are not necessarily representative of how biochar could influence soil hydrology during natural rainstorm events. Owing to the relatively low height of the rainfall simulator used in this study, raindrops would not have reached terminal velocity before striking the soil (see section 8.4.3). As previously discussed, although the rainfall intensity used in this study would not be unusual in Mediterranean or tropical climates, it cannot be considered representative of typical rainfall events in temperate climates.

The results of these experiments largely relate to the physical effects that biochar application has on the hydrological response of bare, loose soil under rainfall. Biochar amendments can result in significantly increased root development (Prendergast-Miller *et al.*, 2013) and biochar-amended soils may be preferred by earthworms over those without biochar (Van Zwieten *et al.*, 2010). Biopores such as earthworm burrows (typically > 1mm in radius) and root channels can have a substantial influence on hydraulic conductivity (Brady & Weil, 2008). It is therefore possible that even if the physical effect of biochar application is a reduction in the hydraulic conductivity of a soil, the influence of biochar application on soil flora and fauna could counteract this effect. Furthermore, if biochar application has a beneficial or deleterious effect on above-ground biomass growth, groundcover will be affected, resulting in changes in interception of rainfall by plants with important consequences for development of surface seals and overland flow.

It must also be noted that prior to rainfall simulation, the soil samples were dried and sieved to < 5 mm. The soil aggregates were therefore to some extent artefacts of the drying and sieving process, with differences in aggregate sizes between soils of differing biochar potentially being less pronounced than they might otherwise have been. This could have influenced infiltration rates and hydraulic conductivity.

The findings of this investigation suggest that a biochar application rate of 5 g kg^{-1} would have little or no effect on the hydrological response of medium-textured soils during rainfall. Further work, with greater replication, is needed to identify a threshold application level at which biochar is likely to start to significantly influence infiltration and runoff. Equally, further work is needed to investigate the influence of biochar on coarser and finer textured soils. In more sandy soils which do not themselves form aggregates, such as that used in Chapters 5 & 6, the effect of biochar application might be very different.

7.6 Summary

Biochar application rate had no effect on soil wettability. Although retention of rainwater by the soil tended to increase with increasing application rate, overland flow was generated more quickly as biochar application rate increased. This can be attributed to higher biochar application rates causing a reduction in aggregate stability and therefore increasing the speed with which formation of surface seals began, reducing infiltration of rainwater into the soil. However, lower hydraulic conductivity may also have contributed.

Depending on the particle size used, biochar amendments can reduce bulk density and increase water retention, but their effect on aggregate stability can reduce the amount of water that is able to enter the soil. Biochar application may therefore be a less effective means of enhancing water conservation its effect on moisture retention alone might suggest. However, the effects of biochar on development of vegetation above and below ground may moderate or counteract its physical effect on the soil.

8 EFFECTS OF BIOCHAR CONTENT ON SOIL AGGREGATE STABILITY AND EROSION UNDER SIMULATED RAINFALL

8.1 Introduction

Aggregate stability and soil strength are key parameters influencing soil erodibility. Biochar additions have been shown to influence these parameters, but for all soil types the results are conflicting. Liu *et al.* (2012) reported that applying biochar (produced in a traditional charcoal mound from conifer sawdust, then sieved to < 2mm) to a silt loam at rate of 4 g kg^{-1} had no effect on aggregate stability, but increasing the application rate to 8 and 16 g kg^{-1} resulted in significant increases aggregate stability following 11 months of incubation. However, using a different silt loam, the same biochar amendments had no effect on aggregate stability (Liu *et al.*, 2012). Herath *et al.* (2013) reported that applying biochars (produced from corn stover at 350 and 500°C, with 95% of biochar particles being < 2 mm) to a silt loam at rates between 10 and 15 g kg^{-1} resulted in significant increases in aggregate stability following 295 days of incubation. Overall then, the literature suggests that amending silty soils with biochar at rates up to 16 g kg^{-1} can result either in no change in aggregate stability or an increase. However, the effect of higher biochar application rates on the aggregate stability of silty soils is unknown.

The literature on the effects of biochar on soil erosion by water is also unclear. Rumpel *et al.* (2006) reported that biochar is preferentially eroded from soil. However, data on the effect of biochar on soil erosion are scarce. Biochar amendments did not affect erosion of a sandy loam (Smetanová *et al.*, 2012), but erosion of a clayey soil was reduced with increasing biochar content (Jien & Wang, 2013). No published studies have investigated the effect of biochar application on erosion of medium-textured soils.

Few data are available on the effect of biochar amendments on soil crusting and penetration resistance. Biochar was found to reduce the penetration resistance of an acid sulphate soil (Masulili *et al.*, 2010). Busscher *et al.* (2010) found that biochar additions reduced the penetration resistance of a sandy loam soil (Busscher *et al.*, 2010), but a later experiment found that the same biochar increased the penetration resistance of the same sandy loam soil (Busscher *et al.*, 2011). To date, no studies have investigated the effect of biochar application on the penetration resistance of medium-textured soils and none has investigated the penetration resistance of structural crusts.

To address these research gaps, this study uses simulated rainfall to investigate the effect of three different biochar application rates on the aggregate stability and erosion of a silt loam under simulated rainfall, and penetration resistance once the soils were dried following rainfall simulation.

8.2 Methods

The soil and soil-biochar mixtures used in this investigation were the same as those described in Chapter 7 - biochar was produced from deciduous wood in a ring kiln and sieved to < 2 mm because this was this particle size was likely to influence soil moisture retention (see Chapter 6). The biochar was then applied to a silt loam at rates of 0, 5, 25 and 50 g kg^{-1} (see section 7.2.3). Key objectives of this experiment were to investigate the influence of different biochar application rates on aggregate stability and soil crusting following (see Chapter 8). The sandy loam soil used for the experiments in Chapters 5 and 6 did not readily form aggregates, so a silt loam was used instead because it readily formed aggregates, was friable and because soils dominated by silt fractions are particularly susceptible to sealing and subsequent crusting (Gabriels *et al.*, 1998). Using a silt loam thus increased the likelihood of differences in soil aggregate stability, sealing and crusting being observed with different biochar application rates. The experiments described below were conducted after the soils had been incubated for 250 days at 30% of WHC in a darkened constant temperature room at 21°C. This incubation period was chosen to provide as much time as possible for the formation of organo-mineral associations in the soil-biochar mixtures (see section 7.2.1), within the time limitations of the project.

8.2.1 Particle size distribution

The particle size distribution of each soil or soil-biochar mixture was measured using laser diffraction (Malvern Mastersizer 2000, Malvern Instruments Ltd., UK). Forty replicate measurements were made for each application rate.

8.2.2 Aggregate stability

Three subsamples of 100 g were removed from each container (a total of 9 samples for each biochar application rate), dried at 45°C and sieved to obtain the 3.35 - 4 mm fraction for determination of aggregate stability by rainfall simulation (Le Bissonnais, 1996a). Around 10 g of each subsample were weighed out and evenly spread out on a 500 μm sieve. The sieve was placed 1.5 m below the droplet box of a rainfall simulator (described in Chapter 7) and rainfall was simulated for two minutes. The rainfall intensity was measured for 1 minute immediately before and after each 2-minute simulation by measuring the water collected in an 800 x 800 mm V-shaped tray above the sieve. The sieve and the soil remaining in it were then dried at 45°C and the soil aggregates retained in the sieve were sieved again to obtain the fraction > 3.35 mm. This fraction was weighed to enable calculation of the percentage of aggregates that were destroyed.

8.2.3 Electrical conductivity and pH

Electrical conductivity and pH were measured because they can influence aggregate stability through their effect on the cohesion of colloids and clays facilitated by cations. 40 ml of de-ionised water were added to 2.0 g of soil in a centrifuge tube, which was then placed on a shaker for 1.5 hours to ensure that the biochar particle surfaces and the solution were sufficiently equilibrated (Rajkovich *et al.*, 2012). The electrical conductivity of the resultant solution was then measured using a Hanna HI 9835 conductivity meter, and pH was measured using a Camlab pH Boy 501 meter. Five replicate measurements were made for each biochar application rate.

8.2.4 Erosion under simulated rainfall

Splash and slopewash erosion from plots with differing biochar contents were measured during the rainfall simulations described in Chapter 7.

8.2.4.1 Splash erosion

A splash cup lined with filter paper (Whatman no. 541, 110 mm diameter) was positioned on each side of the soil plot (Figure 7.2). The collected sediment was oven-dried for 24 hours at 105°C and weighed.

8.2.4.2 Slopewash erosion

Overland flow was collected for 1 minute every 4 minutes throughout the 60 minute period of simulated rainfall, giving a total of 15 samples per simulation (the timings of overland flow collection differed slightly for Run 2 on soil with 0 g kg^{-1} biochar – see Table A.8.5 in appendices). The collected overland flow samples enabled subsequent determination of sediment yield and concentration, erosion rates and organic matter (OM) content. After the simulation, the collected overland flow was passed through a vacuum filter (lined with Whatman no. 541, 110 mm diameter filter paper) to obtain the sediment. The sediment was then oven-dried for 24 hours at 105°C and weighed. Total sediment yields were estimated by calculating the mean sediment yield of all 15 samples (each assumed to be representative of a 4-minute period) and multiplying this by 4.

8.2.4.3 Determination of organic matter content

Prior to rainfall simulation, 15 x 4 g subsamples were taken from throughout each sample. The organic matter contents of these samples and the collected eroded sediments were determined through loss-on-ignition (LOI). The samples were oven-dried 105°C for 24 hours, cooled in a desiccator and weighed before being heated in a muffle furnace at 750°C for 6 hours and again cooled in a desiccator for 1 hour. The mineral residue was then weighed, allowing the OM content of the sediment to be calculated from the differences in weight before and after LOI.

8.2.5 **Penetration resistance**

To assess crust formation, plots were oven-dried at 30°C for 72 hours following rainfall simulation. Grid meshes comprising 23 x 23 1.21 cm^2 sections were then placed over the plots, and penetration resistance measurements were made to a depth of 6 mm using a hand-held penetrometer (6 mm foot diameter) in every third grid square on alternate rows (Figure 8.1), giving a total of 92 measurements for each plot (Figure 8.1). Where the soil in a section to be measured had cracked during drying, or had been visibly disturbed by previous penetration resistance measurements nearby, a measurement was instead taken from the nearest section with undisturbed soil in the adjacent row.

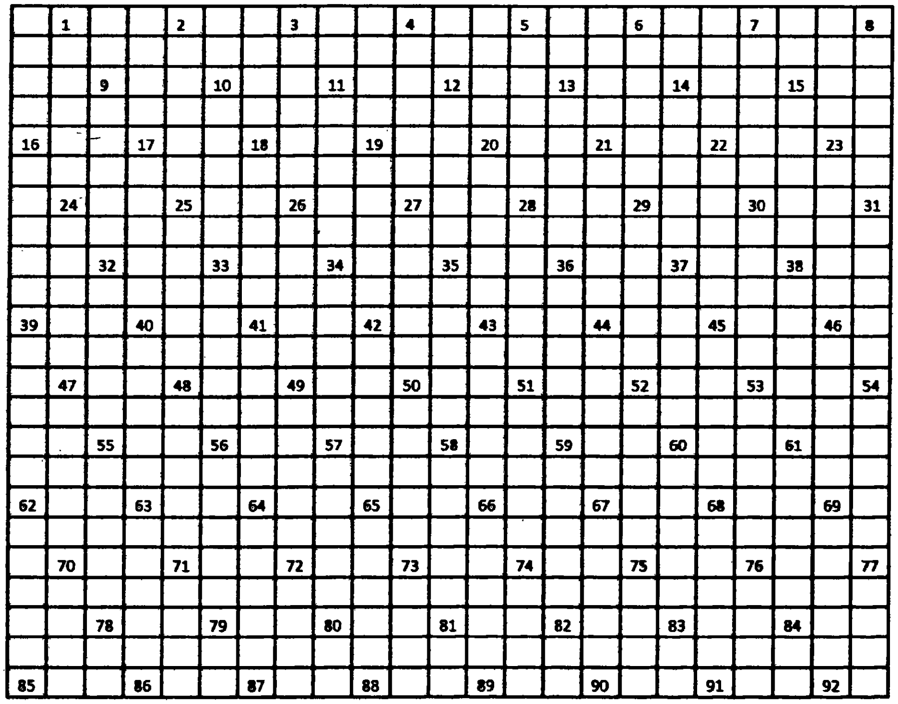


Figure 8.1: Idealised positioning of penetration resistance measurements on a soil plot

8.2.6 Statistical analyses

Kruskal-Wallis tests were used to test for overall differences between treatments (Kruskal & Wallis, 1952), and Mann-Whitney tests were used for pairwise comparisons (Mann & Whitney, 1947). Where multiple comparisons were made, significance values were adjusted using a Bonferroni correction (Dunn, 1961). Trends in the data were tested for using Jonckheere-Terpstra tests (Jonckheere, 1954). Correlation coefficients were calculated using Spearman's rho (Spearman, 1910). For a sample size *n*, the scores X_s, Y_s are converted to ranks x_r, y_r, and *p* is given by:

$$p = 1 - \frac{6 \sum d_r^2}{n\,(n^2 - 1)}$$

Where d_r represents the difference between ranks, $x_r - y_r$. Correlations were compared by first converting each coefficient to a z-score as described by Fisher (1921), then comparing these z-scores using formula 2.8.5 from Cohen & Cohen (1983, p. 54):

$$z = \frac{z^1 - z^2}{\sqrt{\frac{1}{n_1 - 3} + \frac{1}{n_2 - 3}}}$$

Except for correlation comparisons, which were calculated by hand, all statistical analyses were carried out using SPSS, though Jonckheere-Terpstra tests were partly calculated by hand due to an Error in SPSS (see section 4.2.6).

8.3 Results

8.3.1 Particle size distribution

Figure 8.2 illustrates the effect of biochar application rate on the particle size distribution of the soil. Overall, biochar application rate had a significant effect on the percentage of sand-sized particles (0.02 - 2 mm) in the soil ($H(3) = 77.62$, $p < 0.001$). Using a biochar application rate of 5 g kg^{-1} did not significantly influence the percentage of sand particles in the soil (Table 8.1). Applying biochar at a rate of 25 g kg^{-1} significantly affected the particle size distribution, increasing the sand content by 10% compared to soil without biochar additions. A biochar application rate of 50 g kg^{-1} resulted in a further statistically significant increase in the sand content of the soil; the percentage of sand sized particles in soil with 50 g kg^{-1} of biochar was 25% greater than that in unamended soil.

The percentage of silt-sized particles (0.002 - 0.02 mm) in the soil was significantly influenced by biochar application rate ($H(3) = 61.16$, $p < 0$ 0.001). An application rate of 5 g kg^{-1} did not affect the silt content relative to the unamended soil (Table 8.2). Applying biochar at a rate of 25 g kg^{-1}, however, resulted in a statistically significant reduction in silt content, which was 2% less abundant than in soils to which biochar was applied at rates of 0 or 5 g kg^{-1}. Doubling the application rate to 50 g kg^{-1} resulted in a further statistically significant reduction in the prevalence of silt in the soil by 2%.

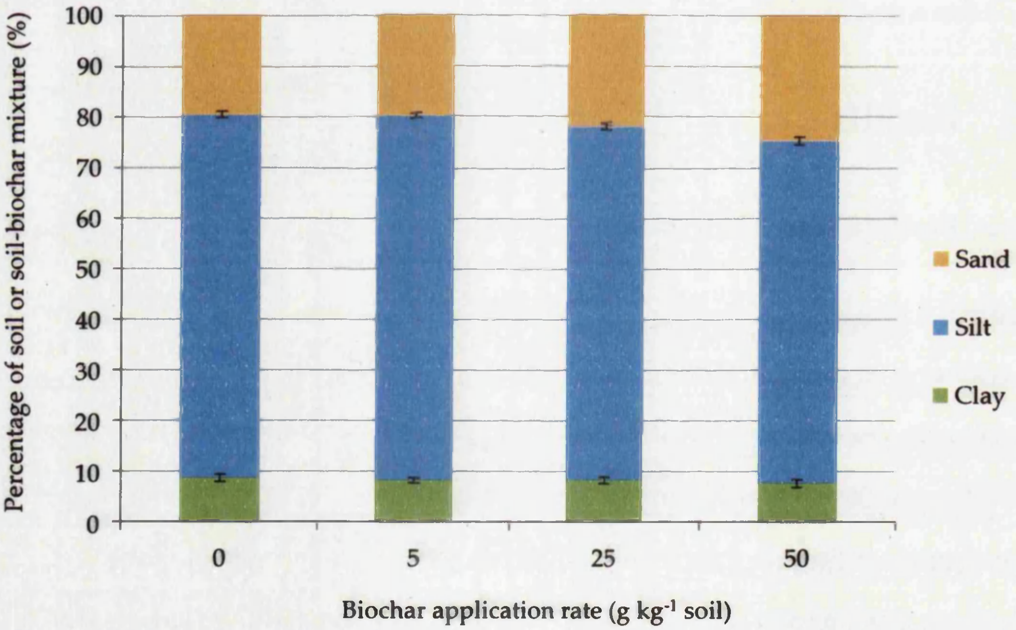


Figure 8.2: Particle size distribution of a silt loam with different biochar application rates (Error bars represent 95% CIs, n = 40)

Biochar application rate also had a significant effect on the proportion of clay-sized (< 0.002 mm) particles ($H(3) = 21.02$, $p < 0.001$). Application rates of 5 and 25 g kg^{-1} did not significantly affect the clay content of the soil (Table 8.3). However, an application rate of 50 g kg^{-1} resulted in a statistically significant reduction in clay content, reducing its prevalence by over 10% compared to unamended soil. Furthermore, there was a statistically significant trend for the clay content of the soil to decrease with increasing biochar application rate ($S = 2798$, $p < 0.001$).

