

# Biochar Production and Use: Environmental Risks and Rewards

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Biochar is a carbon dense solid that is produced via the slow-pyrolysis of organic materials for application to soil. Organic carbon structures, such as those found in animal manures or wood, are modified by exposure to elevated temperatures in an oxygen-limited environment. This processing causes a loss of mass through a preferential loss of hydrogen along with a loss of volatile carbon molecules. The carbon remaining in the solid forms stable, conjugated aromatic structures, which are more recalcitrant to degradation in the natural environment than the pre-processed feedstock material. The surface area of the biochar material is also greatly increased compared to the feedstock, especially at the micro-pore scale. The mineral ash content of the original organic materials is preserved in the biochar, increasing in concentration with the loss of volatile components of the feedstock.

Biochar production and use offers many opportunities for enhancing soil health and sequestering carbon. The evidence to support the application of biochar as a soil amendment to enhance crop productivity is growing. Its potential as a carbon reservoir, able to sequester carbon in soils, and hence reduce atmospheric concentrations of greenhouse gases is a relatively new area of scientific investigation, on which lies significant socio-political interest due to the agenda to find cost effective climate change solutions.

This thesis makes a significant contribution to the field of biochar production and use in developing several aspects of its physical characterization, environmental sustainability, risks, and opportunities. The investigation builds the evidence and methods required to understand the potential contribution biochar can make to atmospheric greenhouse gas reduction and agricultural sustainability.

Key findings include a comprehensive review of the physical characteristics of biochars and how they are influenced by processing conditions and feedstocks choice. Also, the discovery and investigation of *Terra Preta Australis* sites, which provide an Australian analogy to the *Terra Preta de Indio* soils, that provide a case study demonstrating the long-term impact on soil health and potential for carbon sequestration in that environment. Other major outcomes from the work include the development of risk assessment and greenhouse gas accounting methodologies that can be applied to biochar production and use. Extensive collaborative work has been included, particularly concerning the agronomic assessment of a number of biochars derived from commercially relevant feedstocks.

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## Abstract

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Biochar is a carbon dense solid that is produced via the pyrolysis of organic materials for application to soil. Organic carbon structures, such as those found in animal manures or wood, are modified by exposure to elevated temperatures in an oxygen-limited environment. This processing causes a loss of mass through a preferential loss of hydrogen along with a loss of volatile carbon molecules. The carbon remaining in the solid forms stable, conjugated aromatic structures, which are more recalcitrant to degradation in the natural environment than the pre-processed feedstock material. The surface area of the biochar material is also greatly increased compared to the feedstock, especially at the micro-pore scale. The mineral ash content of the original organic materials is preserved in the biochar, increasing in concentration with the loss of volatile components of the feedstock.

Biochar production and use offers many opportunities for enhancing soil properties and sequestering carbon. The evidence to support the application of biochar as a soil amendment to enhance crop productivity is growing. Its potential as a carbon reservoir, able to sequester carbon in soils, and hence reduce atmospheric concentrations of greenhouse gases is a relatively new area of scientific investigation, on which lies significant socio-political interest due to the agenda to find cost effective climate change solutions.

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collaborative work has been included, particularly concerning the agronomic assessment of a number of biochars derived from commercially relevant feedstocks.

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# Chapter 1

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## *Introduction*

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### *Biochar from the Slow-pyrolysis of Biomass*

#### **Biochar Production**

Pyrolysis technology facilitates the heating of biomass (organic sources of solid carbon) in a very low oxygen environment to temperatures over 400°C (Bridgwater, 2007). The resulting thermal decomposition yields solid char, liquid bio-oils and tars, and gaseous syngas. When the char is applied for environmental management and productivity benefits to soil it is described as biochar (Lehmann and Joseph, 2009). The reaction conditions of the pyrolysis production process can be engineered to change the product ratios and properties (Bridgwater, 2007; Di Blasi, 2008). Slow-pyrolysis technology, referring to the lower heating rates used in comparison to other pyrolysis reactor designs, is optimised for biochar and syngas production over bio-oil production.

The production of charcoal, as a solid fuel and metallurgical reductant, is one of the oldest industries (Food and Agriculture Organisation, 1983). Charcoal making via traditional means is renowned for the creation of air pollution (Moscowitz, 1978; Food and Agriculture Organisation, 1983; Adam, 2009; Brown, 2009). Production techniques have therefore advanced from these early industrial processes to ensure the increasing regulatory requirements can be met. Dramatic improvements have been achieved in both pollution control and energy efficiency, for example, through the adoption of controlled continuous kilns compared to batch kilns (Moscowitz, 1978; Brown, 2009).

Modern applications of biochar production technology also achieved enhanced environmental and economic outcomes via their ability to utilize the energy co-products, bio-oils and syngas, to displace fossil fuel use and/or meet growing energy demand (Brown, 2009; Laird *et al.*, 2009).

### Biochar Use

The high carbon content and surface area of the char produced via slow-pyrolysis makes it suitable for a range of purposes that would sequester the carbon it contains. Examples include using char as a concrete aggregate, or as a thermal insulation material. However, there is growing interest in its use as a soil amendment, which enhances plant growth and nutrient use efficiency (Chan *et al.*, 2007; Chan *et al.*, 2008; Blackwell *et al.*, 2009; Van Zwieten *et al.*, 2010) and reduces nitrous oxide emissions from soils (Van Zwieten *et al.*, 2009; Singh *et al.*, 2010). Charcoal has been widely used as a soil amendment for orchid growing mix and for growing turf grass for many decades. In Japan, a strong tradition in the use of charcoal as an authorised soil improver for horticultural and agricultural applications means that at least 15,000 tonnes of carbonized material is annually applied to soil (Okimori *et al.*, 2003).

Issues such as food security, declining soil fertility, climate change adaptation and profitability are all drivers for implementing new technologies or new farming systems. Research trials have shown that the application of biochar to soil has effects ranging from very positive, through to neutral and even negative impacts for crop production (Sohi *et al.*, 2009). It is therefore essential that the mechanisms for biochar interactions in soil be understood before it is recommended for wide-spread application.

It should be noted, however, that charcoal is a natural constituent of most soils. Charcoal has been found to persist in almost all soils of the world (Schmidt and Noack, 2000; Skjemstad, 2001; Lehmann *et al.*, 2008), due to the occurrence of natural fires over history. The application of biochar to soils cannot therefore be considered alien to the natural soil ecosystem.

### Terra Preta Soils

There are several examples in which the anthropogenic addition of large quantities of biochar to soils has occurred over long time frames. These include the *Terra Preta de Indio* soils of Brazil (Sombroek *et al.*, 2002), the Plaggen soils of Europe (Davidson *et al.*, 2006) and the ancient agricultural soils of the Andes (Sandor *et al.*, 1995). These examples cover different climatic regions, soil types and land management practices. The outcomes of improved soil quality for agriculture are universal across these studies, demonstrating not

only the potential to employ the technique to enhance agricultural productivity today, but also that the risk of adverse side-effects over the long-term is low.

*Terra Preta* soils have garnered interest because of their anthropology, increased fertility over extended periods and demonstrated long-term soil C sequestration (Lehmann *et al.*, 2003a). The enhanced fertility of *Terra Preta* in the Amazon has been explained by higher levels of soil organic matter (SOM), improved holding capacity of nutrients such as nitrogen, phosphorus, calcium and potassium, higher pH and higher moisture-holding capacity compared to the surrounding soils (Sombroek, 1966; Smith, 1980; Zech *et al.*, 1990; Glaser *et al.*, 2001; Lehmann *et al.*, 2003a; Lehmann *et al.*, 2003b).

These soils demonstrate the potential benefits of adding charred organics to soils, both in terms of C sequestration and improving soil fertility, and have been directly linked to the idea of biochar amendment to modern agricultural soils. Although the *Terra Preta* soils provide the opportunity to investigate the long-term implications of biochar addition, the outcomes will almost certainly be influenced by soil type, climatic conditions and the anthropological process by which they are created. Also, the differences observed between the *Terra Preta* soils and the adjacent soils may take hundreds of years to develop. Therefore, the clear benefits of biochar amendment in the *Terra Preta* soils of the Amazon will not necessarily occur in other regions. Hence, there is great interest in finding examples where anthropological biochar addition has occurred in different soils and climates. The comparison of soils amended with freshly applied biochars with ancient *Terra Preta* soils is also of interest to determine the influence of natural processes, such as oxidation and adsorption, over time. The agronomically beneficial soil qualities achieved in ancient *Terra Preta* soils may only occur over a time horizon that is not relevant to modern day land managers.

### Biochar for Greenhouse Gas Mitigation

The formation of charcoal is a known pathway for sequestering atmospheric C into terrestrial reservoirs via stabilisation of short-term cycling biogenic C into a longer-term C pool (Saldarriaga and West, 1986; Carcaillet and Talon, 2001; Graetz and Skjemstad, 2003; Long *et al.*, 2007). The highly aromatic chemical structure of the carbon in charcoal relates to its high recalcitrance to environmental degradation. Conversion of biomass to biochar

moves the biogenic carbon it contains from the short-term C cycle of degradation and release, into the long-term C cycle of recalcitrance resulting in a sink.

The upper 100 cm of the world's soils represent an estimated 1200-1600 Gt organic C global pool (Post *et al.*, 1982; Batjes, 1996; Eswaran *et al.*, 2000), which offers enormous sequestration potential (Cole *et al.*, 1996; Lal *et al.*, 2007) when considered in relation to the estimated  $270 \pm 30$  Gt CO<sub>2</sub>-C emissions from fossil fuel combustion between 1850 and 2000 (IPCC, 2001). Increasing soil carbon (C) levels has benefits beyond climate change mitigation as it improves agricultural productivity and sustainability (Paustian *et al.*, 1997; Lal *et al.*, 2007). As these benefits relate directly to profitability, they have the potential to motivate land managers to incorporate the practices of increasing soil C, without the need for high C emissions offset prices.

Although the potential for specific soil types to store carbon is an area of increasing understanding (West and Six, 2007), the potential limit for C sequestration by soils is often assumed to be the C holding capacity of native, pre-cultivation soils (Paustian *et al.*, 1997; Lal *et al.*, 2007), which results in an estimated global storage potential of 40-60 Gt (Cole *et al.*, 1996). It has been demonstrated, however, that incorporation of high levels of organic matter, and in particular chemically recalcitrant forms of organic matter, can result in greatly enhanced soil C levels (Sombroek, 1966; Sombroek *et al.*, 1993). This is evident by the ancient case studies, such as *Terra Preta* soils, discussed above (Pape, 1970; Sombroek *et al.*, 1993; Sandor *et al.*, 1995; Davidson *et al.*, 2006).

Although climate-engineering has been discussed by scientists and politicians since the 1960's, the necessity of major geo-engineering solutions has attracted serious research and debate since Crutzen put them firmly on the agenda through his editorial in *Climate Change* in 2006 (Crutzen, 2006). Since then, biochar has been added to the arsenal of geo-engineering solutions by several authors (Lehmann *et al.*, 2005; Hansen *et al.*, 2008; Read, 2008; Lenton and Vaughan, 2009). Biochar is considered as a longwave geo-engineering option for climate change mitigation, because it results in the removal of CO<sub>2</sub> from the atmosphere hence increasing levels of longwave radiation leaving the planet (Lenton and Vaughan, 2009). Biochar technology has been recognised as having potential to be implemented on a climate-changing scale (Hansen *et al.*, 2008; Read, 2008; Lehmann and Joseph, 2009; Lenton and Vaughan, 2009). The global potential for annual sequestration of

atmospheric CO<sub>2</sub> via this method has been estimated at the billion-tonne scale (10<sup>9</sup> t yr<sup>-1</sup>) within 30 years (Sohi *et al.*, 2009; Woolf *et al.*, 2011), even when strict criteria for sustainable biomass use and production are applied (Woolf *et al.*, 2011)

To enable accounting for individual entities contribution to atmospheric concentrations of greenhouse gases, methodologies need to be applied to all anthropogenic activities that cause a significant greenhouse gas (GHG) flux to the atmosphere. Methodologies are applied to calculate the net emissions of activities, so that they can be appropriately incentivised or discouraged. Alternative management practices can be compared and assessed by the net difference in atmospheric flux of GHG they are responsible for. An alternative management practice might result in abatement or additional emissions compared to usual practice. Activities involving the production and use of biochar need to be accredited, measured, monitored and verified so that they can either, produce offsets and contribute to reduction targets set on National Greenhouse Gas Inventories (NGGI) and voluntary reduction commitments, or be held liable for excessive emissions.

The structure of crediting mechanisms or emission trading schemes often lack frameworks for accounting for the prevention of biogenic emissions, as they are not recognised as a liability because the short-term cycling of biomass C is considered to be carbon neutral over the relevant timeframe. Biomass C pools are one of the most challenging parts to account for in inventories due to their dynamics and large range of management alternatives over long periods of time (Pingoud and Wagner, 2006). Some considerations have been made for long-lived carbon products and how they can be accounted for in inventories (Marland and Marland, 2003). For example, in the first commitment period of the Kyoto Protocol (2008–2012), C stock effects of harvested wood products (HWP) were ignored, and forest harvesting was treated as an instantaneous emission of carbon dioxide (Tonosaki, 2009). However, in the next commitment period of the United Nations Framework Convention on Climate Change (proposed to commence from 2013), the C stock changes resulting from HWP will be taken into account in the NGGI (Tonosaki, 2009).

The ability to obtain accreditation from C trading and offset schemes for biochar production and use could provide some additional economic incentives for the development of this industry. To date, no biochar project proponent has publically announced the successful accreditation of an accounting methodology.

### *Thesis Organisation*

In this thesis, several key questions regarding the physical structure of biochar products, and the environmental sustainability of biochar production and use are addressed. Tools for assessing environmental sustainability include; risk assessment, greenhouse gas balances, agronomic trials and case studies for integration into existing industry.

This thesis has been compiled in a publication-based format. Thirteen peer-reviewed publications are presented as the body of work under consideration in this submission. Five first-authored publications comprise the principal chapters of the thesis and the remaining co-authored works, provided as appendices, are used to develop the discussions and conclusions.

Although different publishers have published the thirteen publications independently of each other over several years, all of the papers combine around a common theme and each provides insight into one or more aspects of this topic. Collectively, the body of work contained within this thesis represents a significant contribution by the author to the knowledge of the field.

The most significant effort to compile the body of biochar research knowledge to date has been by the editors of the Earthscan published book, *Biochar for Environmental Management: Science and Technology*, published in 2009. The first peer-reviewed publication, Chapter 2 of this thesis, titled *Characteristics of Biochar – Physical and Structural Properties*, forms a chapter of that book. As is evident from the title of this chapter, this contribution describes in detail how the structure and properties of biochar depend on feedstock and processing conditions.

An aspect of biochar that was not covered in a dedicated section of the aforementioned book was a compilation of the possible risk factors raised by implementing biochar technology. A highly significant paper published on climate change geo-engineering solutions raised the need for comprehensive risk assessments to be conducted (Lenton and Vaughan, 2009). To address this void in the knowledge, a risk assessment that gauged the magnitude of the net benefit achievable through biochar production and use in relation to the associated risks was developed by the author. This work has been accepted for

publication in the leading, peer-reviewed, environmental sciences journal *Critical Reviews in Environmental Science and Technology*, which has a very high impact factor of 7.091. This publication forms Chapter 3 of this thesis.

The study of historical *Terra Preta* sites, where charcoal has been concentrated in a soil environment by anthropogenic activity hundreds of years ago, has assisted in developing an understanding of the risks and opportunities presented by biochar production and use (Glaser *et al.*, 2001; Lehmann *et al.*, 2005). The discovery and investigation of *Terra Preta* type soils in Australia, termed here as *Terra Preta Australis*, reported in this thesis as Chapter 4, is therefore highly significant to the field. This publication, which has been peer-reviewed and published by the international journal *Agriculture, Ecosystems and Environment* (impact factor 3.13), provides a case study that assesses the impact of aboriginal oven mounds created hundreds of years ago on soil. Aspects of both enhancing soil properties for supporting agricultural productivity and C holding capacity have been assessed. The paper redefines the potential of Australian soils in a temperate climate to sequester carbon and provides support for the development of biochar as a soil amendment in this climatic zone.

Very little information is available in the published literature about how feedstocks could be sustainably sourced through existing industries and logistically and economically be processed into value added biochar products for use. To address this gap in the literature a detailed synthesis of the commercial aspects to be considered in the production of biochar and its applicability to various industries was conducted. Chapter 5 of this thesis contains the peer-reviewed chapter, *Biochar: A co-product to bioenergy from slow-pyrolysis technology*, of a book to be published by Springer entitled, *Advanced Biofuels and Bioproducts*. The effective integration of biochar production with existing industries will be a critical factor in ensuring both the economic and environmental sustainability of the emerging industry. This chapter assesses biochar as a product to be marketed and in doing so highlights the important parameters for its commercialization and adoption by consumers.

A barrier to the adoption of biochar production and use is the inability of industry to monetise the greenhouse gas abatement achieved. Accreditation of biochar production and use by C offset trading mechanisms requires the approval of accounting methodologies.



Chapter 6 of this thesis consists of a paper, entitled *Greenhouse gas balance methodologies for biomass management and use*, which has been submitted for peer-review and publication to the international journal, *Biomass and Bioenergy* (impact factor 3.33). This paper proposes and examines three alternative methods for accounting for the greenhouse gas abatement in biomass carbon systems such as biochar. It develops methods, compares them using first principals and worked examples and makes recommendations as to which method is the most appropriate for implementation.

As industry moves to adopt biochar production technology, the agronomic benefits of biochars produced from industry relevant feedstocks needs to be established. A key feature to this thesis is the level of collaboration achieved with experts in soil science and agronomy. Consideration of industry relevant feedstocks and production technology has successfully been brought together with enhanced soil properties and crop productivity assessment. Chapter 7 of this thesis provides a summary of the collaborative work undertaken and published in peer-reviewed journals. As a co-author, contributions to these publications included; producing the biochar samples, assisting with experimental design, characterisation of biochars, such as conducting and reporting on scanning electron microscopy analysis, along with contributing to, reviewing and editing the manuscripts. For each publication, a summary of the contributions made by the author is provided in Chapter 7.