Table 8.1: Tests for differences between the sand content of soil under different biochar application rates (p is 1-tailed and Bonferroni-adjusted)

Biochar application rates compared (g kg^{-1})	Mann-Whitney *U*	*p*
0 vs. 5	697.0	0.486
0 and 5 vs. 25	694.0	< 0.001
25 vs. 50	284.0	< 0.001

Table 8.2: Tests for differences between the silt content of soil under different biochar application rates (p is 2-tailed and Bonferroni-adjusted)

Biochar application rates compared (g kg^{-1})	Mann-Whitney *U*	*p*
0 vs. 5	770.0	1.000
0 and 5 vs. 25	819.0	< 0.001
25 vs. 50	351.0	< 0.001

Table 8.3: Tests for differences between the clay content of soil under different biochar application rates (p is 2-tailed and Bonferroni-adjusted)

Biochar application rates compared (g kg^{-1})	Mann-Whitney *U*	*p*
0 vs. 5	674.0	0.693
0 and 5 vs. 25	1410.0	0.876
0, 5 and 25 vs. 50	284.0	< 0.001

8.3.2 Aggregate stability

Biochar application rate had a significant effect on the aggregate stability of the silt loam ($H(3) = 23.58$, $p < 0.001$). An application rate of 5 g kg^{-1} had no effect on aggregate stability (Figure 8.3); as with the control treatment, 30% of aggregates were destroyed per millimetre of rainfall. An application rate of 25 g kg^{-1} significantly reduced aggregate stability (Table 8.4), with ~34% of aggregates destroyed per millimetre of rainfall. Doubling the application rate to 50 g kg^{-1} did not result in any further statistically significant reduction in aggregate stability (Table 8.4), but there was a significant overall trend for aggregate stability to decrease with increasing application rate ($S = 334$, $p < 0.001$).

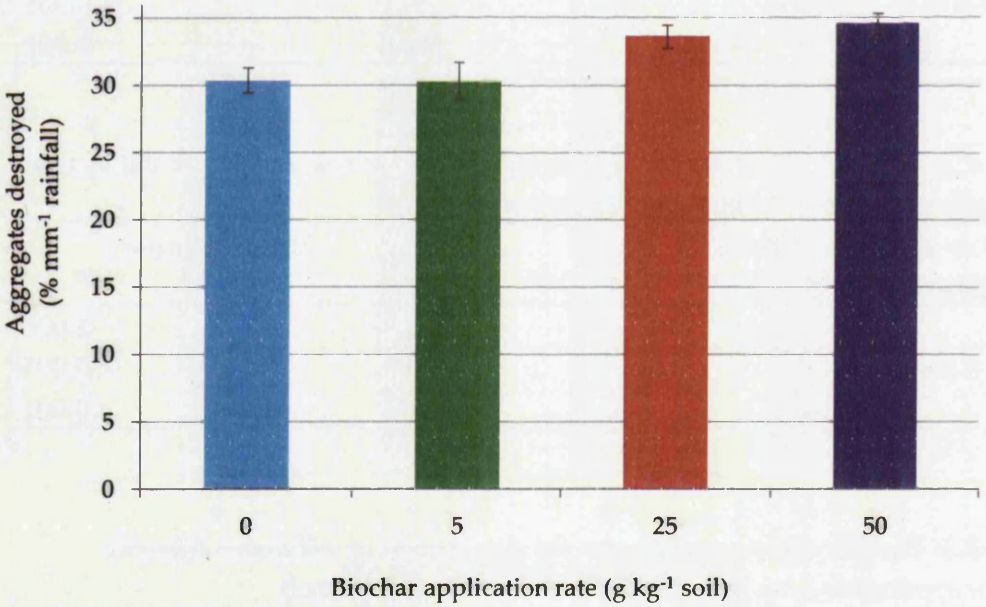


Figure 8.3: Destruction of aggregates under simulated rainfall (Error bars represent 95% CIs, n = 9)

Table 8.4: Tests for differences between aggregate stability of soil at different biochar application rates (p is 1-tailed and a Bonferroni adjustment has been applied)

Biochar application rates compared (g kg^{-1})	Mann-Whitney *U*	*p*
0 vs. 5	37.0	1.000
0 and 5 vs. 25	11.0	< 0.001
25 vs. 50	19.0	0.18

8.3.3 Electrical conductivity

The ECs of soils containing biochar were higher than that of soil without biochar additions, but these differences were not statistically significant ($H(3) = 6.11$, $p = 0.106$).

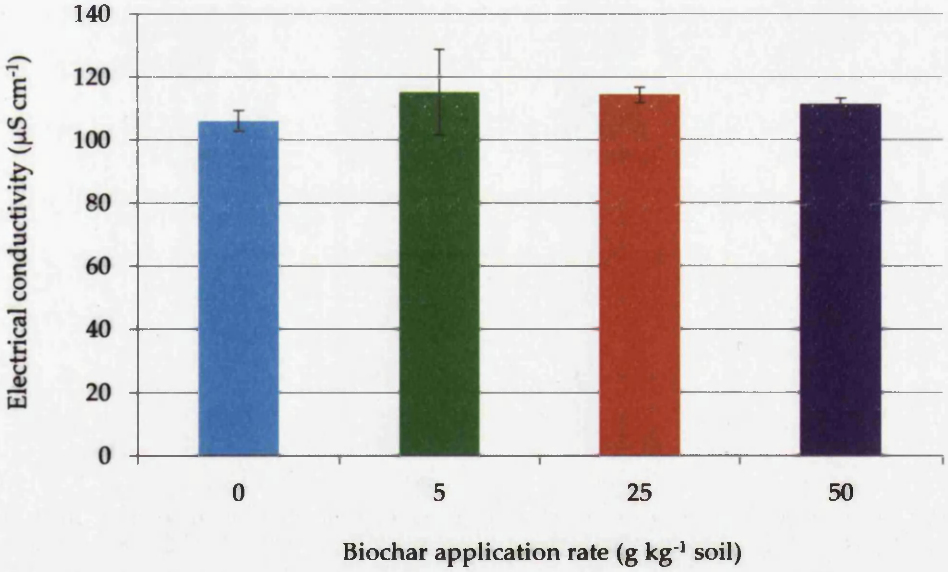


Figure 8.4: Electrical conductivity of soils of differing biochar content (Error bars represent 95% CIs, n = 5)

8.3.4 pH

Significant differences were observed between the pH values of soils of differing biochar content ($H(3) = 16.24$, $p < 0.001$). As Figure 8.5 illustrates, biochar application rates of 5 and 25 g kg^{-1} resulted in small but statistically significant changes in the mean pH of the soil, increasing it to 0.11 and 0.18 respectively (Table 8.5). The differences in pH between soils under biochar application rates of 5 and 25 g kg^{-1} were not statistically significant. However, increasing the application rate to 50 g kg^{-1} resulted in a further small but statistically significant increase in mean pH to 8.18 (Table 8.5).

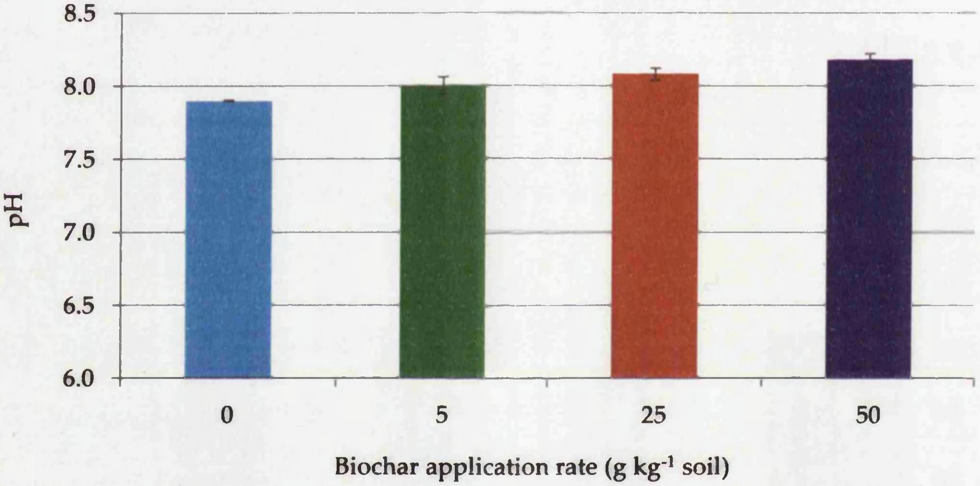


Figure 8.5: pH of soils under different biochar application rates (Error bars represent 95% CIs, n = 5)

Table 8.5: Tests for differences between pH of soils of differing biochar contents (p is 1-tailed and Bonferroni-adjusted)

Biochar application rates compared (g kg^{-1})	Mann-Whitney *U*	*p*
5 vs. 25	4.5	0.249
5 and 25 vs. 0	2.5	0.006
5 and 25 vs. 50	2.5	0.006

8.3.5 Splash erosion

Figure 8.6 shows that biochar application rate did not influence the total mass of sediment eroded from the plots by splash erosion ($H(3) = 1.106$, $p = 0.292$).

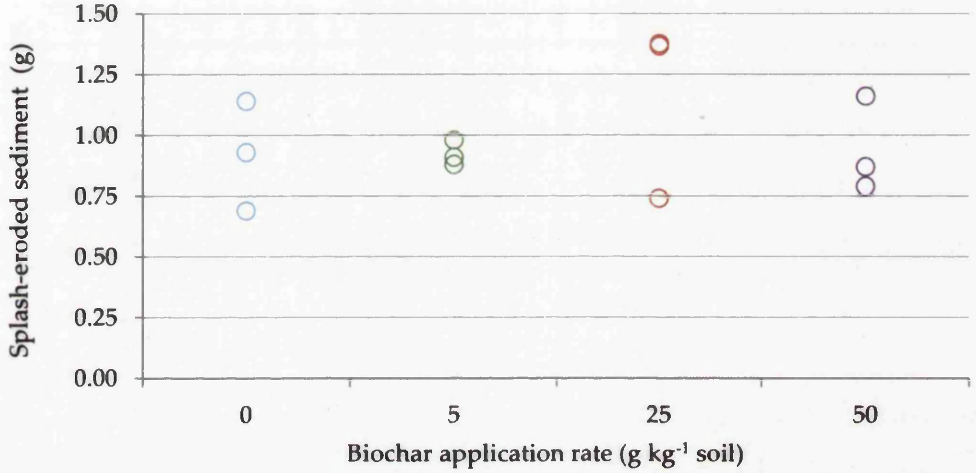


Figure 8.6: Total collected splash-eroded sediment during simulated rainfall from soils under different biochar application rates

8.3.6 Slopewash erosion

As Figure 8.7 illustrates, there was a statistically significant trend for slopewash erosion to be generated more quickly as biochar content increased ($S = 24$, $p = 0.042$). For plots with biochar contents of 0 and 5 g kg^{-1}, the median rainstorm duration before any recorded erosion was 24 minutes, for 25 g kg^{-1} plots the median time was 20 minutes, and for 50 g kg^{-1} plots it was 16 minutes.

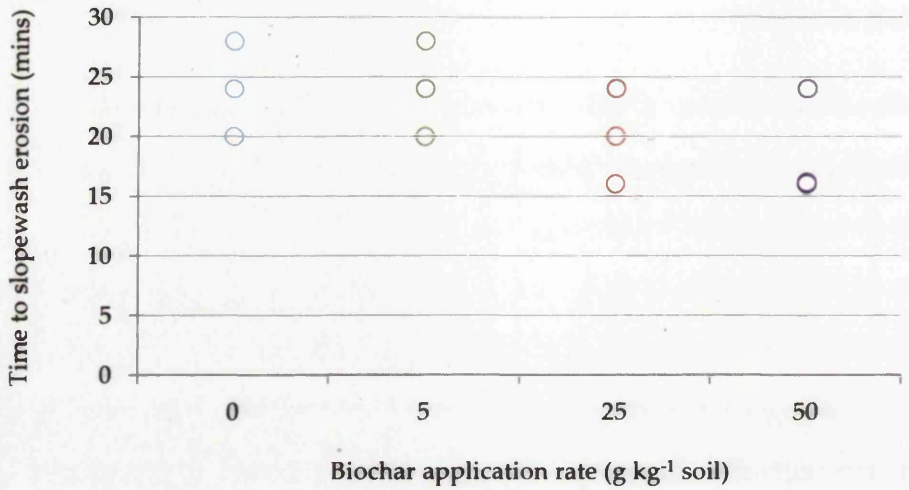


Figure 8.7: Time to onset of slopewash erosion

As Figure 8.8 demonstrates, biochar application rate did not influence the estimated total amount of slopewash erosion from soil plots in absolute terms ($H(3) = 1.77$, $p = 0.669$). Biochar content did not affect estimated total erosion per unit volume of overland flow either ($H(3) = 3.31$, $p = 0.385$).

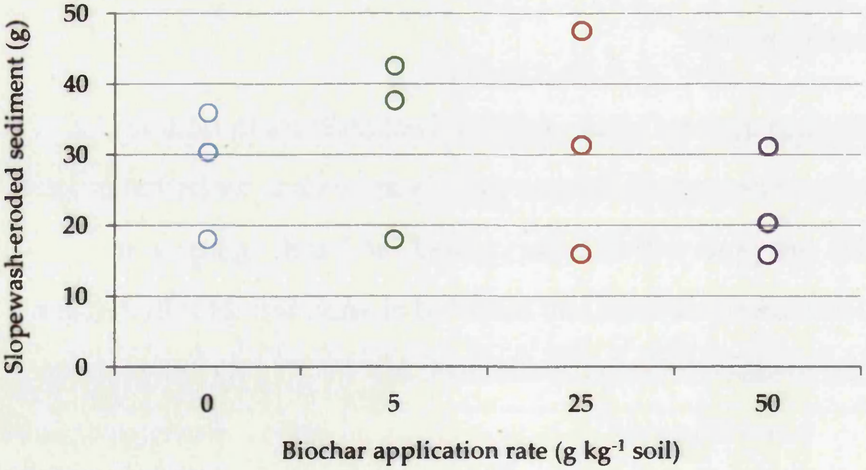


Figure 8.8: Estimated total slopewash erosion from soils under different biochar application rates

Figure 8.9 illustrates how the strength of the correlation between rainstorm duration and the amount of erosion (per minute) was reduced with each increase in biochar application rate (Table 8.7). For plots with a biochar content of 5 g kg^{-1}, the correlation was similar to that for plots with no added biochar (Table 8.8). The correlation for soil plots with biochar contents of 50 g kg^{-1} was significantly weaker than the correlation for soil plots without biochar (Table 8.8). There were no statistically significant differences in the correlations between overland flow volume and erosion for soils of differing biochar content.

Table 8.6: Correlations between rainfall duration and erosion

Biochar content of soil (g kg^{-1})	n	Spearman's rho	*p*
0	45	0.884	< 0.001
5	45	0.827	< 0.001
25	45	0.782	< 0.001
50	45	0.730	< 0.001

Table 8.7: Comparisons of correlations between rainstorm duration (mins) and erosion rate (g min^{-1}) in soils of differing biochar content (p is 1-tailed and Bonferroni-adjusted)

Biochar content of soil (g kg^{-1})	z	*p*
0 vs. 5	0.986	1.000
0 vs. 25	1.573	0.174
0 vs. 50	2.152	0.050

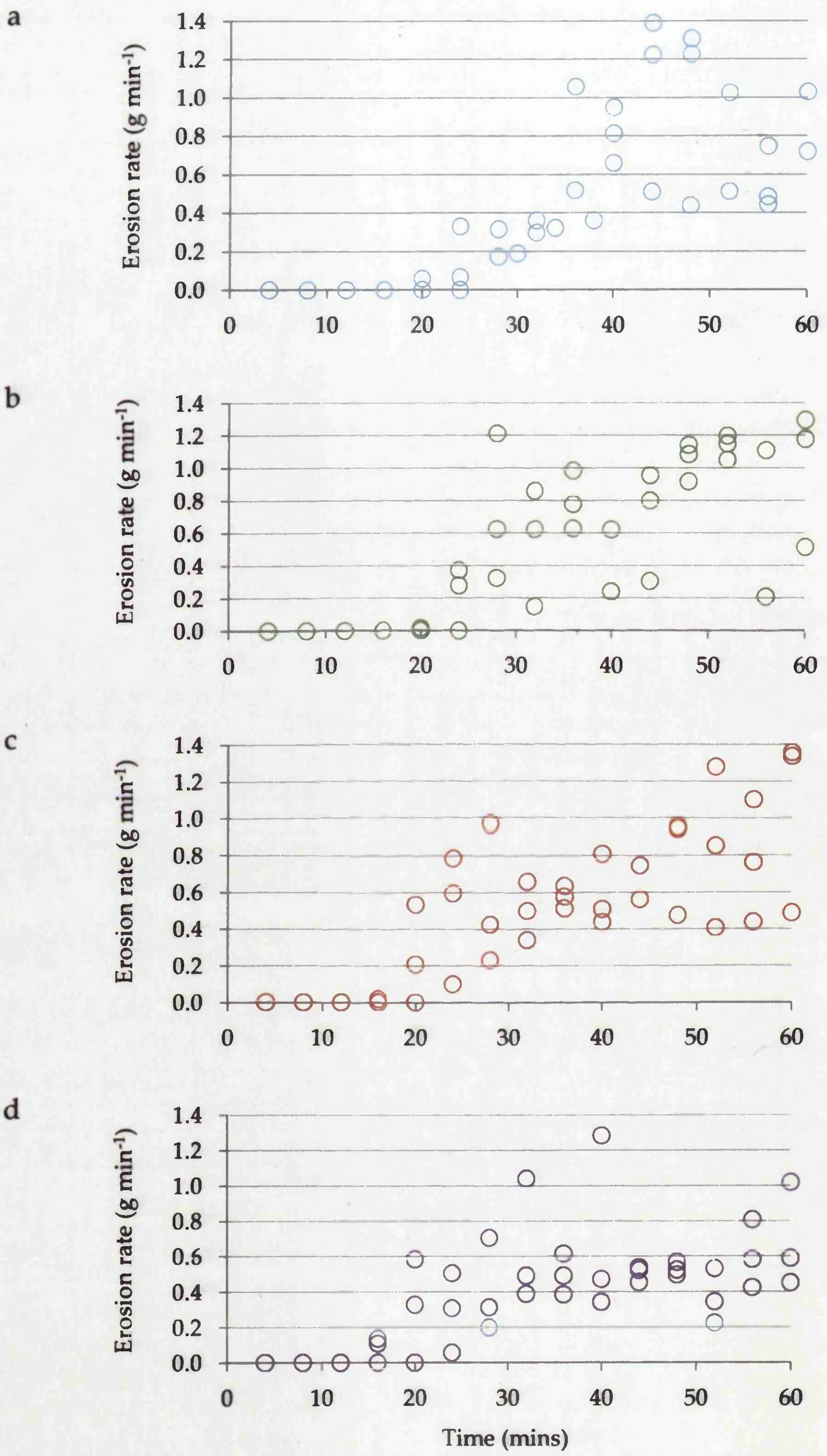


Figure 8.9: Slopewash erosion rates during rainfall simulations for soils with biochar contents of (a) 0 g kg^{-1}, (b) 5 g kg^{-1}, (c) 25 g kg^{-1} and (d) 50 g kg^{-1}.