A concluding chapter has been compiled to draw together the key findings of each of the papers into a comprehensive body of work. Bringing the collections of publications together has allowed for a synthesis of results that demonstrates a significant contribution to the field and provides recommendations for future avenues of investigation.

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## Chapter 2

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### *Characteristics of Biochar – Physical and Structural Properties*

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# Physical Properties of Biochar

*Adriana Downie, Alan Crosky and Paul Munroe*

## Introduction

The physical properties of biochars contribute to their function as a tool for environmental management. Their physical characteristics can be both directly and indirectly related to the way in which they affect soil systems. Soils each have their own distinct physical properties depending upon the nature of mineral and organic matter, their relative amounts and the way in which minerals and organic matter are associated (Brady and Weil, 2008). When biochar is present in the soil mixture, its contribution to the physical nature of the system may be significant, influencing depth, texture, structure, porosity and consistency through changing the bulk surface area, pore-size distribution, particle-size distribution, density and packing. Biochar's effect on soil physical properties may then have a direct impact upon plant growth because the penetration depth and availability of air and water within the root zone is determined largely by the physical make-up of soil horizons. The pres-

ence of biochar will, by affecting these physical characteristics, directly affect the soil's response to water, its aggregation, workability during soil preparation, swelling-shrinking dynamics and permeability, as well as its capacity to retain cations and its response to ambient temperature changes. In addition, indirectly, many chemical and biological aspects of soil fertility can be inferred from physical properties, such as the physical presentation of sites for chemical reactions and the provision of protective habitats for soil microbes (Brady and Weil, 2008).

This chapter focuses on the physical (structural) characteristics of freshly made biochars, relating how their qualities are influenced by both the original organic material and the processing conditions under which the biochar is made. Where possible, these physical characterizations are discussed in the context of soil systems.



## Biochars: Old and new

Two approaches that one could take in examining biochars in soils include the study of biochars that have been anthropogenically or naturally incorporated within soil systems and the study of biochar made from known feed material under known conditions. Both approaches have their advantages and challenges and complement one another in developing an understanding of how the physical nature of biochars influences soil systems over time. The Black Carbon Steering Committee, for example, has developed refer-

ence materials, including wood and grass biochar produced under standardized atmospheric conditions in a pilot-scale pyrolysis oven that are intended to represent natural samples (created by forest fires) for the purpose of cross-calibration of analysis techniques (Hammes et al, 2007). As the science advances and experimental research continues, hopefully results from the two approaches will align and ancient biochar-amended soils can be more thoroughly understood to the advantage of modern agriculture.

## Relevance of extended literature

There are a limited number of peer-reviewed research papers directly presenting data on the physical characterization of biochars. Some creativity, therefore, has to be applied in literature reviews, with insightful data available from papers discussing chars made for gunpowder (Gray et al, 1985) as one example. The majority of the work on pyrolysed biomass carbons (C) has been done in the interest of developing more effective activated carbons. From a physical perspective, activated carbons are black C with both high internal surface area and microporosity, and are widely used as adsorbents in separation and purification processes for gases, liquids and colloidal solids. They also often serve as catalysts and catalyst supports. Activated carbon, however, is an expensive commodity and it is unlikely that land managers will ever afford its application to soil. Activated carbons are made from char precursors, which are analogous to biochars – hence, the literature on activated carbons is often relevant to the study of biochars. The char precursors used for making activated carbon have been characterized by several research groups (Pastor-Villegas et al, 1993; Lua et al,

2004), including a range of biomass sources such as agriculture and forest residues. These precursor products are likely to be comparable to the biochars used in anthropogenically amended soils. However, some physical activation probably occurred in traditional kilns due to steam and CO<sub>2</sub> evolving from wet biomass feedstocks, along with some gasification due to partial oxidation with the ingress of air.

There are some characterization studies available that have endeavoured to produce synthetic chars that replicate chars produced in natural systems due to the occurrence of fire (Brown et al, 2006). However, the physical characterization of biochars has generally been performed on samples produced in reactors replicating commercial processes, which have faster heating rates and shorter residence times than traditional methods that may have been used by pre-Columbian Indians, amongst others, to produce biochar. Some characterization work has been done on traditionally made wood charcoals (see Pastor-Villegas et al, 2006); however, the reporting of these methods for biomass residues other than wood is rare. The large-

scale economic manufacture of biochar will probably be carried out in modern engineered systems due to the environmental, health and safety issues associated with traditional manufacturing methods. As a result, the study of biochars made under the faster reaction times and controlled conditions of modern processing will probably be relevant for an increasing number of biochar systems (see Chapter 9) as the science moves forward.

Another consideration is that the majority of characterization work has been performed on biochars made from biomass with high C contents and low inorganic contents (ash) in order to meet the demands of the highly specified activated carbon markets. Biochar also includes products made from high-ash (inorganic) biomass feedstocks. To date, the body of physical characterization work on these types of biochars is limited but growing.

### Caution on comparing data

When reviewing the literature regarding the physical characterization of biochar, care should be taken not only because experimental conditions are highly variable, but also because they are not always reported in sufficient detail. This applies to the conditions under which the samples were prepared and the conditions under which they are analysed. For example, a commonly used physical analysis technique for determining surface areas of biochars is gas sorptometry. Adsorption experimentation is only as good as the interpretation of the results and differ-

ent methods often yield very different results. Therefore, care should be taken to only compare literature values obtained by the same method. It is known that, for microporous solids, a value of surface area does not always describe a unique property of the material but, rather, depends upon how the adsorption isotherm is determined and interpreted (Marsh, 1987). Critical review of the techniques used is beyond the scope of this chapter; however, further discussion of the issues can be found in Marsh (1987), Macias-Garcia et al (2004) and many others.

### Origin of biochar structure

The physical characteristics of biochar depend not only upon the starting organic material (biomass), but also upon the carbonization or pyrolysis system by which they are made (including the pre- and post-handling of the biomass and biochar). The degree of alteration of the original structures of the biomass, through microstructural rearrangement, attrition during processing, and the formation of cracks all depend upon the processing conditions to which they are exposed.

Since biochar is a term used to refer to the high-C solid formed as the result of the

pyrolysis of organic matter, the material can have originated from a diverse range of biomass materials. The original structure of most types of materials is imprinted on the biochar product (Laine et al, 1991; Wildman and Derbyshire, 1991) and, thus, has an overwhelming influence on its final physical and structural characteristics. During pyrolysis, mass is lost (mostly in the form of volatile organics) and a disproportional amount of shrinkage or volume reduction occurs. Hence, during thermal conversion, the mineral and C skeleton formed retains the

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rudimentary porosity and structure of the original material. The residual cellular structures of botanical origin that are present and identifiable in biochars from woods and coals of all ranks contribute the majority of the macroporosity present (Wildman and Derbyshire, 1991). Confirming this, microscopy analysis of physically activated carbon has illustrated the presence of aligned honeycomb-like groups of pores on the order of 10  $\mu\text{m}$  in diameter, most likely the carbonaceous skeleton from the biological capillary structure of the raw material (Laine et al, 1991). These large-sized pores serve as a feeder to lower-dimension pores (i.e. meso- and micro-pores) (Fukuyama et al, 2001; Martínez et al, 2006; Zabaniotou et al, 2008).

The chemical composition of the biomass feedstock has a direct impact upon the physical nature of the biochar produced. At temperatures above 120°C, organic materials begin to undergo some thermal decomposition, losing chemically bound moisture. Hemicelluloses are degraded at 200°C to 260°C, cellulose at 240°C to 350°C, and lignin at 280°C to 500°C (Sjöström, 1993). Therefore, the proportions of these components will influence the degree of reactivity and, hence, the degree to which the physical structure is modified during processing. The proportion of inorganic components (ash) also has implications for physical structure. Some processing conditions result in ash fusion or sintering, which can be the most dramatic change within the physical and structural composition of biochar.

Operating parameters during the pyrolysis process that influence the resultant physical properties of biochar of any given biomass feedstock include heating rate, highest treatment temperature (HTT), pressure, reaction residence time, reaction vessel (orientation, dimensions, stirring regime, catalysts, etc.), pre-treatment (drying, comminution, chemical activation, etc.), the flow rate of ancillary inputs (e.g. nitrogen, carbon dioxide, air, steam, etc.), and post-

treatment (crushing, sieving, activation, etc.).

Although all of these parameters contribute to the final biochar structure, the pyrolysis HTT is expected to be the most important of the factors studied because the fundamental physical changes (i.e. the release of volatiles, the formation of intermediate melts and the volatilization of the intermediate melts) are all temperature dependent. The temperature ranges, however, under which these stages occur vary with feedstock. Heating rates and pressures are expected to have the second greatest influence since they affect the physical mass transfer of volatiles evolving at the given temperature from the reacting particles (Antal and Grønli, 2003; Biagini and Tognotti, 2003; Lua et al, 2004; Boateng, 2007).