8.3.7 Organic matter content of eroded sediments

There were significant differences between different biochar application rates in terms of how the OM contents of splash-eroded sediments differed from the OM contents of the plot soils (*H*(3) = 7.31, *p* = 0.033). As Figure 8.10 illustrates, the OM contents of splash-eroded sediments from plots without biochar additions were not significantly different from the OM contents of the soils in the plots themselves. However, for plots with biochar application rates of 5, 25 and 50 g kg^{-1}, the mean OM contents of splash-eroded sediments were, respectively, 163, 119 and 94% higher than the OM contents of the plots themselves (Figure 8.10). These differences were statistically significant (in each case, *U* = 0.00, *p* = 0.05).

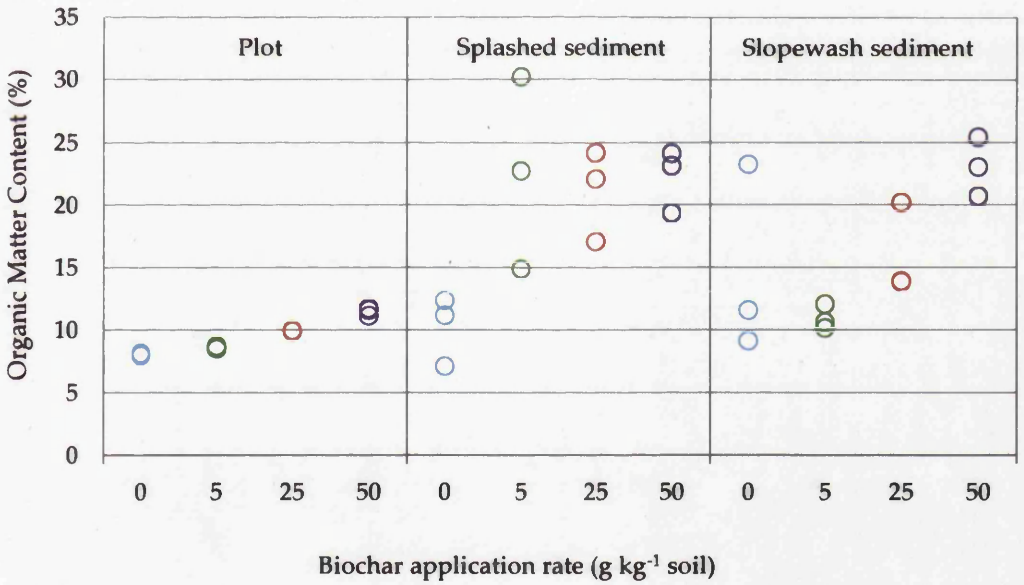


Figure 8.10: The effect of biochar application rate on the organic matter content of soils and eroded sediments

As Figure 8.10 illustrates, for all biochar application rates (including 0 g kg^{-1}), the OM contents of slopewash sediments were significantly higher than the

OM contents of the plots from which they were eroded (in each case, U = 0.00, p = 0.05). However, there were no statistically significant differences between different biochar application rates in terms of how the OM contents of slopewash sediments differed from the OM contents of the plots ($H(3)$ = 4.74, p = 0.209).

8.3.8 Penetration resistance

As Figure 8.11 illustrates, biochar application rate had a significant effect on the penetration resistance of soil ($H(3) = 398.91$, $p < 0.001$). The penetration resistance of soil with a biochar content of 5 g kg^{-1} did not significantly differ from that of the control treatment; both soils had a mean penetration resistance of ~0.8 kg^{-1} force cm^{-2}. Applying biochar at a rate of 25 g kg^{-1} reduced penetration resistance by one-quarter, to 0.61 kg^{-1} force cm^{-2}, but there was no further reduction in penetration resistance when the biochar application rate was increased to 50 g kg^{-1}.

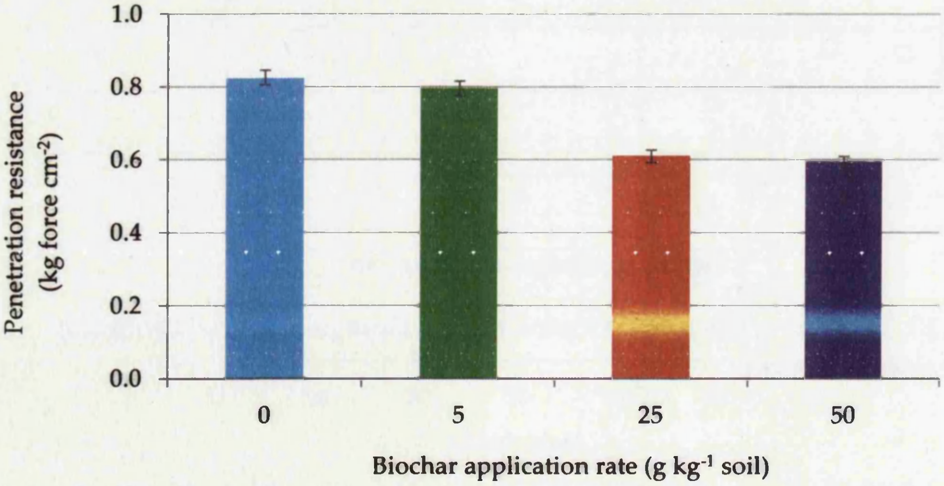


Figure 8.11: The effect of biochar application rate on soil penetration resistance (Error bars represent 95% CIs, n = 276)

Table 8.8: Comparisons of penetration resistance between soils of differing biochar content (p is 1-tailed and Bonferroni-adjusted)

Biochar content of soil (g kg^{-1})	Mann-Whitney U	p
0 vs. 5	34,737.0	0.228
0 vs. 25	11,618.0	< 0.001
0 vs. 50	9,314.0	< 0.001
5 vs. 25	14,350.0	< 0.001
5 vs. 50	12,084.5	< 0.001
25 vs. 50	36,330.0	1.000

8.4 Discussion

8.4.1 Aggregate stability

In the present study, 5 g kg^{-1} of biochar did not significantly affect aggregate stability. This corresponds to the finding of Liu *et al.* (2012) that biochar application rates up to 4 g kg^{-1} did not affect aggregate stability in either of the two silt loam soils they studied. The reductions in aggregate stability associated with higher biochar application rates (25 and 50 g kg^{-1}) observed in the present study are somewhat in contrast with the findings of previous studies which reported either no change or significant increases in the aggregate stability of silt loam soils with biochar application rates between 8 and 16 g kg^{-1} (Liu *et al.*, 2012; Herath *et al.*, 2013). The application rates used in the present study were substantially higher than those used by Liu *et al.* (2012) and Herath *et al.* (2013). It is possible that aggregate stability is unaffected by low biochar application rates, then increases with increasing application rate up to a certain point, after which further increases in application rate result in decreases in aggregate stability. The findings of the present study are not necessarily comparable however with those of Liu *et al.*

(2012) and Herath *et al.* (2013), who incubated their soil-biochar mixtures in open containers for around 11 and 10 months respectively. The soil-biochar mixtures in the present study were incubated for a shorter period of time (~8 months) in lidded containers (which were occasionally aerated), meaning that there may have been less oxidation of biochar particle surfaces than in the studies conducted by Liu *et al.* (2012) and Herath *et al.* (2013). Compared to those studies, limited oxygen availability in the present study could have diminished the potential for: (i) increases in aggregate stability arising from microbially-produced polysaccharides; and (ii) organo-mineral associations between biochar and soil particles promoted by the formation of carboxylic and phenolic functional groups on biochar surfaces (Glaser *et al.*, 2000; Lin *et al.*, 2006). As such, the findings of the present study may only be indicative of the effects of biochar on soil hydrology and erosion relatively soon after application.

It should however be remembered that the biochar in the present study was initially stored for 12 months in a heated greenhouse to enhance oxidation of its surfaces. If there was indeed little formation of functional groups on biochar particles in the present study, it is likely that the particles which were hydrophobic (see section 7.3.1) would have remained so after incubation (Cheng *et al.*, 2006). Decreasing the wettability of soil aggregates can enhance their stability (Chenu *et al.*, 2000), which suggests that hydrophobic biochar particles at the surface of aggregates may promote aggregate stability. However, the effect of hydrophobic particles within otherwise wettable soil aggregates has not been investigated. It is possible that hydrophobic biochar particles within otherwise wettable aggregates contribute to aggregate break-up by repelling water, causing dispersion of adjacent soil particles.

Reductions in aggregate stability arising from high biochar application rates may be attributable to substantial changes in the soil's particle size distribution caused by biochar 'displacing' the original soil, particularly the clay fraction, with larger sized particles. Clay particles have an important aggregation and bonding effect, but sand is more easily detachable (Le Bissonnais, 1996b; Brady & Weil, 2008). Coarser textured soils tend to have lower aggregate stability as they have less clay and silt to bind larger, sand-sized particles together (Skidmore & Layton, 1992). In silty soils, aggregate stability decreases with decreasing clay content (Le Bissonnais, 1988). A biochar application rate of 5 g kg^{-1} did not significantly affect the aggregate stability of the soil; this can be attributed to the fact that this application rate was too low to make any substantial difference to the particle size distribution of the soil. Conversely, at application rates of 25 and 50 g kg^{-1}, there were substantial declines in clay content and increases in sand content which may have caused the substantial reductions in aggregate stability. An application rate of 25 g kg^{-1} increased the sand content of the soil by 10% and reduced the aggregate stability by 11%. An application rate of increased the sand content of the soil by 25% and reduced the soil's aggregate stability by 14%.

Further research is needed to determine whether threshold application rates exist, above which the influence of biochar amendments (of a certain particle size distribution) on the particle size distribution of the soil begins to affect aggregate stability significantly (where there is little oxidation of the biochar surfaces). For example, it may be the case that finer biochar particle size fractions than were used in this study have less effect on aggregate stability, or even increase it, if they increase the clay content of a soil.

Soil pH increased with increasing biochar application, which would have had the effect of increasing CEC through an increase in pH-dependent charges (Brady & Weil, 2008), increasing the ability of bivalent cations (such as calcium ions) to act as bridges between organic colloids and clays (Shainberg & Levy, 1996). However, although the effects of increasing biochar application on soil pH were statistically significant, they were small. It is therefore assumed that any effect of biochar application increasing soil pH and therefore aggregate stability was outweighed by its effect on particle size distribution. The influence of biochar on soil pH may have greater implications for aggregate stability in more acidic soils.

Although sodium increases the tendency of aggregates to slake, other soluble salts can help prevent dispersion of soil colloids (Goldberg *et al.*, 1988; Brady & Weil, 2008). It is therefore possible that increasing salinity with increasing biochar application rate (inferred from increasing electrical conductivity) could have moderated to some extent the effect of biochar in altering the particle size distribution of the soil, thereby reducing aggregate stability. However, although biochar additions increased the electrical conductivity of the soil, the increases were not statistically significant. On the other hand, neither the exchangeable sodium percentage nor the sodium adsorption ratio were measured, thus the possibility that increasing salinity with increasing biochar application rate contributed to reductions in aggregate stability cannot categorically be ruled out. However, the Na content of biochar tends to be low compared to the combined contents of Ca and Mg (Enders & Lehmann, 2012), the ions of which moderate the adverse effects of Na ions (Brady & Weil, 2008). Moreover, it should be noted that none of the soil or soil-biochar mixtures used in this study was particularly saline (all were far below the 4000 μS cm^{-1} threshold commonly used to define soils as saline) and the differences in salinity between soils of differing biochar content were small. It therefore seems unlikely that the influence of biochar application on soil salinity had a substantial effect on aggregate stability either way. For biochars of higher salt or cation content (Bird *et al.*, 2011, Yuan *et al.*, 2011) high application rates could have a more substantial influence on aggregate stability. However, as salts and cations are progressively leached from the soil, such effects may not be important in the long-term (Lehmann *et al.*, 2011).

Under field conditions, the effect of biochar amendments on aggregate stability will be more complex. Biochars may promote aggregation through their effect on soil biota such as fungi (see Chapter 4). Earthworms can assist aggregate formation through the formation of worm casts and although some studies have observed earthworm avoidance of biochar-amended soils, others have observed earthworm preference for biochar-amended soils (see section 3.7). Root growth has a positive effect on aggregate stability (Reid & Goss, 1981), so the effect of biochar amendments on plant root development will also be important. Furthermore, these experiments were conducted on bare soils; where vegetation is present to intercept rainfall and overland flow, the effects of biochar application on aggregate stability, overland flow and erosion may be different. Moreover, biochar will be incorporated into soil aggregates much more slowly if it is not mixed with the soil as it was in the present study. If biochar is applied via top-dressing, drilling or deep-banding for example, it will exist as horizontal or vertical layers within the soil profile, becoming mixed with the surrounding soil only through subsequent tillage or bioturbation.

8.4.2 Water erosion

Applying biochar at a rate of 5 g kg^{-1} did not affect the rapidity slopewash erosion initiation because it did not affect aggregate stability, which meant the speed of surface sealing and subsequent onset overland flow were also unchanged. As biochar application rates of 25 and 50 g kg^{-1} did significantly reduce aggregate stability, surface sealing occurred more rapidly. This resulted in quicker onset of overland flow, meaning that slopewash erosion also began more quickly.

Although slopewash erosion began sooner in plots with higher biochar content, there was no difference between different biochar application rates in terms of the (estimated) total amount of soil eroded over one hour of rainfall. These findings resemble those of Smetanová *et al.* (2012), who found that adding biochar of an unspecified particle size at rates of 5 and 10% (by volume) to a sandy loam soil had no significant effect of sediment yields during rainfall simulation. However, the findings of the present study contrast with those of Jien & Wang (2013), who found that applying biochar ground to < 2 mm to a silty clay soil at a rate of 25 g kg^{-1} reduced soil erosion rates by around 50%, while an application rate of 50 g kg^{-1} reduced erosional losses by nearly two-thirds. This contrast may be related to the effect of biochar application on soil pH. The soil studied by Jien & Wang (2013) was acidic, but biochar application had a substantial liming effect, which could have enhanced aggregate stability (Shainberg & Levy, 1996; Brady & Weil, 2008). Conversely, although in the present study biochar application increased soil pH, the effect was very small (as the unamended soil already had a relatively high pH) and thus unlikely to significantly influence aggregate stability, so other factors were more important.

The relationship between rainstorm duration and erosion rate became weaker as biochar content increased, indicating that while short rainfall events may result in more erosion in soils with high biochar content (25 or 50 g kg^{-1}) at the beginning of rainfall events or during short rainfall events, as rainfall duration increases, it becomes more likely that the total amount of erosion will be similar regardless of the biochar content of the soil. The weaker correlation between rainfall duration and slopewash erosion in soils with high biochar contents can be attributed to the fact that these soils were less responsive to higher volumes of overland flow than soils with low (5 g kg^{-1}) or zero biochar content. This may be because lower aggregate stability enabled more rapid reorganisation of aggregates into a complete surface seal than in soils with low / no biochar content. Partial seal formation would lead to generation of overland flow, which could cause erosion. However, as sealing becomes more complete, it can reduce soil erodibility (Römkens *et al.*, 2001). In near-saturated soils, sealing affords a protective layer of dense material, increasing shear strength such that shallow overland flows are unable to erode the soil (Bradford *et al.*, 1987; Neave & Rayburg, 2007). Moreover, fewer loose particles are available for transport by saltation due to raindrop impact dispersing aggregates then compacting the resultant loose material (Smith *et al.*, 1990).

A further factor to consider is that at 0.4 m^2 scale examined here, few erosion processes are active because plots are too small for overland flow to form eroding rills (Rumpel *et al.*, 2006). Consequently, slopewash erosion was largely limited to transporting sediments already detached by raindrops. No significant differences were observed in the amount of sediment eroded by splash, making it unlikely that there could be differences in slopewash erosion. At field scale however, the effect of biochar on aggregate stability (which accelerated the formation of structural seals) could have resulted in increased erosion as a result of increased overland flow. Nonetheless, the relationships between surface sealing and fluvial erosion are usually more complicated than those between sealing and overland flow generation; either a positive or negative relationship between seal development and erosion is possible (Neave & Rayburg, 2007).

It should be remembered that amounts of splash and slopewash erosion were measured by weight rather than by volume. Biochar particles are light compared to soil particles of a similar volume. Therefore, even if the weight of eroded sediment from plots containing biochar was similar to the weight of sediment from plots without biochar, there might have been substantial differences in the volume of sediment eroded from plots with differing biochar contents.

The present study confirms the finding of Rumpel *et al.* (2006) that biochar itself is preferentially eroded. The OM contents of sediments eroded by splashing from biochar amended plots were significantly higher than that of the plots themselves, but for soil without biochar additions there was no significant difference. The mean OM content of splash-eroded sediment from soil plots without biochar was 26% higher than the OM content of the plots themselves, but for plots with biochar additions the differences were 3 to 6 times greater. This can be attributed to preferential erosion of biochar, which can be explained by its low specific gravity, meaning less energy is required to transport a biochar particle than a typical soil particle of the same size (Kookana *et al.*, 2011), and its hydrophobicity.

Hydrophobic particles are preferentially eroded because a greater proportion of them are ejected from the soil surface by splashing than is the case for hydrophilic particles, and they also travel further than hydrophilic particles once ejected (Ahn *et al.*, 2013). As explained above, overland flow erosion would have been largely limited to transporting sediment detached by rainsplash, so differences in the OM content of slopewash sediments reflected those of splash-eroded sediments. The data suggest however that preferential erosion of biochar was less prevalent in slopewash sediment than in rainsplash sediment. This is presumably because a substantial proportion of the biochar available at the soil surface was removed from the soil plot by splashing prior to commencement of overland flow. It can therefore be assumed that at the field-scale, preferential erosion of biochar by overland flow would not be less important than preferential erosion by splashing.