Lua et al (2004) evaluate the relative importance of temperature, hold time, nitrogen ( $\text{N}_2$ ) flow rate and heating rate during pyrolysis by assessing the standard deviations and coefficients of variation of several physical parameters (e.g. Brunauer, Emmett and Teller equation (BET) surface area, and micropore surface area and yield). They found the pyrolysis temperature to have the most significant effect, followed by pyrolysis heating rate. The  $\text{N}_2$  flow rate and the hold (residence) time show the least effects. It should be noted that these results are only directly relevant for their given feedstock and process conditions.

On the other hand, BET surface areas of olive kernel biochars measured by Zabaniotou et al (2008) increased with increasing mass loss (burn-off), regardless of the activation temperature. This indicates that with systems that include some higher oxidative gasification conditions, the burn-off of the fixed C has the most significant effect on increasing the surface area. Indeed, the surface area depends largely upon the C mass removed during processing, creating pores in the material (Zabaniotou et al, 2008).

An additional mechanism producing the structural complexity of biochars is the

occurrence of cracking. Biochar is typically laced with macro-cracks, which can be related to both feedstock properties and the rate at which carbonization is carried out (Byrne and Nagle, 1997). Wood biochar is generally broken and cracked due to shrinkage stresses developed because the surface of the material decomposes faster than its interior. Brown et al (2006) concluded that high-temperature (1000°C) surface area is controlled primarily by low-temperature (<450°C) cracking and high-temperature microstructural rearrangement. Through

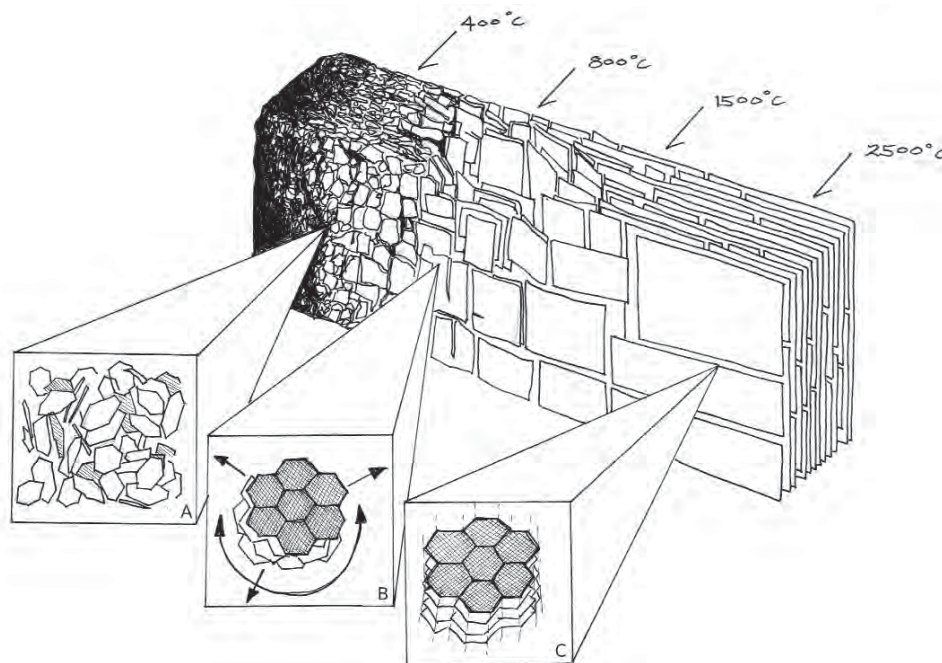
experimentation, they found the cracks formed to be too large and too numerous to be sealed off by microstructural rearrangement at higher carbonization temperatures (Brown et al, 2006). Byrne and Nagle (1997) have developed preparation methods for wood feedstocks based on its fundamental characteristics, such as density and strength, under which C monoliths (biochars with no cracks) can be produced for advanced applications. The importance of biochar structure for macro-scale porosity is discussed later in this chapter.

## Influence of molecular structure on biochar morphology

The fundamental molecular structure of biochar creates both its surface area and porosity. Carbonaceous solid materials such as coals, charcoals, cokes, etc. contain crystalline particles (crystallites) in the order of nanometres in diameter, composed of graphite-like layers arranged turbostratically (layers are not aligned) (Warren 1941; Biscoe and Warren, 1942). The biochar structure, determined by X-ray diffraction, is essentially amorphous in nature, but contains some local crystalline structure (Qadeer et al, 1994) of highly conjugated aromatic compounds. Crystalline areas can be visualized as stacks of flat aromatic (graphene) sheets cross-linked in a random manner (Bansal et al, 1988). Similar to graphite, they are good conductors in spite of their small dimensions (Carmona and Delhaes, 1978). Thus, the microcrystallites are often referred to as the conducting phase. The other non-conducting components that complete the biochar C matrix are the aromatic-aliphatic organic compounds of complex structure (including residual volatiles), and the mineral compounds (inorganic ash) (Emmerich et al, 1987). This is complemented with the voids, formed as pores (macro-, meso- and micropores), cracks and morphologies of cellular

biomass origin.

Pyrolysis processing of biomass enlarges the crystallites and makes them more ordered. This effect increases with HTT. Lua et al (2004) demonstrated, for example, that increasing the pyrolysis temperature from 250°C to 500°C increases the BET surface area due to the increasing evolution of volatiles from pistachio-nut shells, resulting in enhanced pore development in biochars. For turbostratic arrangements, the successive layer planes are disposed approximately parallel and equidistant, but rotated more or less randomly with respect to each other (see inset B, Figure 2.1) (Emmerich et al, 1987). The spacing between the planes of turbostratic regions of biochar is larger than that observed in graphite (Emmerich et al, 1987; Laine and Yunes, 1992). In spite of the two-dimensional long-range order in the directions of the graphite-like layers, materials with turbostratic structure are called non-graphitic C because there is no measurable crystallographic order in the third direction (insets B and C, Figure 2.1) (Emmerich and Luengo, 1996). Rosalind Franklin first demonstrated that some varieties of non-graphitic C are converted to graphitic C during pyrolysis, presenting crys-



**Figure 2.1** *Ideal biochar structure development with highest treatment temperature (HTT): (A) increased proportion of aromatic C, highly disordered in amorphous mass; (B) growing sheets of conjugated aromatic carbon, turbostratically arranged; (C) structure becomes graphitic with order in the third dimension*

Source: chapter authors

tallographic order in the third direction (Franklin, 1951). The pyrolysis of all biomass C will finally yield graphite when heated to 3500°C; however, some feedstocks graphitize at HTTs of less than 2000°C (Setton et al, 2002).

The surface of non-graphitized C, such as wood biochars, consists of both the faces and edges of ordered sheets (Boehm, 1994, 2002). The turbostratic linkage of these crystallites leaves random interstices (pores of various sizes). A further possible cause of micropores is from voids (holes) within hexagonal planes (Bourke et al, 2007). Heteroatoms, in particular oxygen (O), are predominantly located on the edges of ordered sheets as components of various functional groups (Boehm, 1994, 2002). The interplanar distance of graphite (0.335nm) is

probably not achieved under typical pyrolysis conditions (<1000°C) due to the formation of O functional groups at the sheet edges, which through steric or electronic effects prevent the close packing of the sheets (Laine and Yunes, 1992).

Pores, of whatever origin, may become filled with tars (condensed volatiles) and other amorphous decomposition products, which may partially block the microporosity created (Bansal et al, 1988). The tars created from thermal biomass C decomposition impede the continuity of pores at low temperatures and these pores become increasingly accessible as the temperatures increase and tar components are volatilized (Pulido-Novicio et al, 2001). Mineral matter may also become occluded in the pores or exposed at the surface of the biochar particles.



## Loss of structural complexity during pyrolysis

Under certain processing conditions, many research groups have reported drastic loss of structural complexity in biochar products, which is often explained by plastic deformation, melt, fusion or sintering. High heating rates, increased pressure, high HTT, high ash contents (or low ash melting points) and long retention times (in combination with high temperatures) have all been held accountable for the loss of surface area and porosity in biochar products. Of the numerous examples in the literature some typical results have been selected to demonstrate each pathway.

Rodríguez-Mirasol et al (1993) investigated the carbonization of eucalyptus kraft lignin at different temperatures and characterized the structure of the microporous biochar product. They found that partial fusion and swelling in the carbonization stage was related to the ash content (inorganic matter) in the starting material (Rodríguez-Mirasol et al, 1993). Therefore, they developed a new pre-treatment method to remove the inorganic matter by washing with diluted acidic solutions prior to carbonization in order to prevent this loss of structural complexity. High ash content is often a significant contributing factor to loss of structure. However, even in very low ash materials, such as the hazelnut shell (Aygün et al, 2003), some thermoplastic properties can be exhibited.