Preferential erosion of biochar could result in there being more erosion from soil with higher biochar contents compared to soils with lower biochar contents. Such an effect was not observed in this study, but this may be because the amounts of sediment eroded were assessed by mass rather than by volume. Biochar has a low bulk density, so even if a large volume of it was eroded, the mass of that volume of biochar sediment would be lower than an equivalent volume of soil sediment. In future work investigating erosion of biochar-amended soils, erosion rates should be determined by both mass and volume.

As the present study was conducted on an unburned, wettable soil with a relatively shallow incline (5°), it demonstrates that preferential erosion of biochar is not limited to the distinctive conditions (burned soils on steep slopes, containing extremely high biochar contents) investigated by Rumpel *et al.* (2006). The preferential erosion of biochar may have significant implications for its potential as a means of greenhouse gas removal. In their modelling work to estimate potential of biochar for climate change mitigation, Woolf *et al.* (2010) assumed a maximum biochar application to the top 0.15 m of agricultural soils of 50 t C ha^{-1}. However, if biochar is preferentially eroded from agricultural soils, biochar may well be reapplied if maintaining a certain biochar concentration is desirable for agronomic purposes. Preferential erosion of biochar could therefore stimulate ongoing demand for biochar production and thus influence its potential for greenhouse gas removal. Although some eroded biochar might accumulate in depressions, much of it could be expected to reach waterways and potentially be transported to the deep ocean, storing carbon for millennia (Masiello & Druffel, 1998).

In the present study biochar was thoroughly mixed with the soil; preferential erosion of biochar will to some extent be dependent on the application method used. For example, if biochar were to be applied by top-dressing, it would probably be even more susceptible to preferential erosion than the findings of the present study suggest, particularly if the biochar were to be hydrophobic, as it would be completely exposed at the soil surface, with no protection from other soil particles. Conversely, if biochar were to be applied by deep-banding, it would be well protected from erosive forces by the soil above it.

8.4.3 Penetration resistance

Soils that are susceptible to sealing and subsequent crusting are typically dominated by fine sand or silt (Valentin & Bresson, 1992). Biochar application rates of 25 and 50 g kg^{-1} reduced by displacement the proportion of silt-sized particles in the soil and increased the proportion of larger, sand-sized particles in the soil. This may have resulted in an increase in the average pore size at the soil surface, reducing penetration resistance (Brady & Weil, 2008). Differences in particle size distribution arising from biochar application would have affected the extent to which particles bound to each other in a single layer in a similar manner to that of aggregate formation. Interestingly, the aggregate stability of soil with biochar applied at a rate of 25 g kg^{-1} was significantly higher than at 50 g kg^{-1}, but there was no significant difference between the strength of the crusts developed following rainfall. As biochar amendments increased water retention, their effect of reducing penetration resistance could be even greater in a field situation. The effect of biochar in reducing crust strength could therefore be a significant benefit promoting its adoption as a soil conditioner.

However, the mean penetration resistance of the unamended soil was 0.82 kg-f cm^2, less than 10% of that necessary to retard seedling emergence (Cass, 1999), so further research is needed to determine whether biochar can effectively reduce penetration resistance when the latter is critically high. Moreover, due to their lower aggregate stability, the soils with higher biochar content in this study were more susceptible to sealing (and subsequent crusting) in the first place, even though their crusts were less severe. On the other hand, the rainfall intensity used in this study was high, and differences in aggregate stability could have been less important had rainfall intensity been lower. Nonetheless, the relatively high rainfall intensity used in this study would have been countered to some extent by the low velocity of drops compared to real rainfall. Although < 1 mm diameter water drops will attain 95% of their terminal velocity within a 2 m falling distance, for drops > 1 mm the required distance increases rapidly; a 2 mm diameter drop requires 5.6 m falling distance to reach terminal velocity (Van Boxel, 1997). Drop-size distribution was not determined for this study, but Clark & Walsh (2007) used identical drop-formers to generate rainfall intensities of 160 and 200 mm h^{-1} and found that most drops were < 1 mm, while drops of 4 - 5 mm diameter were volumetrically more important (it should be acknowledged that these drop-size distributions were calculated under tropical conditions; drop-size distributions may be different in temperate conditions.) The falling distance in this study was 1 – 1.5 m it can be assumed that many of the droplets would have failed to reach terminal velocity before impacting the soil, especially when compared to raindrops in a genuine rainfall event. Finally, it should be noted that it is possible that in the present study, there was limited oxidation of the biochar surfaces during incubation (see section 8.4.1). The effect of biochar on crust formation may be different when the biochar is more fully weathered.

8.5 Limitations

The incubation method and period used in this study may have limited oxidation of biochar particles compared to the approaches used by Liu et al. (2012) and Herath et al. (2013), making direct comparison between studies difficult. If oxidation of biochar particle surfaces was limited by the incubation method adopted, the findings of the present study might only relate to the effects of biochar on soil hydrology and erosion relatively soon after application. The most likely explanation for the effect of biochar additions on aggregate stability (and therefore, erosion) is that the amendments altered the particle-size distribution of the soil. The effects of biochar application on aggregate stability observed in this study are therefore likely to be specific to some extent to (i) the particle size distribution of the biochar used and (ii) the particle size distribution of the soil to which the biochar was applied.

Under field conditions, the effect of biochar amendments on aggregate stability will be more complex than the interactions observed in this laboratory study. Biochars may promote aggregation through their effect on soil biota and as root growth has a positive effect on aggregate stability, the effect of biochar amendments on plant root development will also be important. These experiments were conducted on bare soils but where vegetation is present to intercept rainfall and overland flow, the effects of biochar application on aggregate stability, overland flow and erosion may be different. Moreover, it should be noted that biochar will be incorporated into soil aggregates much more slowly if it is not mixed with the soil as it was in the present study. If biochar is applied via top-dressing, drilling or deep-banding for example, it will be present as horizontal or vertical layers within the soil profile, becoming mixed with the surrounding soil only through subsequent tillage or bioturbation.

Although biochar additions significantly decreased penetration resistance, the penetration resistance of unamended soil was not high enough to limit seedling emergence anyway. Further research is needed to determine whether biochar additions could effectively reduce penetration resistance in soils where penetration resistance is sufficiently high to limit seedling emergence.

It should be noted that at the 0.4 m^2 scale examined in this study, few erosion processes are active because plots are too small for overland flow to form eroding rills. Runoff was thus limited to transporting soil detached by splashing. At larger scales, where sediment is also eroded by runoff, preferential erosion of biochar and differences in erosion rates between soils of differing biochar content may be greater.

The rainfall intensity used in this study was high; differences in aggregate stability could have been less important had rainfall intensity been lower. Nonetheless, the relatively high rainfall intensity used in this study would have been countered to some extent by the fact that many raindrops would not have reached terminal velocity before striking the soil.

The results of these experiments largely relate to the physical effects that biochar application has on the hydrological response of bare, loose soil under rainfall. Biochar amendments can result in significantly increased root development and influence earthworm activity. It is therefore possible that even if the physical effect of biochar application is a reduction in the hydraulic conductivity of a soil, the influence of biochar application on soil flora and fauna could counteract this effect. Furthermore, if biochar application has a beneficial or deleterious effect on above-ground biomass growth, groundcover will be affected, resulting in changes in interception of rainfall by plants with important consequences for development of surface seals and overland flow.

The soil samples in the present study were dried and sieved to < 5 mm prior to being subjected to rainfall simulation. The soil aggregates were therefore to some extent artefacts of the drying and sieving process, with differences in aggregate sizes between soils of differing biochar potentially being less pronounced than they might otherwise have been; this could have influenced infiltration rates and hydraulic conductivity, with subsequent effects on runoff and, therefore, erosion.

The findings of this investigation suggest that a biochar application rate of 5 g kg^{-1} would have little or no effect on the erosional response of medium-textured soils during rainfall. Further work, with greater replication, is needed to identify a threshold application level at which biochar is likely to start to significantly influence infiltration and runoff.

8.6 Summary

Applying biochar at a rate of 5 g kg^{-1} did not affect aggregate stability of the silt loam examined here, confirming the finding of Liu *et al.* (2012) that a low application rate (4 g kg^{-1}) of biochar of a particle size < 2 mm did not significantly affect the aggregate stability of medium-textured soils. However, application rates of 25 and 50 g kg^{-1} resulted in significant reductions in aggregate stability. Soil pH and electrical conductivity increased with increasing biochar application rate. These effects could have promoted increased aggregate stability through their influence on cohesion of colloids and clays, but the increases were too small to have any material effect. It seems likely that the diminished aggregate stability observed with high rates of biochar application (25 and 50 g kg^{-1}) can be attributed to the effects of those application rates on the particle size distribution of the soil, combined with insufficient oxidation of biochar particle surfaces to enable extensive formation of organo-mineral associations which could have increased aggregate stability.

Biochars produced at other temperatures or from alternative feedstocks may be more likely to increase aggregate stability owing to their higher salt or cation content and their effect on soil biota. The liming effect of biochar is likely to have greater implications for aggregate stability in more acidic soils. It is possible that if biochar is ground to particle size typical of clay (i.e. < 0.0002 mm), it will improve aggregate stability when applied to soil by virtue of increasing the clay content. Of course, all of the above would also have implications for erosion.

Slopewash erosion commenced earlier in the silt loam soil with high biochar contents, but no differences were found between treatments in terms of the total amount of sediment eroded over an hour of rainfall. This can be explained by sealing occurring more rapidly in soils with higher biochar content (see Chapter 7), protecting the soil surface from erosion by overland flow by increasing its cohesion. Biochar particles were preferentially eroded from the soil at all application rates because of their hydrophobicity and low particle density, which meant they were ejected over greater distances by splashing.

Due to differences in particle size distribution, the crusts of soils with high biochar content were significantly weaker than those of soils with 0 or 5 g kg of biochar. However, assuming sufficient rainfall intensity and / or duration, soils with higher biochar contents are likely to form crusts more often than soils with low or zero added biochar of a particle size < 2mm.

9 SUMMARY OF THESIS FINDINGS AND QUESTIONS FOR FUTURE RESEARCH

9.1 Conclusions

Greenhouse gas removal may become necessary to ensure that global warming does not exceed 2°C. Some of the technologies for greenhouse gas removal proposed to date can only temporarily sequester carbon, others have adverse ecological impacts, some are prohibitively expensive and / or energy-intensive and others are still in the process of being developed, so it is likely that a suite of these methods will be needed. Biochar does share some of the challenges faced by other greenhouse gas removal methods, but it avoids many of them. Biochar production can potentially sequester carbon for several millennia and can be a self-sustaining or energy-generating process providing a range of saleable services and commodities contributing to its economic viability.

The review of the literature carried out here revealed that biochar can deliver numerous benefits as a soil amendment. It can increase soil nutrient fertility by improving CEC, limiting leaching of nutrients and, to some extent, by directly introducing nutrients to the soil. Biochars may provide substrates and secure habitats for soil microbiota, though observations of earthworm preference for, or avoidance of, biochar amended soils have been mixed. In certain soils biochar amendments will improve soil WHC and aggregate stability.

However, the literature review also identified several research gaps, particularly with regards to the effects of biochar application on soil hydrology and erosion. The overarching objectives of this study were to address some of the research gaps by investigating how the preparation of biochar amendments (i.e. use of different pyrolysis temperatures, feedstocks and particle sizes) can influence their effect on soil hydrology and related properties, and how different biochar application rates influence soil hydrology and degradation during rainfall. These objectives were achieved by addressing three main strands of enquiry:

i. How do feedstock type and HTT influence biochar hydrophobicity, CEC and yield?

ii. In what ways do the HTT and particle size of biochar amendments influence their effects on the hydrological properties of a sandy loam soil?

iii. How do different biochar application rates influence the hydrological and erosional response of a silty loam soil during simulated rainfall, and crust formation after drying?

The experiments conducted to answer these questions led to the conclusions listed below, where an effect is described as significant if $p \leq 0.05$.

Biochar hydrophobicity

I. Feedstock particle size significantly affected the hydrophobicity of fresh biochar. Biochar produced from 10 - 20 mm feedstock particles was less hydrophobic than biochar produced from 2 - 5 or 5 - 10 mm feedstock particles. However, these differences were very small and it seems unlikely that they would substantially influence the hydrological properties of the biochars as soil amendments.

II. Time since production did not influence the hydrophobicity of biochar stored for 21 days.

III. Pyrolysis temperature significantly affected biochar hydrophobicity; biochar particles became increasingly wettable (i.e. less hydrophobic) with increasing HTT (from 350°C to 800°C).

IV. Feedstock type significantly influenced biochar hydrophobicity. *Salix* feedstock produced the least wettable (i.e. most hydrophobic) biochar, while *Picea* feedstock tended to produce biochar that was slightly more wettable than that produced from *Miscanthus* feedstock.

V. Biochar hydrophobicity cannot be solely attributed to surface chemistry; the surface topography of biochar particles also has an influence.

Biochar yield

VI. Biochar mass yields decreased with increasing HTT. For all three feedstocks examined here (*Salix, Picea* and *Miscanthus*), the largest reductions in median yield occurred between HTTs of 350 and 500°C. Further reductions in median yield with increasing temperature were smaller.

VII. *Picea* feedstock tended to produce the largest yields, while yields from *Salix* and *Miscanthus* feedstock were similar.

Biochar CEC

VIII. Biochar CEC varied by feedstock for a given HTT. The CEC of biochar produced from *Picea* feedstock tended to be less than half of that of biochars produced from *Salix* and *Miscanthus* feedstocks, which were similar to each other.

IX. *Salix* and *Miscanthus* biochar CECs more than doubled between HTTs of 350 and 500°C, but further increases in HTT had no significant effect.

X. Differences between the CECs of biochars produced from different feedstocks and / or at different HTTs were negligible compared to the CECs of aged biochars reported in the literature, which may be orders of magnitude greater.

The effects of pyrolysis temperature on biochar soil amendments

XI. Biochars significantly reduced the bulk density of the soil tested. However, this effect was greater with biochars produced at 600 and 700°C than those produced at 400 and 500°C.

XII. Only biochar produced at 500°C significantly increased soil WHC, but all biochars significantly augmented matric suction (at a water content of 0.17 $cm^3\ cm^{-3}$). The overall trend was for increases in soil moisture retention as biochar HTT was increased from 400 to 500°C, but decreases with subsequent increases in HTT. These effects may arise from an increase in biochar porosity at HTTs up to 500°C and widening of soil or biochar pores, or reduction in pore interconnectivity with further increases in biochar HTT.

XIII. The effect of 400°C, 600°C and 700°C biochars increasing matric suction was counteracted by a reduction of osmotic suction, which can be attributed to these biochars displacing native soil, reducing solute concentrations. This indicates that biochars may be able to increase

WHC without increasing total suction. However, 500°C biochar did increase total suction, presumably because it significantly enhanced osmotic suction (presumably by introducing condensed volatiles to the soil solution) as well as matric suction. 500°C biochar could, therefore, increase plant moisture stress, particularly for seedlings.

XIV. After 14 days of incubation, prolific fungal growth was observed in soils amended with 500°C biochar, but not in soils amended with biochars produced at other HTTs. This can be attributed to pyrolysis condensates on the surface of the 500°C biochar which provided a carbon and energy substrate.

The effects of biochar soil amendment particle size

XV. Biochars of all particle sizes (< 0.2, 0.4 - 1, 2 - 3 and 4 - 5 mm) significantly diminished the soil's bulk density. However, biochars of a smaller particle size reduced bulk density more effectively than those of a larger diameter; <0.2 mm biochar reduced bulk density by ~8%, whereas 4 - 5 mm biochar reduced bulk density by only 4%.

XVI. Only biochars with a particle size of 0.4-1 mm significantly augmented the soil's WHC. Water drained from the soil more quickly that it was able to permeate larger biochar particles.

XVII. All biochar amendments resulted in significantly increased matric suction (at a water content of 0.17 $cm^3 cm^{-3}$), indicating that when wet conditions persist, moisture uptake by larger biochar particles may match that of smaller particles.

XVIII. Biochars of particle sizes < 1 mm increased both matric and osmotic suction and therefore significantly increased total suction. However, biochars of particle sizes between 2 and 5 mm did not significantly affect total suction because their effect of increasing matric suction was countered by a reduction of osmotic suction. These contrasts between biochars of differing particle size probably relate to differences in the extent to which pyrolysis condensates held in biochar pores were released by grinding.

The effect of biochar application rate on the hydrology and erosional response of a silt loam under simulated rainfall

XIX. Pyrolysing mixed deciduous wood in a traditional kiln produced biochar with highly heterogeneous wetting characteristics.

XX. Despite this biochar being partially hydrophobic, applying at rates up to 50 g kg^{-1} had no effect on soil wettability

XXI. An application rate of 5 g kg^{-1} did not affect the soil's bulk density. However, an application rate of 25 g kg^{-1} significantly reduced bulk density, with an additional reduction when this rate was doubled.

XXII. Soil water retention tended to increase with increasing biochar application rate.

XXIII. A biochar application rate of 5 g kg^{-1} did not affect the aggregate stability of the soil. However, applying biochar at rates of 25 and 50 g kg^{-1} resulted in significant reductions in aggregate stability and there was an overall trend for aggregate stability to decrease with increasing biochar application rate. This may be attributed to biochar amendments altering the soil's particle size distribution, with insufficient oxidation of biochar particles to enable organo-mineral associations between the biochar and soil particles.

XXIV. Overland flow was generated more quickly as the biochar application rate increased beyond 5 g kg^{-1}. This can be attributed to more rapid onset of surface sealing arising from biochar applications, which caused reductions in aggregate stability. Reductions in hydraulic conductivity may also have contributed.

XXV. As a result, slopewash erosion commenced earlier in soils with high biochar contents (25 and 50 g kg^{-1}). However, there were no statistically significant differences between treatments in terms of total amount (weight) of sediment eroded during rainfall simulation.

XXVI. Biochar particles were preferentially eroded from the soil at all application rates because of their low particle density and in many instances, their hydrophobicity, which meant they were ejected over greater distances by splashing.

XXVII. Penetration resistance testing demonstrated that the crusts formed following rainfall simulation were ~25% stronger on plots with biochar contents of 0 or 5 g kg^{-1} than on plots with 25 or 50 g kg^{-1} of biochar.