The lack of structure in biochars made at high heating rates has been explained by the melting of the cell structure and by plastic transformations (Biagini and Tognotti, 2003; Boateng, 2007). Cetin et al (2004) reported that at low heating rates ( $20^{\circ}\text{C sec}^{-1}$ ), the natural porosity of pine sawdust allows a volatile release with the occurrence of no major morphological changes. However, at high heating rates ( $500^{\circ}\text{C sec}^{-1}$ ), the cell structure is destroyed by devolatilization (Cetin et al, 2004). Biagini and Tognotti

(2003) recorded the same phenomenon in their experimentation and noted the re-solidification of the solid structure and formation of more compact biochar particles (Biagini et al, 2003). They also stated that melting and swelling are more pronounced for biomass species that contain higher levels of volatile matter.

High HTT, coinciding with the ash melting points of the various biomass feedstocks, also causes decreases in structural complexity. For a pistachio-nut feedstock, Lua et al (2004) found that increasing HTT from  $500^{\circ}\text{C}$  to  $800^{\circ}\text{C}$  progressively decreased the BET surface area. They attributed this to the decomposition and softening of some volatile fractions to form an intermediate melt in the biochar structure (Lua et al, 2004). Brown et al (2006) reported similar findings with biochars made from pine. At heating rates of  $30^{\circ}\text{C hr}^{-1}$  and  $200^{\circ}\text{C hr}^{-1}$ , surface areas were found to be markedly lower at a HTT of  $1000^{\circ}\text{C}$  compared with those observed at lower final temperatures (Brown et al, 2006).

Increasing the reaction retention time has also been demonstrated to cause deformation in the physical structure; however, this may be the result of heat transfer rates being too slow for the solid to reach a high HTT. Guo and Lua (1998) found that at  $900^{\circ}\text{C}$ , the high surface area of oil palm stone biochar deteriorated with increasing reaction retention time. They attributed this to both the sintering effect, followed by a shrinkage of the biochar, and realignment of the biochar structure, which resulted in reduced pores. With their reactor configuration, they found that maximum surface areas were obtained when oil palm stones were pyrolysed at  $800^{\circ}\text{C}$  with a retention time of three hours (Guo and Lua, 1998).

Work by Lewis (2000) with redwood has shown, however, that the pores do not collapse as suggested by Guo and Lua (1998). Lewis

(2000) provides evidence against such collapse by showing that the pores can be reopened by a  $\text{CO}_2$  activation process in a manner that allows  $\text{N}_2$ -accessible surface area to increase from  $2\text{m}^2\text{g}^{-1}$  to  $540\text{m}^2\text{g}^{-1}$ . This suggests that the pores are still present (not collapsed) and that they are only closed off at higher temperatures (Lewis, 2000).

The fusion of multiple particles, which did not occur under atmospheric conditions,

has also been reported at pressures of 10bar to 20bar (Cetin et al, 2004). Cetin et al (2004) found that at these pressures, eucalyptus sawdust particles melt and fuse, losing their own distinctions. Similar results were obtained at atmospheric pressures for the fast heating rate of  $\sim 500^\circ\text{C min}^{-1}$ . A number of particles fused together can form a hollow and smooth-surfaced particle (Cetin et al, 2004).

### Industrial processes for altering the physical structure of biochar

Processes for increasing surface areas and porosity have been frequently investigated, driven by the many commercial applications of activated carbons that require large sorptive capacities. Although, as already highlighted, process conditions such as HTT, heating rate, etc. influence biochar's physical structure, commercially viable internal surface areas are almost always generated in high C-containing biochar precursors through physical or chemical activation.

Physical activation, which is carried out most frequently in industry, is obtained when the initial pyrolysis reactions, occurring in an inert atmosphere at moderate temperatures ( $400^\circ\text{C}$  to  $800^\circ\text{C}$ ), are complemented by a second stage in which the resulting biochars are subjected to a partial gasification at a higher temperature (usually  $>900^\circ\text{C}$ ) with oxidizing gases such as steam,  $\text{CO}_2$ , air or a mixture of these. This produces final products with well-developed and accessible internal pores (Bansal et al, 1988).

The activation of biochar with  $\text{CO}_2$  involves a  $\text{C}-\text{CO}_2$  reaction (Rodríguez-Reinoso and Molina-Sabio, 1992). This leads to the removal of C atoms or burn-off, in this way contributing to the development of a porous structure. According to Rodríguez-Reinoso et al (1992),  $\text{CO}_2$  can open closed

pores as well as widen existing pores by the activation, increasing the accessibility of the small pores to the molecules of an adsorbate. Both the surface area and the nature of porosity are significantly affected by the conditions of  $\text{CO}_2$  activation, the extent of which depends upon the nature of the precursors (Zhang et al, 2004). Steam is suggested to play a double role: it promotes both the release of volatiles with partial devolatilization and enhances crystalline C formation (Alaya et al, 2000).

The physical and adsorptive properties of biochars depend upon activation time and quantity of steam used for activation. BET surface areas of activated olive kernel carbons were found to be increasing with activation time and temperature from a minimum value of  $1339\text{m}^2\text{g}^{-1}$  at one hour and  $800^\circ\text{C}$  to a maximum of  $3049\text{m}^2\text{g}^{-1}$  at four hours and  $900^\circ\text{C}$  (Stavropoulos, 2005). Zhang et al (2004) confirmed these trends for biochars made from oak, maize hulls and maize stover residues. They found BET surface areas of all activated carbons obtained at  $700^\circ\text{C}$  were lower than those obtained at  $800^\circ\text{C}$  (Zhang et al, 2004). With physical activation for one to two hours, surface areas were increased with activation time (Zhang et al, 2004). This expansion in surface area with increased activation time can also be explained by the

increasing burn-off (mass loss) (Zabaniotou et al, 2008).

Chemical activation entails the addition of materials such as zinc salts or phosphoric acid to the C precursors ( $\text{H}_3\text{PO}_4$ ,  $\text{ZnCl}_2$  and alkali metal hydroxides). KOH (and NaOH) has been used for preparing activated carbons with unusually high surface areas called 'super active' carbons by some authors (Rouquerol et al, 1999). During activation, potassium (K) is intercalated and forces apart the lamellae of the crystallites that form the C structure. After washing the samples, K is eliminated, leaving free interlayer space that contributes to the porosity of the product (Marsh et al, 1984). Precursor material properties such as microcrystalline structure, reactivity and pore accessibility are shown to affect the results of these treatments. The most suitable raw materials for KOH activation are those having small-sized crystallites, medium reactivity and high accessibility to the internal pore structure (Stavropoulos, 2005).

Chemical activation offers several advantages since it is carried out in a single step, combining carbonization and activation, is performed at lower temperatures and, therefore, results in greater development of porous structure. Chemical activation methods are not, however, as common, possibly due to the possibility of generating secondary environmental pollution during disposal (Zhang et al, 2004).

Reactor type has also been demonstrated to have an influence on the physical surface and porosity of chars. Gonzalez et al (1997) conducted their investigation of  $\text{CO}_2$  activation with both vertical and horizontal furnaces and concluded that a horizontal furnace is advantageous for micropore development.

Biochars resulting from fast pyrolysis reactors (high heating rates) have different physical properties from those made under

slow pyrolysis conditions. The surface areas of switchgrass biochars made under fast pyrolysis conditions were found to be low, typically between  $7.7\text{m}^2\text{ g}^{-1}$  and  $7.9\text{m}^2\text{ g}^{-1}$  (Boateng, 2007). Further examples that are typical for fast pyrolysis, because of the high heating rates of the rather small particles (less than 1mm), were produced by a fluidized sand-bed reactor operating at approximately  $500^\circ\text{C}$ , with inert  $\text{N}_2$  as the fluidizing agent (Zhang et al, 2004). Oak, maize hull and maize stover biochars exhibited low surface areas of  $92\text{m}^2\text{ g}^{-1}$ ,  $48\text{m}^2\text{ g}^{-1}$ , and  $38\text{m}^2\text{ g}^{-1}$ , and total pore volumes of  $0.1458\text{cm}^3\text{ g}^{-1}$ ,  $0.0581\text{cm}^3\text{ g}^{-1}$  and  $0.0538\text{cm}^3\text{ g}^{-1}$ , respectively (Zhang et al, 2004).

Gas pressure during the pyrolysis reactions also has an influence on the structure of the biochar products. For example, biochar particles that were generated at 5bar pyrolysis pressure at a heating rate of  $500^\circ\text{C sec}^{-1}$  to  $950^\circ\text{C}$  were shown to have larger cavities with thinner cell walls than biochars that were generated at atmospheric pressure. This effect was increased at 20bar (Cetin et al, 2004).

The pyrolysis system, particularly the activation method, has an influence on the physical nature of biochars. The degree of influence that it has, however, depends upon the feedstock used, with different feedstocks producing different results. For example, Pastor-Villegas et al (2006) found that the influence of the carbonization reaction method on the non-micropore structure is not significant when the raw material is eucalyptus wood, while there are considerable differences when the raw material is holm-oak wood (Pastor-Villegas et al, 2006). When studying biochars, it is essential to note the feedstock, preparation conditions and analysis methods used to ensure that meaningful conclusions are drawn which can be compared with that of other studies.



## Soil surface areas and biochar

Surface area is a very important soil characteristic as it influences all of the essential functions for fertility, including water, air, nutrient cycling and microbial activity. The limited capacity of sandy soil to store water and plant nutrients is partly related to the relatively small surface area of its soil particles (Troeh and Thompson, 2005). Coarse sands have a very low specific surface of about  $0.01\text{m}^2\text{g}^{-1}$ , and fine sands about  $0.1\text{m}^2\text{g}^{-1}$  (Troeh and Thompson, 2005). Clays have a comparatively large specific surface, ranging from  $5\text{m}^2\text{g}^{-1}$  for kaolinite to about  $750\text{m}^2\text{g}^{-1}$  for Na-exchanged montmorillonite. Soils containing a large fraction of clay may have high total water-holding capacities but inadequate aeration (Troeh and Thompson, 2005). High organic matter contents have been demonstrated to overcome the problem of too much water held in a clay soil, and also increase the water contents in a sandy soil (Troeh and Thompson, 2005). Indications exist that biochar will similarly change the

physical nature of soil, having much of the same benefit of other organic amendments in this regard (Chan et al, 2007). Biochar specific surfaces, being generally higher than sand and comparable to or higher than clay, will therefore cause a net increase in the total soil-specific surface when added as an amendment.

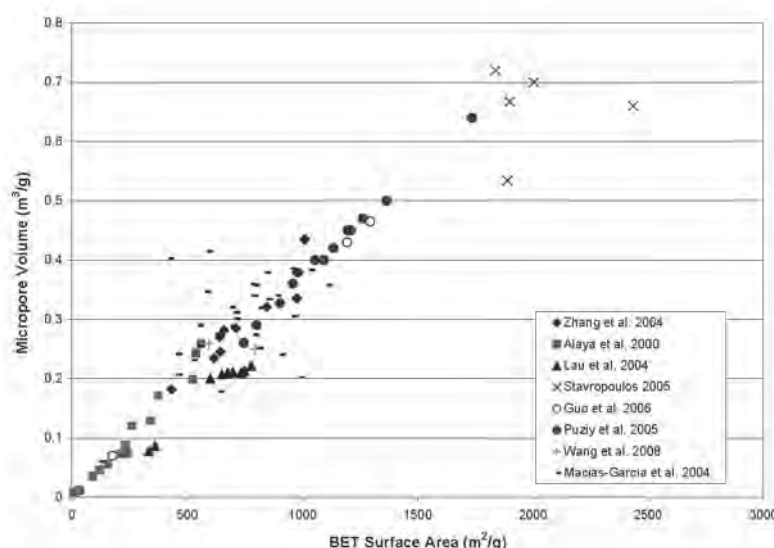
The influence of biochar on microbial populations in soils is presented in Chapter 6. However, it should be noted here that soil microbial biomass commonly increases with increasing clay content under both field and laboratory conditions (Amato and Ladd, 1992; Juma, 1993; Müller and Höper, 2004), and this response is generally attributed to the increased surface area (Juma, 1993). The higher surface areas of finer-textured soils can result in increased total water content and improved physical protection from grazers. Biochar has been experimentally linked to improved soil structure or soil aeration in fine-textured soils (Kolb, 2007).

## Biochar nano-porosity

The pore-size distribution of activated carbons has long been recognized as an important factor for industrial application. It is logical that this physical feature of biochars will also be of importance to their behaviour in soil processes. The relationship between total surface area and pore-size distribution is logical. As shown in Figure 2.1, as the HTT increases more structured regular spacing between the planes results. Interplanar distances also decrease with the increased ordering and organization of molecules, all of which result in larger surface areas per volume.

Micropores (known to material scientists as all pores  $<2\text{nm}$  in diameter) contribute

most to the surface area of biochars and are responsible for the high adsorptive capacities for molecules of small dimensions such as gases and common solvents (Rouquerol et al, 1999). It should be noted that soil scientists refer to all pores  $<200\text{nm}$  in diameter as micro-pores; however, for the purpose of this chapter, the total pore volume of the biochar will be divided into micropores (pores of internal diameter less than  $2\text{nm}$ ), mesopores (pores of internal width between  $2\text{nm}$  and  $50\text{nm}$ ) and macropores (pores of internal width greater than  $50\text{nm}$ ) (Rouquerol et al, 1999), as this provides a level of differentiation required to discuss molecular and structural effects. However, the importance



**Figure 2.2** Relationship between biochar surface area and micro-pore volume

Source: chapter authors

and range of macroporosity in the context of biochar in soil systems cannot be overemphasized, and will be discussed in detail in a later section.

Figure 2.2 compiles some of the data available in the literature to demonstrate the relationship between micropore volume and total surface area of biochars. This provides evidence that pore sizes distributed in the micropore range make the greatest contribution to total surface area. The development of microporosity with higher temperatures and longer retention times has been demonstrated by several research groups (see plotted examples in Figure 2.3). Elevated temperatures provide the activation energies and longer retentions allow the time for the reactions to reach completion, leading to greater degrees of order in the structures. For example, the ratios of micropore volume to total pore volume of CO<sub>2</sub>-activated carbons produced from maize hulls generated at 700°C were lower than those of activated carbons prepared at 800°C (Zhang et al, 2004).

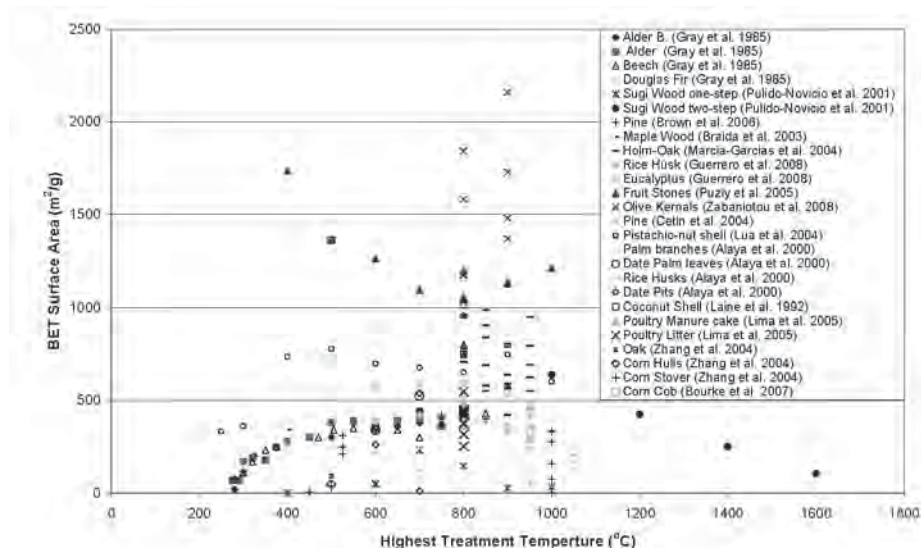
The analysis of gas adsorption isotherms is the typical methodology used for assessing surface areas of C materials. The range of

adsorbents, degassing regimes, temperatures, pressures and algorithms used makes comparison of literature values challenging. However, some general trends can be observed through compiling literature values (see Figure 2.3).

The surface area of biochars generally increases with increasing HTT until it reaches the temperature at which deformation occurs, resulting in subsequent decreases in surface area. A typical example is provided by Brown et al (2006), who produced biochar from pine in a laboratory oven purged with N<sub>2</sub> at a range of final temperatures varying from 450°C to 1000°C, and heating rates varying from 30°C hr<sup>-1</sup> to 1000°C hr<sup>-1</sup>. Brown et al found that independent of heating rate, maximum surface area, as measured by BET (N<sub>2</sub>), was realized at a final temperature of 750°C. At the lowest HTT (i.e. 450°C), all of the surface areas were found to be less than 10m<sup>2</sup> g<sup>-1</sup>, while those produced at intermediate temperatures of 600°C to 750°C had a surface area of approximately 400m<sup>2</sup> g<sup>-1</sup> (Brown et al, 2006).

Under some conditions, a high temperature causes micropores to widen because it

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**Figure 2.3** Biochar surface area plotted against highest treatment temperature (HTT): it should be noted that different methods of treatment and surface area analysis were used in each study

Source: chapter authors

destroys the walls between adjacent pores, resulting in the enlargement of pores (Zhang et al, 2004). This leads to a decrease in the fraction of volume found in the micropore range and an increase in the total pore volume. In samples of maize hulls and maize stover, Zhang et al (2004) found microporosity to be appreciably greater after one hour of physical activation than after two hours. They proposed that the rate of pore formation exceeded that of destruction due to pore enlargement and collapse at the earlier stage and vice versa at the later stage (Zhang et al, 2004).

Heating rates also determine the extent of micropore formation. One example was

provided by Cetin et al (2004), who found that biochars generated at atmospheric pressure under low heating rates mainly consisted of micropores, whereas those prepared at high heating rates were largely comprised of macropores as a result of melting (Cetin et al, 2004).

Mesopores are also present in biochar materials. These pores are of importance to many liquid–solid adsorption processes. For example, pistachio-nut shells have a mixture of micropores and mesopores, with micropores dominating, indicating that these activated carbons can be used for both gas and liquid adsorption applications (Lua et al, 2004).