9.2 Limitations

The apparent effect of biochar hydrophobicity being lower when larger feedstock particles are used may in practice be eliminated by grinding of biochar following production. The finding that biochar hydrophobicity is not affected by time since production may not apply to all biochar production systems. Where no purge gas is used, a greater proportion of evaporated volatiles will condense on biochar surfaces. This could potentially result in (i) freshly produced biochar being more hydrophobic than when produced using purge gas and (ii) a reduction in biochar surface hydrophobicity over time since production resulting from the absorption of condensed volatiles. This study provides only a theoretical explanation of the potential for differences in biochar surface topography to contribute to differences in hydrophobicity. Quantitative analyses of differences in biochar surface topography related to pyrolysis temperature and feedstock are needed to enable experimental demonstration of the relationship between biochar surface roughness and biochar hydrophobicity. The hydrophobicity and CEC data presented in this study provide an understanding of the properties of fresh biochar, but are of limited value in determining the likely long-term effects of biochars on soil properties. Biochar surfaces are progressively oxidised in the soil environment, so the formation of functional groups is likely to render them progressively less hydrophobic, while increasing their CEC (Cheng *et al.*, 2008). Biochar CEC may also be influenced by progressive leaching of ash. Changes in biochar properties following application to the soil may thus be more important than the initial surface properties arising from the production technique used.

Differences between the effects of biochars of different particle size or produced at different pyrolysis temperatures observed in the present study might not be evident if lower, currently more commercially realistic application rates are used. Moreover, differences between biochars may be less important in soils where biochar application has little or no effect on moisture retention. Furthermore, differences between the effects of biochars produced at different pyrolysis temperatures may be different where different biochar particle size fractions are used; differences in moisture retention arising from differences in biochar pore connectivity could be augmented where larger biochar particles are used, or reduced where smaller particles are used. The findings of the present study suggest that biochar particles > 2 mm are not as effective in increasing soil WHC as those of a diameter < 1 mm. The larger particles may have had more of an influence on soil WHC had saturation conditions persisted for a longer period. Biochar hydrophobicity was not measured, so it is not clear whether or not biochar surface hydrophobicity contributed to the different effects that biochars of differing particle size had on soil water-holding capacity. If hydrophobicity was indeed an influencing factor, then particle size could have less influence on the effect of biochar additions on soil WHC when biochar is produced at higher temperatures and is therefore wettable.

Biochar produced at 500°C increased osmotic suction, whereas those produced at other temperatures did not. Differences in suction observed between biochars of different particle size produced at 500°C are not necessarily representative of the differences that would be observed for biochars produced at other temperatures. A clear limitation of the present study is that while the differences in matric suction between soils containing biochars of different particle size or produced at different temperatures are informative, the measurements themselves cannot be considered valid as absolute values. It must again be acknowledged that the differences in matric and total suction observed in this study are representative of only one particular soil moisture content.

All of the experiments presented in this thesis used soils that were bare, dry, sieved and repacked. The structures, pore architectures, aggregates and inter-aggregate pore size distributions of the soils were therefore to some extent artefacts of the drying, sieving, mixing and repacking process, and do not necessarily resemble the properties of soils amended with biochar *in-situ*, where the direct effects of biochar on water infiltration, conduction and retention will be complicated by indirect effects through the influence of biochar on soil aggregation, aggregate size and aggregate stability. Furthermore, in field situations, the effect of biochar on soil properties will be complicated by its effects on above- and below-ground biota. It should also again be acknowledged that the biochar application rates used in this study were very high and not currently commercially realistic for broadacre agriculture. Differences between the effects of biochars produced at different pyrolysis temperatures observed in the present study may not be observed when lower application rates are used. Moreover, differences between biochars may be less important in soils where biochar application has little or no effect on moisture retention.

Again, it must be remembered that for all the experiments presented in this thesis, biochar was applied to the soil by mixing to mimic biochar being ploughed in. Differences observed between different biochars or different application rates might have been more or less pronounced had a different application method been used. The present study concludes that biochar hydrophobicity does not influence its effect on WHC, possibly because saturation of the soil surrounding biochar causes reorientation of amphiphilic molecules on biochar surfaces, rendering them wettable. Conversely, where application methods result in layering of biochar within the soil profile, such an effect might only occur at the biochar layer margins. As with previous studies which mixed hydrophobic biochar with soil, the present study found that biochar did not influence soil wettability.

Hydrophobic biochars might have a greater influence on soil wettability however if they are applied by top-dressing rather than mixing. Biochar would probably be more susceptible to preferential erosion if applied by top-dressing, and less susceptible if applied by deep-banding, than the results of the present study suggest. Equally, if biochar were applied by drilling, top-dressing or deep-banding, it would be so readily incorporated into soil aggregates and would thus have less influence on soil aggregation and aggregate stability than the results of the present study suggest.

The results of the experiments presented in Chapters 7 & 8 are not necessarily representative of how biochar could influence soil hydrology during natural rainstorm events. Due to the relatively low height of the rainfall simulator used in this study, many droplets would not have reached terminal velocity before striking the soil. The findings of this investigation suggest that a biochar application rate of 5 g kg^{-1} would have little or no effect on the hydrological response of medium-textured soils during rainfall, but further work is needed to identify a threshold application level at which biochar is likely to start to significantly influence infiltration and runoff.

9.3 Final Discussion

HTT has numerous implications both for the properties of biochar itself and for its subsequent influence on soil properties. Biochar surface hydrophobicity was observed to decrease with increasing HTT, confirming the findings of Kinney *et al.* (2012). However, while Kinney *et al.* (2012) attributed biochar surface hydrophobicity solely to the presence of alkyl functionalities, the present study has shown that rough biochar surface topography also contributes to hydrophobicity. Furthermore, the present study has demonstrated that, contrary to the conclusions of Kinney *et al.* (2012), biochar hydrophobicity does continue to reduce with increases in HTT beyond 500°C. The present study found that a partially hydrophobic biochar had no effect on soil wettability at application rates up to 50 g kg^{-1}, confirming the findings of Kinney *et al.* (2012), Smetanová *et al.* (2012) and Abel *et al.* (2013) that hydrophobic biochars do not significantly affect soil wettability even at high application rates. Gray *et al.* (2014) concluded that the hydrophobicity of biochar is more important than its porosity in determining its water uptake. Contrastingly, the findings of the present study suggest that for soil WHC, the effect of increasing HTT on biochar and / or soil porosities has greater significance than its effect on hydrophobicity.

All this is not to say that biochar surface hydrophobicity is not important. Indeed, biochar hydrophobicity is likely to play a significant role in determining the extent to which biochar is preferentially eroded from the soil, particularly during the first year after application. Furthermore, HTT can influence the extent to which biochars provide fungal substrates. As fungal growth can affect biochar and soil wettability, the effects of HTT on biochar and / or soil wettability may be both direct and indirect. Indeed, the persistent hydrophobicity of 8 year old biochar in soil reported by Briggs *et al.* (2005) might have been due to the presence of fungal hyphae colonizing the biochar rather than being related to the surface chemistry and / or topography of the biochar itself.

The HTT used to produce a biochar can have various implications for soil nutrient dynamics. Biochars produced from *Salix, Miscanthus* and *Picea* feedstocks at HTTs of 500 - 800°C were observed to have higher CECs than biochars produced at 350°C. Biochar produced from softwood pellets at 500°C was associated with prolific fungal growth when applied to soil, but those produced at 400, 600 and 700°C had no visually discernable effect, indicating that 500°C biochar introduced more nutrients to the soil than the other biochars did. As mycorrhizal fungi can influence plant nutrient availability, so the effect of biochar application of fungal activity may have important indirect effects on soil nutrient dynamics.

The present study has demonstrated that HTT can significantly affect the influence of biochar soil suction. The higher solute concentrations in soils containing 500°C biochar led to much higher total suction, which would increase the energy-cost of water uptake by plants. Conversely, although biochars produced at 400, 600 and 700°C all increased matric suction, they reduced osmotic suction and therefore did not augment total suction. The HTT used to produce biochar may therefore have implications for the energy cost of water-uptake by plants. Although differences between the CECs of biochars produced using different HTTs are initially small, differences may increase if biochar surfaces weather at different rates over time, resulting in differences in surface charge, which could result in greater differences in WHC than those observed in the present study.

In summary, it is clear that HTT has several important impacts on the influence of biochar on soil properties. However, it should be remembered that even if certain biochar properties associated with different HTTs are considered desirable, biochar production costs may rise with increasing HTT because energy costs are likely to be higher, and biochar yields will be lower. Of course, under some production scenarios, precise control of HTT and resultant biochar properties will not be possible anyway, as demonstrated by the extreme heterogeneity in wettability of biochar produced from mixed deciduous wood in a traditional kiln. Also, the effect of HTT on biochar properties varies with feedstock type.

The particle size of feedstock materials and biochars affects both the properties of biochars and their influence on soil properties. Smaller *Salix* feedstock particles (2 - 10 mm) produced biochars that were slightly more hydrophobic than those produced from larger *Salix* particles (> 10 mm). However, it is unlikely that these small differences would have a significant influence on soil hydrology, especially compared to the direct effect of biochar particle size itself. The findings of the present study indicate that biochar porosity is more important than hydrophobicity in influencing the effects of biochar amendments on soil hydrology, but biochar particle size does significantly affect soil properties, because larger particles have less effect on bulk density and water takes longer to permeate larger particles. The findings of the present study correspond to those of Zheng *et al.* (2010) who found that larger biochar particle sizes increased pesticide sorption equilibrium times by several days because of the greater length of time necessary for pesticides to reach their innermost regions. Differences in osmotic suction arising from use of different biochar particle sizes may be specific to the pyrolysis system and / or the feedstock used in the present study. For example, in a furnace continuously purged with N_2, there may be less blocking of biochar pores by pyrolysis condensates as volatiles are transported out of the furnace by the purge gas rather than condensing on biochar surfaces.

Overall, the present study has demonstrated that, contrary to the conclusions of Lehmann *et al.* (2003) and Joseph *et al.* (2009), particle size can significantly influence the effects of biochar applications on soil properties.

Larger biochar particles are less likely to be preferentially eroded than smaller particles. Smaller particles are lighter and thus more susceptible to transport by splashing, while the distance travelled by a particle in suspension is dependent on its settling velocity in water; the lower the density and size of a particle, the slower it settles out of suspension and the further it travels. Assuming no grinding of biochar particles following pyrolysis, differences in biochar hydrophobicity arising from differences in feedstock particle size could augment these differences between the preferential erosion of large and small biochar particles. Conversely, it is possible that these factors may be counteracted by the large specific surface area of smaller biochar particles causing them to be more cohesive than larger particles.

The influence that the particle size distribution of biochar amendments has on soil texture can important implications for aggregate stability and consequently, the hydrological and erosional response of soils under rainfall. The present study confirms the finding of Liu *et al.* (2012) that biochar applications rates ≤ 5 g kg^{-1} do not significantly affect the aggregate stability of silt-loam soils. However, the findings of the present study contrast with those of previous studies which reported either no effect (Liu *et al.*, 2012) or increased aggregate stability (Liu *et al.*, 2012; Herath *et al.*, 2013) when higher biochar application rates (8 - 15 g kg^{-1}) were used to amend medium-textured soils. In the present study, applying biochar ground to < 2 mm at rates of 25 and 50 g kg^{-1} to a silt loam inevitably gave the soil a more sandy texture, reducing its aggregate stability.

Taken in conjunction with the findings of Liu *et al.* and Herath *et al.*, the reductions in aggregate stability observed in the present study with biochar applications of 25 and 50 g kg^{-1} may indicate that biochar application only increases aggregate stability up to a certain point, after which further increases in application rate have a deleterious effect on aggregate stability. Conversely, it is also possible that the reductions in aggregate stability at higher biochar application rates observed in the present study relate to low oxidation of biochar particle surfaces, in which case the findings of the present study might therefore be indicative only of the effects of biochar on soil hydrology and erosion relatively soon after application. It should, however, be noted that the HTT at which biochar is produced can significantly influence both its CEC and its utility as a fungal substrate. CEC can influence aggregate stability through their effect on the cohesion of colloids and clays facilitated by cations. Fungal hyphae can bind soil particles together, increasing aggregate stability. The influence of biochar amendments on aggregate stability may therefore vary according to their HTT.

Although the effects of biochar application on erosion observed in the present study resemble those of Smetanová *et al.* (2012), they contrast with those of Jien & Wang (2013), who found that biochar application reduced erosion in an acidic silt clay loam. This contrast may be related to the fact that biochar application substantially increased pH (which would have contributed to increased aggregate stability) in the study conducted by Jien & Wang (2013), but only had a small effect on the pH of the more alkaline soil used in the present study, in which high biochar application rates reduced aggregate stability.

The effect of biochar amendments on aggregate stability will have a substantial effect on their influence on both soil hydrology and erosion. Soil water retention increased with increasing biochar application rate, but there are indications that reductions in aggregate stability arising from high biochar application rates can reduce the amount of rainwater that infiltrates the soil in the first place, by causing surface sealing which results in overland flow being generated sooner (assuming sufficient rainfall intensity and duration). However, although soils containing high biochar contents sealed more quickly than those with low or zero biochar, the crusts that were formed by drying of those seals were significantly weaker in soils with high biochar contents. Although overland flow was generated more quickly on soils with high biochar contents, there was no more erosion from these soils than from those with low or zero biochar. However, the present study confirms the finding of Rumpel *et al.* (2006) that biochar itself is preferentially eroded and demonstrates that preferential erosion of biochar can also occur on shallower slopes.

The preferential erosion of biochar may have significant implications for its potential as a means of greenhouse gas removal. If biochar is preferentially eroded from agricultural soils, biochar may well be reapplied if maintaining a certain biochar concentration is agronomically desirable and economically viable. Preferential erosion of biochar could therefore stimulate ongoing demand for biochar production, resulting in it having a greater potential for greenhouse gas removal than was estimated by Woolf *et al.* (2010).

9.4 Implications and suggestions for future research

Biochar hydrophobicity is influenced both by feedstock type and HTT. Previous research has demonstrated that hydrophobic particles are preferentially eroded compared to wettable particles (Ahn *et al.*, 2013). The biochar used in the rainfall simulation experiments, comprising both wettable and hydrophobic particles, was preferentially eroded from the soil. Additional research is needed to determine the extent to which preferential erosion of biochar can be reduced by producing it from certain feedstocks and / or at certain HTTs, to ensure it is wettable. Using higher HTTs to eliminate biochar hydrophobicity could result in a higher unit cost of biochar, because biochar yields would be lower and energy costs could be higher. However, if biochar produced at higher HTTs is eroded less quickly, it will not need to be reapplied as frequently as biochar produced at lower HTTs. On the other hand, hydrophilic biochar is likely to break down into smaller particles more quickly than hydrophobic biochar. As discussed above, smaller particles are more easily eroded than larger particles. Future research could investigate the costs associated with maintaining a certain biochar content in the soil, depending on whether it was produced using a higher or lower HTT. Furthermore, increased hydrophilicity of biochar is not necessarily a positive outcome. It could augment the biological, physical and chemical weathering of biochar such as particle size reduction and dissolution (Cheng *et al.*, 2006). There also appears to be a trade-off between maintaining the ability of biochar to sorb hydrophobic molecules such as organic contaminants and reducing the hydrophobicity of biochar (Major *et al.*, 2009; Verheijen *et al.*, 2010). Research is needed to determine in which contexts it is preferable for biochar to be an initially hydrophobic or hydrophilic material.

The HTT at which biochar amendments were produced had a significant effect on the extent to which they influenced the physical and hydrological properties of a sandy loam. However, it should be remembered that the application rates used in these experiments were high (50 g kg^{-1}). Further research is necessary to understand how important these differences would be if lower, more commercially realistic biochar application rates and / or soils were used. Indeed, an application rate of 5 g kg^{-1} seemed to have little effect on the hydrological response of a silt loam under simulated rainfall. Differences between biochar types may thus be less important at lower application rates. On the other hand, certain biochars may significantly influence soil hydrology even at very low application rates, while others may require higher application rates to have an impact. Research could also be conducted to investigate how differences between the hydrological properties of soils amended with biochars produced under different pyrolysis conditions vary over time. For example, biochar surface charges will increase over time, contributing to increased soil WHC, while ash and pyrolysis condensates will be progressively leached from biochar pores, resulting in increased available porosity.

Biochar produced at 500°C from softwood pellets was found to have a positive effect on fungal growth, which was observed to aid aggregation, binding biochar together with other soil particles. Future research could investigate how biochars which affect fungal growth influence aggregate stability and the hydrological and erosional response of soils under rainfall. If biochar application leads to increased fungal activity promoting aggregation and aggregate stability, their use could result in reduced soil erosion. Binding of biochar within and to soil aggregates by fungi could also reduce the extent to which it is preferentially eroded. On the other hand, certain fungi can be associated with enhanced soil water repellency (Doerr *et al.*, 2000). Biochar application could thus indirectly lead to increased soil water repellency (resulting in increased overland flow and erosion) if it sufficiently affects fungal activity. The effect of HTT on biochar CEC may also have important implications for soil aggregation; biochars which have or develop high concentrations of negative surfaces charge are likely to promote soil aggregation more effectively than those with lower concentrations.

Additional research is necessary to determine whether the differences in suction observed between biochars produced at different HTTs and biochars of differing particle size would apply across the whole moisture release curve. Also, it is not clear whether the differences between the effects of biochars produced using different HTTs would be the same if a different particle size (< or > 0.4 - 1mm) was used. Equally, it is not known if the different effects of biochars of differing particle size observed in this investigation would apply to biochars produced using different HTTs. Furthermore, the periods of time over which these differences would persist remain unclear. For example, if differences in osmotic suction between soils containing biochars of differing particle size were indeed related to the extent to which pyrolysis condensates were either retained in the pores of larger particles or were instead available to the soil solution in the case of smaller particles, these differences would not apply to biochars produced at higher HTTs (which contain less condensates). Moreover, the influence of pyrolysis condensates may in any case be short-lived if they are quickly leached from the soil. If biochars produced at higher HTTs had less pore interconnectivity (due to intermediate melts), it might be expected that the differences between the effects between smaller (< 1 mm) and larger (> 3 mm) biochar particles on properties such as WHC would be even more pronounced than those observed in the present study. On the other hand, biochar particles produced using higher HTTs tend to be more fragile than those produced at lower temperatures, so larger particles would break down into smaller fragments more quickly than particles produced at lower temperatures would. The bulk density of biochar-amended soils might be expected to reduce over time as biochar particles break down into smaller fragments. However, this effect would be complicated by the direct and indirect influences of different sized biochar particles on aggregation and aggregate stability.