## Biochar macroporosity

In the past, when biochars and activated carbons were assessed mainly for their role as adsorbents, macropores (>50nm diameter)

were considered to be only important as feeder pores for the transport of adsorbate molecules to the meso- and micro-pores

**Table 2.1** *Surface areas and volumes of different sizes of biochar pores*

	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Volume (cm <sup>3</sup> g <sup>-1</sup> )
Micropores	750–1360	0.2–0.5
Macropores	51–138	0.6–1.0

Source: Laine et al (1991)

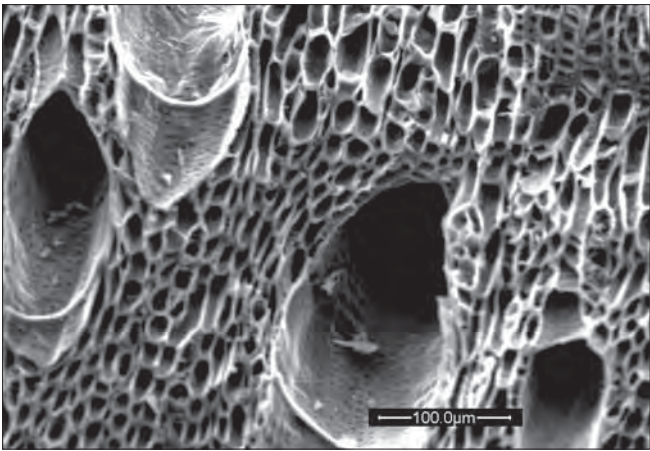
(Wildman and Derbyshire, 1991). However, macro-pores are very relevant to vital soil functions such as aeration and hydrology (Troeh and Thompson, 2005). Macropores are also relevant to the movement of roots through soil and as habitats for a vast variety of soil microbes. Although micropore surface areas are significantly larger than macropore surface areas in biochars, macropore volumes can be larger than micropore volumes (see Table 2.1). It is possible that these broader volumes could result in greater functionality in soils than narrow surface areas.

As anticipated from the regular size and arrangement of plant cells in most biomass from which biochars are derived, the macropore size distribution is composed of discrete groups of pores sizes rather than a continuum (Wildman and Thompson, 1991). The obvious macroporous structure of a wood biochar imaged using a scanning electron microscope (SEM) can be seen in Figure 2.4.

To put this in perspective with typical soil particles, these discrete groups of pore diameters observed in this sample of ~5µm to 10µm, and ~100µm compare to very fine sand or silt particle sizes, and fine sand particle sizes, respectively.

Another consideration is the type of microbial communities that utilize soil pores as a preferred habitat (see Chapter 6). Microbial cells typically range in size from 0.5µm to 5µm, and consist predominantly of bacteria, fungi, actinomycetes and lichens (Lal, 2006). Algae are 2µm to 20µm (Lal, 2006). The macropores present in biochars pictured in Figure 2.4 may therefore provide suitable dimensions for clusters of micro-organisms to inhabit. Chapter 6 provides more detail on microbial communities and biochar.

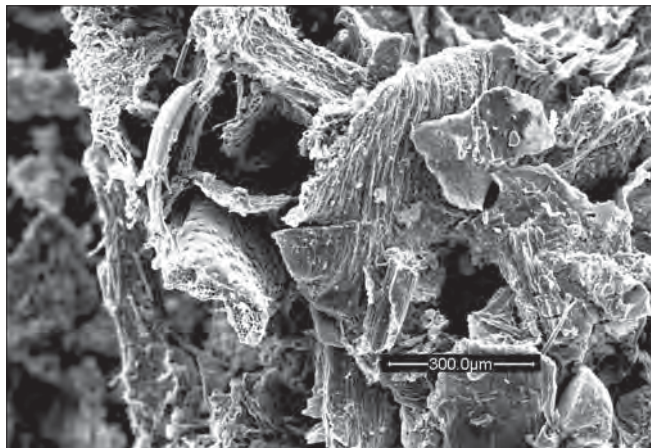
On the scale of soil systems, the macroporosity seen in the SEM image of a poultry litter char (see Figure 2.5), with cavities up to 500µm in the agglomerated particle, is very relevant. However, very few investigations at this scale are presented in the literature. Soil structure is defined in terms of peds, which are arrangements of primary soil particles, and soil porosity is often defined as the openness between these peds (Troeh and Thompson, 2005). The interaction and stacking of heterogenous agglomerated biochar particles and peds in the soil will have a direct impact upon the bulk soil structure.



**Figure 2.4** *Scanning electron microscope (SEM) image showing macroporosity of a wood-derived biochar produced by 'slow' pyrolysis: The biochar samples were chromium coated and imaged with a beam energy of 20kV on a FEI Quanta 200 environmental scanning electron microscope (ESEM)*

Source: chapter authors





**Figure 2.5** SEM image showing macroporosity in biochar produced from poultry manure using slow pyrolysis

Source: chapter authors

### Particle-size distribution

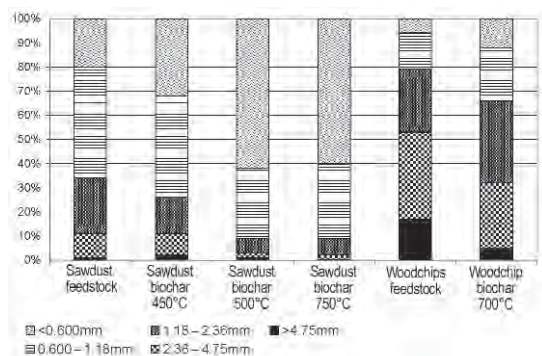
The particle sizes of the biochar resulting from the pyrolysis of organic material are highly dependent upon the nature of the original material. Due to both shrinkage and attrition during pyrolysis, particle sizes of the organic matter feedstock are likely to be greater than the resultant biochar. In some cases, particles may agglomerate; therefore, increased particle sizes are also found (Cetin et al, 2004). Depending upon the mechanical intensity of the pyrolysis technology employed, a degree of attrition of the biomass particles will occur during processing. This is especially true in the post-handling of the material as the biochar is significantly more friable than the original biomass.

Evidence for the dependency of particle-size distribution of the biochar upon the organic matter feedstock is presented in Figure 2.6. Biochar derived from sawdust and wood chips was prepared with different pre-treatments, producing contrasting particle sizes. The pyrolysis processing, through the BEST Energies continuous slow ( $5^{\circ}\text{C min}^{-1}$  to  $10^{\circ}\text{C min}^{-1}$  heating rate) pyrolysis pilot plant, resulted in an increasing proportion of particles in the smaller size distributions for both of the feedstocks, as measured by dry sieving. It can also be seen

that as the pyrolysis HTT increased ( $450^{\circ}\text{C}$  to  $500^{\circ}\text{C}$  to  $700^{\circ}\text{C}$ ), the particle sizes tended to decrease. This may be explained by the decreasing tensile strength of the material as it is more completely reacted, resulting in less resistance to attrition during processing.

Depending upon the technology employed, biomass feedstock is prepared in different ways. The faster the heating rate required, the smaller the feedstock particles need to be to facilitate the heat and mass transfer of the pyrolysis reactions. Fast pyrolysis feedstocks, for example, are pre-processed to a fine dust or powder; therefore, the resultant biochar is very fine. Continuous slow pyrolysis technologies, which employ slower heating rates ( $\sim 5^{\circ}\text{C min}^{-1}$  to  $30^{\circ}\text{C min}^{-1}$ ), can accommodate larger particles up to several centimetres in dimension. Traditional batch processes can allow weeks for the heat and mass transfer of the process to occur (see Chapter 8) and, hence, receive whole branches and logs.

The investigation by Cetin et al (2004), for example, on the first-step pyrolysis of a two-stage gasification process used biomass fuel particles with sizes between  $50\mu\text{m}$  and  $2000\mu\text{m}$  depending upon the reactor type and techniques used. This small size is



**Figure 2.6** Influence of biomass pre-treatment and HTT on the particle size distribution of different biochars

Source: chapter authors

required to achieve the high heating rates, ranging from  $500^{\circ}\text{C sec}^{-1}$  to extremely high heating rates of ( $\approx 1 \times 10^5^{\circ}\text{C sec}^{-1}$ ) and short residence times (Cetin et al, 2004).

If larger particles are used, it is possible that the reactions will be limited by the heat transfer into the particles and the mass transfer of volatiles out of the biochar. For

example, in a study of the pyrolysis of oil palm stones, it was found that the biochar yields were affected by both the particle size of the stones and the maximum pyrolysis temperature (Shamsuddin and Williams, 1992). Longer retention times would perhaps have overcome the influence of the larger particle sizes.

An increase in linear shrinkage of the particles being pyrolysed can be seen to take place in conjunction with the loss of volatile matter (Emmerich and Luengo, 1996; Freitas et al, 1997). For example, as pyrolysis temperatures increase from  $200^{\circ}\text{C}$  to  $1000^{\circ}\text{C}$ , the linear shrinkage of particles was demonstrated to increase from 0 to 20 per cent for peat biochars (Freitas et al, 1997).