Although biochar HTT and particle size can directly influence the effects of biochar application on soil properties such as WHC or bulk density, the effect of different biochars on soil aggregation and aggregate stability may be of equal or greater importance to properties such as WHC or bulk density under field conditions. For example, feedstock and HTT significantly affect biochar CEC, which will mean that different biochars will influence soil aggregation to varying extents. Again, it must be remembered that the findings of the present study are not necessarily representative of the influence of biochars when applied to soils *in-situ,* where the direct effects of biochar application will be complicated by pre-existing soil structure, and the effects of biochar on above- and below-ground biota. Much further research is needed to explore all these interactions.

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11 APPENDIX: SUPPLEMENTARY DATA

This appendix contains supplementary data from the experiments described in Chapters 4 to 8. Tables A.4.1 to A.4.3 contain data presented in Chapter 4, Tables A.5.1 to A.5.4 contain data presented in Chapter 5 and so on.

Table A.4.1: Biochar yields (mass % of feedstock mass) by feedstock type and HTT

Salix				Miscanthus				Picea			
350°C	500°C	650°C	800°C	350°C	500°C	650°C	800°C	350°C	500°C	650°C	800°C
45.15	29.94	-	27.02	41.87	30.31	28.50	23.57	56.78	48.60	47.17	29.15
39.08	30.01	27.70	26.41	37.79	31.41	30.14	31.15	47.36	33.71	30.91	29.34
38.63	29.69	-	25.64	41.69	30.86	28.39	27.46	34.88	37.22	31.50	29.63

Table A.4.2: Contact angles of water droplets on biochar surfaces by feedstock type and HTT

Salix				Miscanthus				Picea			
350°C	500°C	650°C	800°C	350°C	500°C	650°C	800°C	350°C	500°C	650°C	800°C
94.4	69.3	45.2	33.3	90.0	0.0	0.0	8.6	88.1	0.0	70.3	16.4
90.0	93.3	42.4	28.1	82.7	0.0	49.2	47.4	93.1	0.0	90.0	19.5
90.0	90.0	88.9	49.2	91.8	48.5	52.8	40.3	72.4	0.0	74.9	13.3
92.2	65.1	86.5	32.9	75.6	49.8	0.0	40.6	84.9	0.0	69.6	31.8
78.8	70.2	85.6	91.4	77.5	59.0	0.0	40.4	78.5	0.0	85.7	41.5
103.1	67.5	85.2	102.5	76.1	48.9	0.0	0.0	66.7	0.0	64.2	44.4
63.5	75.2	86.1	0.0	80.6	75.6	21.6	0.0	72.9	0.0	33.9	45.0
100.6	77.1	85.1	0.0	93.0	70.4	27.6	0.0	70.1	0.0	35.7	39.1
75.0	82.9	85.9	13.9	95.8	69.4	28.0	0.0	63.6	0.0	52.5	31.5
68.8	90.0	90.0	20.9	95.6	64.5	19.4	0.0	73.8	0.0	54.2	14.7

Salix				Miscanthus				Picea			
350°C	500°C	650°C	800°C	350°C	500°C	650°C	800°C	350°C	500°C	650°C	800°C
111.2	77.1	98.2	0.0	92.9	67.3	0.0	0.0	80.5	12.8	58.2	17.7
125.9	92.7	71.6	0.0	89.0	66.7	0.0	34.1	78.2	23.3	50.9	26.0
98.1	79.1	76.6	0.0	83.7	53.7	13.1	33.0	73.6	47.8	49.8	20.5
107.0	80.9	78.5	0.0	95.3	54.6	17.5	56.4	71.1	40.2	56.0	42.5
104.9	74.1	0.0	51.3	93.9	64.2	29.8	63.6	97.8	0.0	50.2	32.6
126.1	75.7	0.0	60.3	95.1	19.7	27.2	64.5	93.9	0.0	41.4	40.5
95.4	65.7	0.0	71.7	95.2	85.5	34.1	45.5	100.4	11.7	0.0	31.8
99.0	56.6	0.8	67.2	85.3	128.9	38.0	35.9	122.9	12.5	0.0	0.0
87.0	78.7	47.3	74.5	91.1	41.6	63.3	41.6	138.2	56.5	2.0	0.0
98.5	81.4	34.7	83.4	90.1	58.2	50.1	66.0	133.0	41.9	2.0	33.7
94.3	97.9	59.8	70.3	95.5	58.8	36.1	66.8	142.2	58.4	2.0	31.2
97.9	96.1	58.3	77.7	92.5	66.4	54.4	56.5	85.8	48.5	2.0	0.0
100.2	88.3	58.3	45.1	91.1	54.3	26.6	50.8	78.4	43.2	55.0	0.0
118.0	98.3	53.9	60.8	97.0	47.2	23.1	54.3	63.1	55.2	51.5	24.0
104.3	66.1	78.9	2.0	98.5	58.3	60.8	51.3	70.7	52.0	52.0	13.2
101.3	72.9	71.1	2.0	96.4	45.3	51.9	61.2	64.2	68.3	60.6	0.0
92.4	67.9	72.6	42.4	92.3	48.7	54.2	72.0	66.3	83.6	48.5	0.0
93.1	65.4	69.1	46.8	86.8	60.5	47.1	52.8	61.5	87.0	39.4	20.4
99.5	58.3	86.6	0.0	84.6	59.3	38.3	47.4	67.3	73.6	39.2	21.8
105.4	68.9	93.7	0.0	86.9	54.0	50.7	0.0	70.2	73.0	46.4	10.4
117.6	67.2	81.6	36.3	81.2	58.6	61.6	0.0	80.3	82.2	0.0	18.2
125.5	83.3	77.6	29.9	96.2	62.3	74.3	0.0	72.5	88.0	0.0	0.0
107.7	74.9	87.5	27.4	91.1	58.8	63.5	0.0	85.5	59.9	37.7	0.0
116.3	90.0	86.3	22.0	92.8	67.3	71.4	21.2	90.0	66.6	23.8	0.0
101.8	91.9	50.3	67.4	90.7	56.4	64.4	26.8	76.1	61.7	0.0	0.0
106.7	95.9	47.6	73.1	94.6	67.7	60.1	33.0	120.0	63.1	0.0	4.7
102.3	95.8	67.7	0.0	95.0	71.4	49.2	31.4	87.1	76.7	0.0	10.5
90.0	91.1	70.0	0.0	93.0	67.1	31.0	48.5	95.5	101.8	0.0	10.8
100.1	83.2	68.2	35.5	96.9	56.9	19.2	13.8	76.1	66.0	30.9	0.0
97.8	74.7	71.0	31.6	86.6	54.4	32.4	2.0	84.2	52.9	12.8	0.0
98.1	88.2	71.0	27.9	82.5	67.9	33.5	2.0	81.5	59.5	18.6	19.0

Salix				Miscanthus				Picea			
350°C	500°C	650°C	800°C	350°C	500°C	650°C	800°C	350°C	500°C	650°C	800°C
95.2	70.1	61.3	14.0	105.5	60.2	45.1	22.9	68.9	62.6	43.5	22.0
105.3	79.0	71.7	53.8	96.2	65.6	51.3	25.4	77.6	49.9	39.5	0.0
98.9	80.6	71.6	42.5	100.3	70.3	26.2	46.8	136.4	43.1	63.6	0.0
114.7	70.1	51.0	43.8	94.0	68.5	29.2	41.8	83.0	0.3	0.0	0.0
115.4	78.0	49.9	46.0	95.3	78.8	48.7	8.0	73.7	0.3	0.0	0.0
136.8	125.9	54.4	30.2	91.0	88.1	63.7	2.0	72.7	13.2	2.0	0.0
132.7	125.8	55.7	43.2	97.4	55.6	51.6	38.1	66.7	13.2	2.0	0.0
114.2	123.5	89.0	18.3	95.3	66.1	46.9	19.6	76.4	64.2	46.0	0.0
110.2	145.5	93.9	20.8	90.0	37.3	0.0	13.5	74.1	49.2	48.0	0.0
105.7	108.4	93.6	65.5	92.1	45.0	0.0	17.2	70.1	72.2	48.2	28.1
104.5	101.4	102.4	68.6	90.0	44.1	56.3	0.0	71.0	79.0	77.0	32.9
115.1	96.1	62.8	59.5	89.5	41.7	45.0	0.0	73.4	89.9	64.5	29.5
106.6	111.6	61.1	64.0	82.3	46.5	44.6	0.0	88.0	69.4	68.3	45.9
101.0	121.3	60.5	0.0	88.3	49.3	46.0	0.0	99.6	61.2	69.4	0.0
120.3	83.5	66.0	0.0	129.5	57.2	57.2	0.0	95.0	72.3	72.2	0.0
106.1	95.2	56.5	81.2	123.8	54.3	67.5	46.1	84.5	47.1	46.0	16.8
98.4	94.7	72.6	90.5	112.4	54.3	0.0	53.1	83.4	33.8	36.6	25.1
100.9	86.8	111.4	20.2	116.8	50.4	0.0	49.4	89.3	53.3	24.3	0.0
98.0	88.4	99.0	19.7	119.7	49.5	0.0	43.5	76.7	70.1	15.5	0.0
90.0	88.4	122.6	62.1	117.0	48.6	0.0	31.5	77.1	59.4	2.0	46.2
100.3	98.3	107.0	67.0	116.1	62.9	0.0	35.2	86.5	73.4	2.0	34.0
96.6	111.0	38.8	110.4	116.1	42.4	0.0	3.7	86.1	53.5	76.3	42.5
90.0	119.6	57.3	113.6	115.0	51.8	0.0	0.0	66.1	44.2	78.7	40.8
100.8	108.2	110.3	56.4	116.3	56.0	0.0	19.5	99.6	49.4	43.1	39.7
103.1	112.8	107.8	62.6	122.7	50.6	0.0	33.1	83.9	43.9	38.1	22.5
96.9	91.3	0.0	34.2	117.9	65.7	0.0	21.8	91.6	59.6	52.9	46.7
96.8	119.5	0.0	23.9	131.7	76.7	0.0	0.0	75.5	60.1	49.2	0.0
121.2	106.8	0.0	0.0	122.5	77.2	68.5	0.0	59.1	69.6	66.5	0.0
127.7	105.8	0.0	0.0	93.2	45.6	71.5	0.0	78.2	35.7	57.9	38.7
122.0	95.7	20.2	65.5	95.3	50.9	0.0	0.0	79.9	43.7	66.5	33.6
107.9	102.0	22.1	59.3	92.1	52.0	0.0	34.1	77.5	40.2	74.1	43.1

Salix				Miscanthus				Picea			
350°C	500°C	650°C	800°C	350°C	500°C	650°C	800°C	350°C	500°C	650°C	800°C
97.1	93.6	29.3	0.0	91.5	48.6	0.0	19.1	86.1	50.3	0.0	27.3
90.0	92.7	37.1	0.0	77.6	52.4	43.8	29.1	81.2	54.0	0.0	24.4
94.4	84.6	0.0	41.9	104.8	39.4	41.0	41.5	86.0	51.4	63.5	13.8
88.5	92.2	0.0	35.8	100.6	50.2	44.8	0.0	76.7	44.4	68.4	20.5
101.0	105.0	54.1	29.1	109.6	57.2	45.7	0.0	85.7	66.8	0.0	27.0
100.3	104.5	67.5	40.4	106.3	52.3	36.6	0.0	126.5	63.1	0.0	0.0
135.0	94.4	77.9	120.7	92.1	58.2	0.0	0.0	70.4	53.9	13.8	0.0
111.5	90.2	90.0	111.8	88.8	50.4	0.0	28.8	87.4	59.9	26.0	0.0
119.7	111.1	87.1	72.9	108.5	56.4	35.5	20.1	83.0	64.5	71.8	0.0
114.9	114.6	90.0	64.5	101.9	79.7	27.3	51.1	93.0	66.8	73.0	42.2
77.5	89.0	76.0	0.0	91.9	76.1	21.1	52.8	97.5	67.8	82.6	29.0
99.7	89.5	93.2	0.0	103.4	72.7	39.6	66.6	81.3	48.9	82.5	0.0
111.4	98.9	59.3	61.1	87.6	69.2	34.5	66.8	79.9	40.6	70.1	0.0
114.7	88.3	59.0	74.8	117.0	60.5	0.0	0.0	84.3	35.9	73.9	26.4
118.4	46.1	69.9	49.5	120.2	73.2	0.0	0.0	74.4	76.3	0.0	19.2
87.8	64.0	58.2	54.2	95.4	46.6	0.0	35.2	70.9	52.2	0.0	35.8
89.3	76.1	55.1	90.6	119.1	46.4	0.0	31.9	70.0	57.3	18.9	34.0
96.8	92.5	43.6	81.5	78.7	51.4	2.0	13.2	74.6	45.1	21.8	0.0
135.0	98.0	49.2	44.4	86.5	53.9	2.0	20.8	65.2	62.3	0.0	0.0
120.6	103.6	49.6	62.3	87.8	65.8	0.0	0.0	77.8	53.2	0.0	0.4
135.0	78.0	77.5	36.2	86.5	45.7	0.0	0.0	67.4	54.0	0.0	9.9
132.3	82.0	76.0	38.0	86.7	47.9	27.8	33.5	84.9	64.4	0.0	0.0
94.3	96.8	77.7	65.8	89.8	56.6	28.4	42.0	80.7	59.6	16.5	0.0
91.6	96.6	90.9	52.4	86.0	51.8	69.3	0.0	73.0	68.3	12.0	9.7
106.8	83.0	100.9	75.6	81.0	51.3	47.7	0.0	92.4	59.2	0.0	12.5
120.0	87.9	95.7	71.0	90.0	59.8	50.2	0.0	94.3	2.7	0.0	17.2
107.9	79.7	89.7	71.6	94.5	43.8	0.0	0.0	77.3	2.7	30.3	22.4
116.6	78.8	81.1	67.4	96.2	64.4	0.0	0.0	82.0	49.1	28.5	14.6

Table A.4.3: Contact angles of water droplets on Salix biochar surfaces at 0, 7 and 21 days after production

0	7	21
87.4	102.8	79.7
91.1	117.2	97.4
90.0	115.7	95.4
86.8	127.7	96.5
81.5	142.1	100.5
90.9	140.6	92.9
77.7	94.1	93.9
92.0	97.5	98.0
79.6	93.3	90.0
94.5	93.6	94.7
90.0	89.1	90.0
113.6	89.3	85.1
97.8	98.4	89.5
78.7	125.2	87.8
95.2	119.0	107.2
90.0	113.2	134.2
95.5	97.5	111.2
74.6	87.9	104.7
98.5	90.0	112.5
105.9	89.9	116.8
108.4	90.0	94.9
130.1	85.1	94.7
132.7	86.0	108.1
126.8	144.7	120.5
87.9	88.3	95.9
80.5	85.0	113.6
95.5	86.0	98.4
96.4	84.4	108.8
91.0	89.1	97.6
89.4	146.9	105.9

0	7	21
106.3	119.1	101.9
94.4	111.1	117.3
99.8	93.0	123.3
106.1	116.9	112.9
112.4	104.0	105.6
93.1	105.2	110.4
108.8	115.5	79.2
129.0	109.2	77.3
128.2	101.4	84.4
92.3	97.1	88.1
88.1	100.9	78.5
88.4	98.2	81.7
80.5	106.5	82.7
94.4	104.4	90.0
89.4	91.0	92.6
90.6	103.5	80.5
91.7	73.9	93.6
89.4	74.1	94.9
86.6	74.8	108.4
85.1	76.6	88.6
91.3	115.0	90.0
125.1	90.5	86.8
116.8	99.6	92.9
119.2	85.0	88.2
132.1	110.7	96.5
94.2	93.6	90.0
93.1	125.5	94.7
105.7	91.4	91.7
95.0	102.3	81.0
112.4	104.4	88.0
116.3	117.6	84.5
90.0	112.2	85.6

0	7	21
93.0	107.4	104.2
96.2	107.4	99.6
116.6	95.4	106.1
104.6	104.7	109.5
113.6	110.9	115.2
104.7	94.3	105.2
90.0	109.5	109.9
116.2	96.9	94.5
104.2	87.5	102.6
98.8	100.3	103.9
97.6	108.8	94.3
106.8	88.7	92.6
121.6	98.6	117.9
90.0	103.3	123.1
107.6	112.7	102.3
83.8	102.9	104.2
90.0	119.7	82.4
94.4	91.9	90.8
98.4	123.5	82.5
96.1	116.6	93.9
86.8	143.0	84.0
90.0	112.3	81.0
93.4	103.4	93.0
90.5	92.0	87.6
120.1	91.1	99.8
117.6	118.6	94.3
100.4	130.1	104.6
119.9	102.4	88.7
113.6	69.0	105.5
118.2	90.0	108.6
109.6	93.0	110.0
95.6	79.0	106.5

0	7	21
101.7	98.9	87.3
104.9	103.0	88.7
109.1	81.1	79.0
108.2	81.9	84.5
87.1	105.6	83.0
92.4	98.9	84.9

Table A.4.4: Biochar CEC (cmol(+) kg^{-1}) by feedstock type and HTT

Salix				Miscanthus				Picea			
350°C	500°C	650°C	800°C	350°C	500°C	650°C	800°C	350°C	500°C	650°C	800°C
15.64	25.73	51.17	37.39	19.65	41.51	48.05	45.23	2.86	15.36	13.36	19.39
12.85	30.69	66.92	42.41	21.59	59.93	44.80	46.00	1.83	17.38	24.81	12.63
14.27	43.97	62.83	32.87	16.80	38.04	46.75	36.85	3.67	12.05	12.60	11.74
13.46	52.20	34.17	-	26.11	50.35	52.28	-	14.72	22.50	12.06	-

Table A.5.1: Bulk densities (g cm^{-3}) of softwood pellet biochars (ground to 0.4 - 1 mm) produced at different HTTs

400°C	500°C	600°C	700°C
0.42	0.49	0.40	0.40
0.42	0.49	0.40	0.40
0.42	0.49	0.40	0.41
0.42	0.48	0.39	0.41
0.42	0.50	0.40	0.40
0.42	0.49	0.40	0.40

Table A.5.2: Bulk densities (g cm^{-3}) of soils amended with biochars produced at different HTTs

Control	400°C	500°C	600°C	700°C
1.36	1.24	1.26	1.24	1.25
1.35	1.26	1.26	1.24	1.21
1.35	1.29	1.30	1.25	1.25
1.39	1.28	1.30	1.26	1.28
1.35	1.29	1.30	1.25	1.25
1.39	1.31	1.29	1.28	1.27
1.37	1.27	1.29	1.24	1.26
1.34	1.28	1.30	1.29	1.27
1.36	1.23	1.27	1.20	1.22
1.35	1.23	1.25	1.22	1.22
1.32	1.23	1.25	1.19	1.22
1.36	1.28	1.31	1.26	1.27
1.35	1.28	1.25	1.20	1.21
1.28	1.22	1.23	1.21	1.20
1.30	1.23	1.21	1.22	1.23
1.34	1.28	1.27	1.20	1.20
1.28	1.22	1.22	1.17	1.21
1.28	1.19	1.19	1.16	1.18
1.32	1.24	1.23	1.20	1.20
1.34	1.25	1.26	1.23	1.23
1.32	1.20	1.23	1.16	1.19
1.30	1.20	1.25	1.18	1.16
1.34	1.25	1.26	1.22	1.23
1.30	1.25	1.27	1.22	1.23
1.34	1.26	1.21	1.22	1.22

Table A.5.3: Water-holding capacities (cm^3 cm^{-3}) of soils amended with biochars produced at different HTTs

Control	400°C	500°C	600°C	700°C
0.44	0.45	0.51	0.43	0.43
0.45	0.46	0.49	0.47	0.43
0.45	0.44	0.46	0.42	0.43
0.45	0.46	0.52	0.48	0.42
0.43	0.48	0.50	0.41	0.42

Table A.5.4: Suction (kPa, at a water content of 0.17 cm3 cm-3) of soils amended with biochars produced at different HTTs

(i) Total suction

Control	400°C	500°C	600°C	700°C
50.52	48.85	165.17	44.23	43.29
61.30	57.01	110.63	66.59	50.05
58.95	53.72	93.70	57.35	49.05
61.53	58.56	126.41	80.35	52.56
61.63	55.99	87.93	58.76	60.65

(ii) Matric suction

Control	400°C	500°C	600°C	700°C
2.40	3.60	7.78	5.22	6.82
2.21	2.85	6.68	5.14	4.55
2.31	3.05	6.00	4.05	3.39
2.45	2.71	6.71	6.49	3.90
2.21	3.62	6.69	6.51	3.85

Table A.6.1: Bulk densities ($g\ cm^{-3}$) of soils amended with biochars of differing particle size

Control	< 0.2 mm	0.4 - 1 mm	2 - 3 mm	4 - 5 mm
1.36	1.24	1.26	1.23	1.28
1.35	1.23	1.26	1.23	1.27
1.35	1.22	1.30	1.25	1.28
1.39	1.22	1.30	1.24	1.27
1.35	1.22	1.30	1.24	1.27
1.39	1.24	1.29	1.25	1.27
1.37	1.24	1.29	1.24	1.28
1.34	1.24	1.30	1.24	1.30
1.36	1.23	1.27	1.27	1.27
1.35	1.23	1.25	1.25	1.29
1.32	-	1.25	-	-
1.36	-	1.31	-	-
1.35	-	1.25	-	-
1.28	-	1.23	-	-
1.30	-	1.21	-	-
1.34	-	1.27	-	-
1.28	-	1.22	-	-
1.28	-	1.19	-	-
1.32	-	1.23	-	-
1.34	-	1.26	-	-
1.32	-	1.23	-	-
1.30	-	1.25	-	-
1.34	-	1.26	-	-
1.30	-	1.27	-	-
1.34	-	1.21	-	-

Table A.6.2: WHCs ($cm^3\ cm^{-3}$) of soils amended with biochars of differing particle size

Control	< 0.2 mm	0.4 - 1 mm	2 - 3 mm	4 - 5 mm
0.44	0.47	0.51	0.42	0.43
0.45	0.47	0.49	0.43	0.44
0.45	0.46	0.46	0.45	0.43
0.45	0.44	0.52	0.43	0.42
0.43	0.46	0.50	0.42	0.44

Table A.4: Suction (kPa, at a water content of 0.17 $cm^3\ cm^{-3}$) in soils amended with biochars of differing particle size

(i) Total Suction

Control	< 0.2 mm	0.4 – 1 mm	2 -3 mm	4 – 5 mm
50.52	72.38	165.17	66.30	53.49
61.30	125.38	110.63	82.19	83.30
58.95	85.44	93.70	80.05	70.83
61.53	94.78	126.41	60.36	65.16
61.63	-	87.93	61.95	60.65

(ii) Matric suction

Control	< 0.2 mm	0.4 - 1 mm	2 - 3 mm	4 - 5 mm
2.40	7.01	7.78	6.50	6.86
2.21	7.26	6.68	8.61	6.47
2.31	6.15	6.00	8.39	6.23
2.45	6.30	6.71	8.38	6.06
2.21	6.61	6.69	7.87	4.09

Table A.7.1: Contact angles of water droplets on the surface of biochar produced from mixed deciduous in a traditional kiln

Measurement number				
1 - 20	21 - 40	41 - 60	61 - 80	81 - 100
41.99	0.00	0.00	71.05	100.46
56.42	24.53	0.00	95.44	119.55
79.66	36.67	0.00	81.09	66.27
79.55	49.79	0.00	65.27	63.73
109.47	130.39	0.00	52.72	82.69
116.24	120.73	0.00	60.71	62.55
121.08	102.94	0.00	63.60	90.00
119.82	119.23	0.00	70.81	92.42
124.85	134.05	34.37	24.72	96.54
8.45	7.96	0.00	22.51	98.93
15.96	0.00	60.50	17.46	32.81
26.08	0.00	0.00	33.02	60.70
24.69	103.37	0.00	96.39	61.13
15.23	110.82	0.00	68.84	71.85
12.67	72.84	0.00	57.90	74.83
16.22	68.40	0.00	54.00	0.00
10.22	67.54	0.00	56.87	0.00
0.00	78.47	0.00	48.84	101.52
0.00	0.00	107.22	90.91	94.79
0.00	0.00	101.57	92.79	100.79

Table A.7.3: Bulk density (g cm^{-3}) of silt loam soil under different biochar application rates

0 g kg^{-1}	5 g kg^{-1}	25 g kg^{-1}	50 g kg^{-1}
1.23	1.22	1.17	1.14
1.22	1.19	1.17	1.13
1.22	1.22	1.17	1.16
1.24	1.22	1.16	1.14
1.24	1.23	1.17	1.13

Table A.7.4: Drainage (T) and overland flow (R) (mm h^{-1}) during rainfall simulation from silt loam soil under different biochar application rates

(i) Biochar application rate of 0 g kg^{-1} (control)

Time	Simulation 1		Simulation 2		Simulation 3	
(mins)	T	R	T	R	T	R
2	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	-	0.00	-	0.00	-
6	0.67	0.00	0.00	0.00	0.00	0.00
8	2.67	-	0.00	-	14.67	-
10	57.33	0.00	16.00	0.00	41.33	0.00
12	69.33	-	65.33	-	72.67	-
14	80.00	0.00	70.67	0.00	66.67	0.00
16	80.00	-	72.00	-	72.00	-
18	76.67	0.00	73.33	0.00	70.00	7.33
20	77.33	-	72.00	-	58.67	-
22	49.33	0.00	71.33	0.00	42.67	35.33
24	77.33	-	54.00	-	38.67	-
26	62.67	9.33	46.67	28.67	22.67	47.33
28	66.67	-	40.67	-	21.33	-
30	53.33	22.67	22.67	49.33	20.00	53.33
32	49.33	-	26.67	-	23.33	-

Time	Simulation 1		Simulation 2		Simulation 3	
(mins)	T	R	T	R	T	R
34	42.67	63.33	21.33	55.00	21.33	56.00
36	40.00	-	20.00	-	20.00	-
38	32.00	46.67	20.00	56.67	20.00	59.33
40	30.00	-	18.67	-	18.00	-
42	26.67	48.00	17.33	60.00	17.33	52.67
44	23.33	-	15.33	-	17.33	-
46	18.67	60.00	14.67	63.33	16.00	60.00
48	17.33	-	13.33	-	14.67	-
50	16.00	60.00	19.33	53.33	14.00	57.33
52	14.67	-	17.33	-	13.33	-
54	14.00	64.00	16.00	60.00	13.33	63.33
56	13.33	-	14.00	-	13.33	-
58	13.33	62.00	13.33	62.00	13.33	62.67
60	12.00	-	12.67	-	13.33	-

(ii) Biochar application rate of 5 g kg^{-1}

Time	Simulation 1		Simulation 2		Simulation 3	
(mins)	T	R	T	R	T	R
2	0.00	0.00	0.00	0.00	0.00	0.00
4	0.13	-	0.00	-	0.00	-
6	0.07	0.00	0.00	0.00	1.33	0.00
8	5.33	-	2.67	-	1.33	-
10	34.00	0.00	34.67	0.00	10.00	0.00
12	74.67	-	69.33	-	37.33	-
14	76.67	0.00	84.67	0.00	56.00	0.00
16	74.00	-	80.00	-	55.33	-
18	70.00	0.00	80.67	0.00	74.67	0.00
20	67.33	-	79.33	-	76.00	-
22	54.67	16.00	73.33	0.00	61.33	0.00
24	48.67	-	63.33	-	56.67	-

Time	Simulation 1		Simulation 2		Simulation 3	
(mins)	T	R	T	R	T	R
26	40.00	35.33	50.67	27.33	62.00	9.33
28	32.67	-	44.00	-	55.33	-
30	26.67	51.33	37.33	44.00	49.33	13.33
32	22.67	-	28.00	-	38.00	-
34	20.00	53.33	26.67	51.33	36.67	19.33
36	20.00	-	24.00	-	36.00	-
38	18.00	60.00	20.00	64.67	22.67	42.00
40	17.33	-	17.33	-	24.00	-
42	19.33	50.67	14.67	63.33	22.67	26.67
44	16.00	-	14.67	-	21.33	-
46	21.33	62.67	14.67	64.67	20.00	53.33
48	14.00	-	14.00	-	19.33	-
50	13.33	60.00	13.33	63.33	16.00	57.33
52	13.33	-	11.33	-	15.33	-
54	13.33	63.33	10.67	66.67	14.67	55.33
56	14.00	-	10.67	-	13.33	-
58	13.33	56.00	10.00	66.67	12.67	48.00
60	14.00	-	9.33	-	12.00	-

(iii) Biochar application rate of 25 g kg^{-1}

Time	Simulation 1		Simulation 2		Simulation 3	
(mins)	T	R	T	R	T	R
2	0.00	0.00	0.00	0.00	0.00	0.00
4	0.33	-	0.00	-	0.00	-
6	0.33	0.00	0.00	0.00	0.00	0.00
8	0.33	-	3.33	-	2.67	-
10	39.33	0.00	15.33	0.00	28.00	0.00
12	57.33	-	53.33	-	61.33	-
14	69.33	0.67	65.33	0.00	72.67	0.00
16	63.33	-	66.00	-	69.33	-

Time	Simulation 1		Simulation 2		Simulation 3	
(mins)	T	R	T	R	T	R
18	56.00	16.67	66.00	0.00	65.33	8.67
20	46.67	-	68.00	-	59.33	-
22	36.67	41.33	58.00	16.67	48.00	29.33
24	30.67	-	48.00	-	35.33	-
26	26.67	50.67	38.67	30.00	48.67	30.00
28	23.33	-	36.67	-	39.33	-
30	22.67	56.00	31.33	46.00	33.33	45.33
32	19.33	-	26.00	-	28.00	-
34	23.33	46.00	22.67	54.00	26.67	50.67
36	23.33	-	20.67	-	23.33	-
38	22.00	56.67	20.00	59.33	21.33	57.33
40	20.00	-	18.00	-	20.00	-
42	17.33	56.67	14.67	55.33	20.00	55.33
44	16.00	-	14.67	-	20.00	-
46	14.67	64.67	13.33	63.33	17.33	56.67
48	16.00	-	12.67	-	18.67	-
50	14.00	60.00	12.00	60.00	16.67	52.00
52	14.00	-	11.33	-	16.00	-
54	13.33	60.00	10.67	64.00	16.00	60.00
56	13.33	-	11.33	-	15.33	-
58	13.33	62.00	10.67	60.00	16.67	62.00
60	12.67	-	11.33	-	14.67	-

(iv) Biochar application rate of 50 g kg^{-1}

Time	Simulation 1		Simulation 2		Simulation 3	
(mins)	T	R	T	R	T	R
2	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	-	0.00	-	0.00	-
6	0.00	0.00	0.00	0.00	0.00	0.00
8	0.00	-	1.33	-	0.00	-
10	0.67	0.00	5.33	0.00	8.00	0.00
12	19.33	-	20.00	-	50.67	-

Time	Simulation 1		Simulation 2		Simulation 3	
(mins)	T	R	T	R	T	R
14	36.67	0.33	56.67	2.67	65.33	0.00
16	46.00	-	47.33	-	52.00	-
18	55.33	0.33	46.67	20.00	41.33	34.67
20	60.00	-	33.33	-	36.67	-
22	50.00	7.33	36.00	36.00	38.67	40.00
24	40.00	-	21.33	-	32.00	-
26	33.33	32.67	32.00	42.00	22.67	53.33
28	28.00	-	26.67	-	26.67	-
30	26.67	46.00	23.33	51.33	22.67	58.67
32	24.00	-	20.00	-	21.33	-
34	21.33	44.00	18.00	54.67	20.00	59.33
36	19.33	-	15.33	-	18.67	-
38	17.33	48.67	15.33	59.33	18.00	63.33
40	16.00	-	13.33	-	16.67	-
42	14.67	52.67	13.33	58.00	16.00	64.00
44	14.67	-	11.33	-	14.67	-
46	13.33	50.00	12.67	57.33	14.00	68.00
48	12.67	-	12.00	-	14.00	-
50	12.67	57.33	12.00	56.67	13.33	68.67
52	11.33	-	11.33	-	13.33	-
54	10.67	46.67	10.67	59.33	12.67	68.67
56	10.67	-	16.00	-	12.67	-
58	10.00	56.67	16.67	53.33	12.00	66.00
60	10.67	-	15.33	-	11.33	-

Table A.8.1: Particle size distribution (%) of silt loam soil under different biochar application rates

0 g kg^{-1}			5 g kg^{-1}			25 g kg^{-1}			50 g kg^{-1}		
Clay	Silt	Sand	Clay	Silt	Sand	Clay	Silt	Sand	Clay	Silt	Sand
9.00	68.52	22.48	8.07	69.64	22.30	7.70	67.26	25.03	7.18	71.90	20.92
7.54	73.01	19.46	8.65	70.30	21.05	7.27	71.39	21.34	8.64	67.95	23.41
9.12	69.52	21.37	7.33	75.55	17.12	8.07	71.56	20.38	8.61	67.93	23.46

0 g kg^{-1}			5 g kg^{-1}			25 g kg^{-1}			50 g kg^{-1}		
Clay	Silt	Sand	Clay	Silt	Sand	Clay	Silt	Sand	Clay	Silt	Sand
7.42	71.95	20.63	7.17	74.08	18.75	8.76	71.61	19.63	8.62	68.03	23.34
7.58	73.61	18.81	8.70	71.24	20.06	7.01	71.92	21.07	7.19	72.44	20.37
8.98	68.89	22.13	8.50	69.52	21.98	8.40	67.48	24.12	7.11	71.89	21.01
7.58	73.89	18.53	8.72	71.32	19.96	8.35	67.18	24.47	7.14	72.17	20.69
8.99	68.93	22.08	7.27	75.51	17.22	8.33	67.04	24.63	7.16	72.44	20.40
8.95	68.73	22.32	7.26	75.53	17.20	8.28	66.63	25.09	8.62	68.02	23.36
8.76	67.25	23.99	7.09	73.54	19.37	8.26	66.55	25.20	8.72	68.91	22.37
9.75	69.52	20.73	8.91	72.23	18.86	6.81	70.59	22.61	6.30	65.65	28.05
8.16	73.11	18.74	7.75	73.11	19.14	8.38	67.42	24.20	6.35	65.91	27.75
8.42	75.54	16.04	9.74	71.88	18.38	8.38	67.47	24.15	6.32	65.56	28.12
8.33	74.84	16.84	9.75	71.94	18.31	6.94	71.77	21.29	7.52	60.83	31.65
8.25	74.16	17.59	7.95	72.61	19.44	8.54	69.91	21.55	6.42	66.82	26.75
8.31	74.83	16.86	8.06	73.74	18.19	8.50	69.89	21.61	6.36	66.28	27.35
8.24	74.40	17.36	9.70	71.98	18.32	8.43	69.45	22.12	6.31	65.73	27.96
8.44	76.22	15.35	7.97	73.14	18.89	8.47	69.83	21.70	6.37	66.34	27.29
8.23	74.38	17.39	9.84	72.97	17.19	8.41	69.45	22.14	6.45	67.17	26.38
8.08	73.12	18.80	8.11	74.40	17.49	8.51	70.45	21.04	6.35	66.31	27.33
7.41	72.86	19.73	9.72	70.85	19.43	8.63	71.20	20.16	7.98	66.35	25.67
8.35	73.80	17.86	9.74	71.19	19.07	8.43	69.75	21.83	6.55	71.09	22.36
9.04	74.11	16.85	9.60	70.36	20.03	8.43	69.73	21.83	7.92	66.37	25.71
9.37	72.08	18.55	9.65	71.06	19.29	8.47	69.96	21.57	7.86	65.92	26.23
9.60	72.85	17.56	9.56	70.37	20.07	8.79	70.76	20.45	8.01	67.16	24.83
11.28	70.62	18.10	9.62	70.92	19.45	8.69	70.12	21.18	6.50	70.67	22.83
9.48	72.22	18.30	9.52	70.35	20.14	8.59	69.16	22.25	7.91	66.38	25.72
9.35	71.51	19.13	9.49	70.07	20.44	8.69	69.93	21.38	7.81	65.49	26.70
11.29	70.80	17.91	9.46	69.98	20.56	8.78	70.53	20.70	8.01	67.17	24.82
11.23	70.31	18.46	7.80	71.25	20.95	8.86	71.21	19.93	7.74	64.97	27.29
7.55	72.44	20.01	6.41	71.69	21.90	8.78	70.56	20.66	8.26	68.98	22.76
7.40	71.12	21.48	6.39	71.77	21.84	7.17	72.13	20.70	8.23	69.04	22.73
9.16	69.24	21.60	6.31	71.09	22.60	8.75	69.12	22.14	8.18	68.53	23.30
7.56	72.92	19.51	7.86	68.63	23.50	7.14	72.51	20.35	7.97	67.04	24.98
7.51	72.47	20.02	6.41	72.30	21.29	8.72	69.17	22.10	7.99	67.14	24.87
9.03	68.62	22.35	6.39	72.00	21.61	7.26	73.60	19.14	8.12	68.37	23.50
7.43	71.74	20.83	6.35	71.91	21.74	8.62	68.58	22.80	8.20	68.82	22.98
7.53	72.81	19.65	6.41	72.38	21.21	7.15	72.80	20.05	8.15	68.29	23.56

0 g kg^{-1}			5 g kg^{-1}			25 g kg^{-1}			50 g kg^{-1}		
Clay	Silt	Sand	Clay	Silt	Sand	Clay	Silt	Sand	Clay	Silt	Sand
7.44	71.84	20.71	6.50	73.47	20.03	7.26	73.65	19.09	8.20	68.87	22.93
8.87	67.32	23.81	6.44	72.79	20.77	7.27	73.82	18.91	8.20	68.79	23.01

Table A.8.2: Electrical conductivity (EC) and pH of silt loam soil under different biochar application rates

0 g kg^{-1}		5 g kg^{-1}		25 g kg^{-1}		50 g kg^{-1}	
EC	pH	EC	pH	EC	pH	EC	pH
112.5	7.9	99.5	7.9	111.6	8.1	110.5	8.2
103	7.9	105.8	8	117.8	8.0	110.0	8.1
104.4	7.9	107.2	8.1	111.5	8.1	109.4	8.2
105.7	7.9	127.7	8.0	115.3	8.1	114.6	8.2
104.4	7.9	135.4	8.0	115.1	8.1	112.3	8.2

Table A.8.3: Percentage of aggregates destroyed per mm of rainfall on silt loam soil under different biochar application rates

0 g kg^{-1}	5 g kg^{-1}	25 g kg^{-1}	50 g kg^{-1}
31.96	29.21	32.62	32.85
31.39	32.64	35.15	34.39
29.72	28.78	32.88	34.63
27.52	29.30	34.16	36.05
31.04	27.65	30.87	35.29
30.35	29.24	34.52	35.22
28.92	33.19	33.86	34.71
31.57	29.63	33.80	34.99
30.67	32.82	34.36	32.85

Table A.8.4: Total collected sediment splash (g) during rainfall simulations on silt loam soil under different biochar application rates

Simulation	0 g kg^{-1}	5 g kg^{-1}	25 g kg^{-1}	50 g kg^{-1}
1	1.14	0.91	1.37	0.79
2	0.69	0.88	0.74	1.16
3	0.93	0.98	1.37	0.87

Table A.8.5: Slopewash sediment yields during rainfall simulations on silt loam soil under different biochar application rates

Time	0 g kg^{-1}			5 g kg^{-1}			25 g kg^{-1}			50 g kg^{-1}		
(mins)	1	2	3	1	2	3	1	2	3	1	2	3
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
16	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.11	0.13
20	0.00	0.00	0.06	0.02	0.00	0.00	0.53	0.00	0.21	0.00	0.58	0.33
24	0.00	0.07	0.33	0.37	0.28	0.00	0.78	0.10	0.59	0.06	0.51	0.31
28	0.17	-	0.32	1.21	0.63	0.32	0.97	0.23	0.42	0.20	0.70	0.31
30	-	0.19	-	-	-	-	-	-	-	-	-	-
32	0.36	-	0.30	0.86	0.62	0.15	0.66	0.34	0.50	0.49	1.04	0.39
34	-	0.32	-	-	-	-	-	-	-	-	-	-
36	1.06	-	0.52	0.98	0.78	0.63	0.58	0.51	0.63	0.62	0.49	0.38
38	-	0.36	-	-	-	-	-	-	-	-	-	-
40	0.66	0.95	0.81	0.62	1.76	0.24	0.51	0.44	0.81	0.34	1.28	0.47
44	1.39	0.51	1.22	0.80	0.95	0.31	3.17	0.56	0.74	0.54	0.45	0.52
48	1.31	0.44	1.23	1.14	0.92	1.08	0.95	0.47	0.94	0.49	0.57	0.52
52	1.90	0.51	1.02	1.15	1.20	1.05	1.28	0.41	0.85	0.34	0.22	0.53
56	0.48	0.44	0.75	2.19	1.11	0.21	1.10	0.44	0.76	0.42	0.81	0.58
60	1.64	0.72	1.03	1.29	1.18	0.51	1.33	0.49	1.35	0.45	1.02	0.59

Table A.8.6: Mean OM content of silt loam soil under different biochar application rates

Simulation	0 g kg^{-1}	5 g kg^{-1}	25 g kg^{-1}	50 g kg^{-1}
1	8.08	8.71	9.86	11.71
2	7.95	8.47	9.93	11.57
3	8.16	8.68	9.91	11.12

Table A.8.7: Mean OM content of splash eroded sediment from silt loam soil under different biochar application rates

Simulation	0 g kg^{-1}	5 g kg^{-1}	25 g kg^{-1}	50 g kg^{-1}
1	12.36	14.88	17.03	23.12
2	7.09	30.17	22.07	19.33
3	11.15	22.76	24.19	24.12

Table A.8.7: Mean OM content of slopewash sediment from silt loam soil under different biochar application rates

Simulation	0 g kg^{-1}	5 g kg^{-1}	25 g kg^{-1}	50 g kg^{-1}
1	11.58	10.13	13.88	23.04
2	23.27	10.60	20.16	20.69
3	9.13	12.05	13.82	25.43

Table A.8.8: Penetration resistance of silt loam soil under different biochar application rates after drying following simulated rainfall

0 g kg^{-1}			5 g kg^{-1}			25 g kg^{-1}			50 g kg^{-1}		
1	2	3	1	2	3	1	2	3	1	2	3
0.70	0.75	0.75	0.55	0.90	0.75	0.55	0.50	0.50	0.45	0.50	0.55
0.95	0.83	0.88	0.50	1.10	0.65	0.60	0.68	0.63	0.70	0.40	0.50
0.95	0.75	0.75	0.88	0.75	0.88	0.70	0.50	0.70	0.55	0.50	0.63
0.60	0.60	0.68	0.80	0.80	0.70	0.80	0.45	0.60	0.55	0.80	0.50
0.68	0.70	1.05	0.75	0.63	0.63	0.45	0.40	0.80	0.50	0.40	0.83
0.55	0.63	0.95	0.70	0.83	0.75	0.75	0.55	0.63	0.60	0.45	0.60
0.68	0.80	0.60	0.75	0.68	0.95	0.80	0.55	0.60	0.60	0.60	0.55
0.75	0.88	0.80	0.95	0.75	0.83	0.88	0.50	0.68	0.55	0.55	0.58
0.83	0.75	0.83	0.75	0.60	0.75	1.05	0.60	0.70	0.50	0.55	0.68
0.95	0.65	1.00	0.95	0.90	0.68	0.68	0.68	0.55	0.50	0.60	0.55
0.98	0.70	0.70	0.55	0.83	0.55	1.50	0.58	0.50	0.55	0.40	0.80
0.80	0.80	0.83	0.80	0.65	0.88	0.75	0.50	0.45	0.65	0.70	0.75
0.88	0.95	0.95	0.63	0.50	0.80	0.68	0.50	0.50	0.50	0.50	0.58
0.63	0.83	1.30	0.55	0.95	0.75	0.68	0.50	0.50	0.45	0.60	0.63
0.88	1.00	0.75	0.80	0.75	0.80	0.55	0.50	0.45	0.45	0.50	0.45
0.75	0.95	0.75	0.70	0.95	0.80	0.88	0.75	0.40	0.70	0.63	0.75
0.70	0.75	0.63	0.70	0.88	0.70	0.75	0.40	0.58	0.88	0.45	0.75
0.63	0.95	0.75	0.80	0.90	0.60	0.50	0.45	0.65	0.65	0.45	0.45
0.75	0.55	0.75	1.00	0.85	0.68	0.70	0.45	0.60	0.63	0.45	0.60
0.75	0.80	0.80	1.13	0.70	0.75	0.75	0.35	0.95	0.55	0.35	0.50
0.75	0.93	0.83	0.75	0.60	0.63	0.70	0.35	0.45	0.70	0.50	0.45
0.63	1.00	1.00	0.95	0.70	0.63	0.70	0.60	0.48	0.80	0.45	0.65
0.55	0.75	0.60	0.88	0.60	0.88	0.85	0.60	0.55	0.65	0.50	0.60
0.60	0.83	0.68	0.95	0.68	0.83	0.50	0.50	0.98	0.55	0.50	0.55
0.60	0.75	0.75	0.75	0.50	0.70	0.55	0.63	0.65	0.55	0.35	0.55
0.90	0.80	0.68	0.75	1.15	0.68	0.68	0.45	0.75	0.50	0.55	0.68
0.75	0.88	0.75	0.80	1.05	0.75	0.60	0.60	0.55	0.55	0.40	0.80
0.70	0.90	0.65	0.55	0.50	0.90	0.55	0.50	0.55	0.75	0.63	0.55
0.68	0.80	0.68	0.63	0.88	0.70	0.60	0.55	0.50	0.70	0.75	0.75
1.08	0.68	0.85	0.70	1.10	0.58	0.75	0.35	0.68	0.63	0.45	0.50
0.90	0.95	1.00	0.80	0.95	0.75	0.60	0.55	0.55	0.60	0.63	0.40
0.60	0.83	0.80	0.63	0.90	0.63	0.50	0.45	0.88	0.50	0.55	0.43
0.88	0.75	0.95	0.80	1.23	0.93	0.75	0.45	0.68	0.75	0.45	0.65

0.55	0.55	0.95	0.75	1.30	0.75	0.88	0.55	0.50	0.95	0.65	0.60
0.68	0.90	1.10	0.55	0.70	0.70	0.68	0.50	0.50	0.65	0.68	0.65
0.55	0.80	1.00	0.88	0.80	0.68	0.80	0.45	0.80	0.90	0.50	0.55
0.75	0.88	1.15	0.75	0.85	0.60	0.75	0.75	0.68	0.85	0.85	0.65
1.00	0.80	1.15	0.80	0.60	0.80	0.75	0.45	0.50	0.65	0.70	0.40
0.63	0.50	0.95	1.20	1.00	0.70	0.95	0.40	0.68	0.75	0.50	0.55
0.90	0.70	0.95	0.60	0.63	0.50	0.75	0.45	0.58	0.63	0.35	0.75
0.88	0.63	0.95	0.63	1.00	0.75	0.88	0.55	0.70	0.50	0.45	0.60
0.50	0.70	1.48	0.95	1.25	0.75	0.75	0.45	0.68	0.45	0.88	0.75
0.50	0.83	1.25	0.80	1.20	0.95	0.63	0.70	0.55	0.60	0.50	0.55
0.68	0.95	0.95	0.50	1.00	0.80	0.63	0.45	0.60	0.45	0.70	0.63
0.63	0.80	1.25	0.75	1.00	0.75	0.55	0.50	0.80	0.65	0.55	0.50
0.75	0.75	0.85	0.80	0.80	0.55	0.68	0.50	0.65	0.63	0.60	0.53
0.95	0.75	1.00	0.70	0.60	0.65	0.60	0.45	0.60	0.70	0.40	0.55
0.75	0.90	1.65	0.55	0.88	0.75	0.55	0.40	0.75	0.63	0.58	0.50
0.75	0.95	0.88	0.95	1.35	0.58	0.75	0.40	0.58	0.55	0.50	0.55
0.85	1.00	0.95	0.88	0.75	0.65	0.80	0.55	0.68	0.50	0.68	0.58
0.63	0.88	1.00	0.95	1.13	0.68	0.80	0.45	0.45	0.60	0.55	0.70
0.80	0.80	0.75	0.75	0.88	1.03	0.95	0.50	0.70	0.75	0.58	0.50
0.80	0.90	1.00	0.90	0.80	0.80	0.55	0.50	0.50	0.70	0.70	0.50
0.90	0.50	0.75	0.75	0.85	0.75	0.68	0.55	0.55	0.70	0.80	0.58
0.90	0.70	0.85	0.63	1.35	0.75	0.75	0.45	0.75	0.70	0.50	0.50
0.85	0.88	1.15	0.50	0.70	0.65	0.70	0.55	0.75	0.60	0.55	0.65
0.63	0.75	1.05	0.90	0.95	0.83	0.50	0.58	0.45	0.55	0.55	0.80
0.90	1.10	0.93	0.90	0.90	0.58	0.70	0.40	0.45	0.65	0.40	0.68
0.68	0.75	0.83	0.88	0.80	0.80	0.75	0.55	0.55	0.50	0.68	0.58
0.75	0.75	0.83	0.88	0.88	0.60	0.60	0.45	0.50	0.63	0.75	0.70
0.90	0.68	1.00	0.70	1.00	0.80	0.68	0.55	0.60	0.70	0.63	0.50
1.00	0.63	1.05	1.05	0.83	0.83	0.80	0.48	0.68	0.55	0.50	0.55
0.80	0.70	0.75	0.90	1.05	0.95	0.75	0.45	0.75	0.55	0.68	0.50
0.80	0.80	1.33	0.85	0.85	0.80	0.68	0.45	0.75	0.55	0.40	0.75
0.80	0.90	0.75	0.88	1.20	0.75	0.70	0.50	0.70	0.63	0.50	0.50
0.80	0.75	0.80	1.00	0.70	0.55	0.50	0.75	0.50	0.55	0.55	0.50
0.90	0.68	0.75	0.75	0.83	0.93	0.55	0.40	0.60	0.50	0.50	0.65
0.88	0.83	0.95	1.00	0.63	0.65	0.75	0.45	0.50	0.70	0.55	0.45
1.00	1.20	1.33	0.75	0.63	0.75	0.55	0.40	0.50	0.60	0.83	0.75
0.83	0.83	1.43	0.90	0.55	0.55	0.50	0.58	0.65	0.75	0.60	0.85

1.10	0.80	1.10	0.80	0.95	0.45	0.55	0.68	0.68	0.55	0.35	0.55
0.95	0.70	0.55	0.65	0.75	0.60	0.63	0.85	0.63	0.80	0.65	0.60
0.75	0.95	0.68	0.75	0.70	0.83	0.75	0.45	0.55	0.63	0.68	0.60
0.75	0.75	0.85	0.75	0.70	1.03	0.50	0.55	0.63	0.50	1.10	0.70
0.75	0.68	0.95	0.95	0.95	0.70	0.70	0.50	0.60	0.70	0.80	0.80
0.95	0.68	0.75	1.20	0.90	0.50	0.70	0.50	0.75	0.50	0.80	0.50
0.75	0.68	0.85	0.75	0.90	0.85	0.70	0.58	0.50	0.65	0.60	0.60
0.85	0.83	0.75	1.00	0.80	0.75	0.80	0.75	0.68	0.63	0.55	0.50
0.60	0.70	0.75	0.75	0.83	0.60	0.60	0.50	0.60	0.63	0.45	0.65
0.80	1.20	0.75	0.88	1.05	0.70	0.75	0.70	0.65	0.45	0.50	0.80
0.75	0.75	0.60	0.63	0.88	0.70	0.83	0.80	0.83	0.70	0.50	0.50
0.83	1.05	0.88	1.05	1.05	0.83	0.75	0.88	0.68	0.65	0.55	0.65
0.75	0.65	0.68	0.95	0.80	1.10	0.45	0.40	0.80	0.50	0.50	0.60
1.10	0.75	0.80	0.88	1.00	0.90	0.63	0.50	0.50	0.55	0.60	0.55
1.00	0.70	0.75	0.80	0.68	0.75	0.70	0.35	0.50	0.55	0.70	0.45
0.70	0.75	0.85	0.70	0.70	0.70	0.70	0.45	0.55	0.75	0.45	0.58
0.80	0.80	0.80	0.88	1.05	0.75	0.50	0.55	0.80	0.75	0.80	0.50
0.70	0.68	0.75	1.00	0.75	0.90	0.68	0.45	0.55	0.50	0.50	0.50
0.70	0.75	0.75	1.20	0.80	0.68	0.60	0.58	0.75	0.45	0.68	0.58
0.60	1.00	1.05	0.55	0.90	0.75	0.70	0.45	0.68	0.55	0.45	0.50
1.05	0.83	1.25	0.80	0.90	0.65	0.55	0.40	0.45	0.70	0.50	0.68
0.90	0.95	0.68	0.60	0.63	0.68	0.70	0.55	0.55	0.65	1.00	0.63

(see section 5.4). This could have a more significant effect on the hydrologic properties of larger particles as a larger number of pores could be cut off by a melt than would be the case in smaller particles.

The finding that there were no significant differences between the effects of different biochar particle size fractions on matric suction suggests that the two-week incubation period allowed sufficient time for moisture to be absorbed by pores further inside larger particles, with the amount of water held by biochar being equal regardless of particle size and / or that the moisture content of the soil was sufficiently low to mean that only a certain percentage of biochar porosity was holding water, regardless of particle size. As the different size fractions were all produced under the same conditions, their pore size distribution would have been similar, meaning that there would be no differences in matric suction if they had wetted equally.

The differing effects of different sized biochar particles observed in the present study contrast somewhat with the findings of Lehmann *et al.* (2003) who used biochars of < 2 mm and ~20 mm particle size (in absolute terms, a much greater difference in size than was investigated in the present study) and observed no differences in crop growth. Nonetheless, it should be noted that Lehmann *et al.* (2003) irrigated the soils in their study daily to maintain ~60% of WHC. The findings of the present study suggest that the findings of Lehmann *et al.* (2003) might have been different had irrigation instead been applied to nearer 100% of WHC, with soils allowed to dry out more completely (over several days) before rewetting. If larger biochar particles do not necessarily wet as completely as smaller biochar particles, the moisture content of soils containing larger biochar particles would have been lower,