Cetin et al (2004) demonstrated that increasing the pyrolysis pressure (from atmospheric to 5, 10 and 20bars) leads to the formation of larger biochar particles. They accounted for this as swelling, as well as the formation of particle clusters, as a result of melting and subsequent fusion of particles (Cetin et al, 2004).

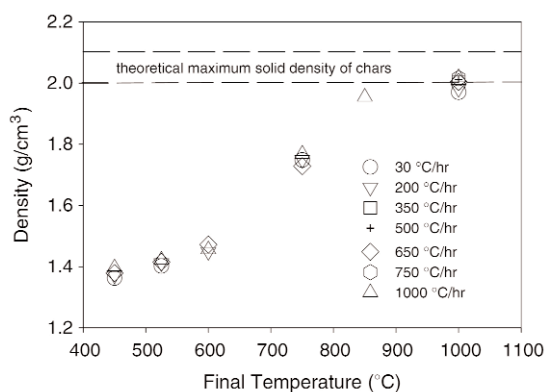
## Biochar density

Two types of density of biochars can be studied: the solid density and the bulk or apparent density. Solid density is the density on a molecular level, related to the degree of packing of the C structure. Bulk density is that of the material consisting of multiple particles and includes the macroporosity within each particle and the inter-particle voids. Often, an increase in solid density is accompanied by a decrease in apparent densities as porosity develops during pyrolysis. The relationship between the two types of densities was demonstrated by Guo and Lua (1998), who reported that apparent densities increased with the development of porosities from 8.3 to 24 per cent at pyrolysis temperatures up to  $800^{\circ}\text{C}$  (Guo and Lua, 1998). However, when the

temperature increased to  $900^{\circ}\text{C}$ , the apparent density of the biochar increased and the porosity decreased due to sintering. This inverse relationship between solid and apparent density was also demonstrated by Pastor-Villegas et al (2006) for eucalyptus biochar manufactured in a continuous furnace having both the lowest values of apparent density (measured as both bulk and mercury displacement) and the highest solid density value (measured by helium displacement).

The loss of volatile and condensable compounds from the unorganized phase of the biochars and the concomitant relative increase in the organized phase formed by graphite-like crystallites leads to the increase in solid density (or true density) of the

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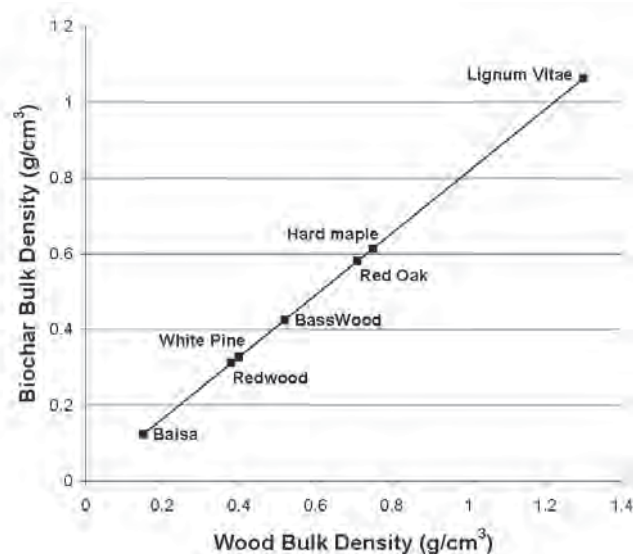
**Figure 2.7** Helium-based solid densities of biochars with HTT

Source: Brown et al (2006)

biochars compared with their feedstocks (Emmerich et al, 1987). The maximum density of C in biochars has been reported to lie between  $2.0 \text{ g cm}^{-3}$  and  $2.1 \text{ g cm}^{-3}$  based on X-ray measurements (Emmett, 1948). Such values are only slightly below the density of solid graphite of  $2.25 \text{ g cm}^{-3}$ . Most solid densities of biochar, however, are significantly lower than that of graphite because of residual porosity and their turbostratic structure (Oberlin, 2002), with typical values

around  $1.5 \text{ g cm}^{-3}$  to  $1.7 \text{ g cm}^{-3}$  (Jankowska et al, 1991; Oberlin, 2002). Lower values such as that of a pine wood biochar collected from a natural fire site at  $1.47 \text{ g cm}^{-3}$  (Brown et al, 2006) are also common. Biochars activated to produce microporosity for the adsorption of gases are denser than for those optimized to produce meso- and macro-porosity for the purification of liquids (Pan and van Staden, 1998).

The density of the biochars depends upon the nature of the starting material and the pyrolysis process (Pandolfo et al, 1994). Solid density of biochar increases with increasing process temperature and longer heating residence times, in accordance with the conversion of low-density disordered C to higher-density turbostratic C (Byrne, 1996; Kercher and Nagle, 2002). Lower amounts of volatiles, which have lower molecular weights than fixed C, and lower ash contents result in higher solid density in biochars (Jankowska et al, 1991). However, Brown et al (2006) showed that density is independent of heating rate, and found a simple and direct dependency of density upon final pyrolysis temperature (see Figure 2.7). Thus, they deduced that the He-based solid density may



**Figure 2.8** Bulk density of wood biochar, plotted against that of its feedstock

Note: Biochar bulk density =  $0.8176 \times$  wood bulk density. Values are for carbonization in a nitrogen atmosphere at  $15^\circ\text{C hr}^{-1}$  to  $900^\circ\text{C}$ .

Source: Byrne and Nagle (1997)

serve as an approximate indicator of the highest temperature experienced by any wood biochar, regardless of the exact thermal history (Brown et al, 2006). This concept may provide a useful tool for characterizing charring conditions in order to understand the production of biochars in archaeological soil such as Terra Preta and possibly provide information about their creation.

Bulk density is also an important physical feature of biochars. Pastor-Villegas et al (2006) found that the bulk densities of biochars made from different types of woods processed in different types of traditional kilns ranged from  $0.30 \text{ g cm}^{-3}$  to  $0.43 \text{ g cm}^{-3}$ .

Bulk density values given in the literature for activated carbons used for gas adsorption range from  $0.40 \text{ g cm}^{-3}$  to  $0.50 \text{ g cm}^{-3}$ , while for activated carbons used for decolourization, the range is  $0.25 \text{ g cm}^{-3}$  to  $0.75 \text{ g cm}^{-3}$  (Rodríguez-Reinoso, 1997). Byrne and Nagle (1997) established a linear relationship between the bulk densities of wood and biochar made from the same material, which spans a range of species. They found that for wood pyrolysed at a heating rate of  $15^\circ\text{C hr}^{-1}$  to a HTT of  $900^\circ\text{C}$ , the carbonized wood had 82 per cent of the bulk density of the precursor wood (Byrne and Nagle, 1997).

## Mechanical strength

The mechanical strength of biochar is related to its solid density. Therefore, the increased molecular order of pyrolysed biomass gives it a higher mechanical strength than the biomass feedstock from which it was derived. For example, Byrne and Nagle (1997) reported that tulip poplar wood carbonized at a HTT of  $1550^\circ\text{C}$  had a 28 per cent increase in strength. Mechanical strength is a characteristic used for defining the quality of

activated carbon as it relates to its ability to withstand wear and tear during use. Agricultural wastes, such as nut shells (almond, hazelnut, macadamia and walnut) and fruit stones (apricot, olive pits, etc.) are of interest as activated carbons because of their high mechanical strength and hardness. These properties can be explained by high lignin and low ash contents (Aygun et al, 2003).

## Future research

The physical properties of biochar products affect many of the functional roles that they may play in environmental management applications. The large variation of physical characteristics observed in different biochar products means that some will be more effective than others in certain applications. It is important that the physical characterization of biochars is undertaken before they are experimentally applied to environmental systems, and variations in outcomes may be correlated with these features. Although the

continued examination of the influence of feedstocks and processing conditions on the physical properties of biochars is essential, an important direction for future research is to develop an understanding of how and by what mechanisms these physical characteristics of biochars influence processes in soils. Further work is also required to determine how the physical properties of biochars change over time in soil systems and how these changes influence their function.



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## Chapter 3

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### *Biochar as a Geo-engineering Climate Solution: Hazard Identification and Risk Management*

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and David M. S. Lau

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## Biochar as a Geoengineering Climate Solution: Hazard Identification and Risk Management

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Q1

*Biochar technology has been proposed as a geoengineering solution that has potential to actively reduce the atmospheric concentrations of greenhouse gases and enhance the sustainability of agriculture. The magnitude of the technologies' net benefit must be considered in relation to the associated risks. Hazards posed by biochar technology need to be managed to a level that the resulting risks are deemed acceptable by society; identification of hazards is an essential first step. Effectively implemented risk management and sustainability guidelines, driven by informed policy directives, will result in biochar technology being an important tool for environmental and atmospheric greenhouse gas management.*

**KEY WORDS:** biochar, climate geoengineering, greenhouse gas mitigation, LCA, pyrolysis, risk assessment

### INTRODUCTION

There has been a lack of progress, to date, to curb anthropogenic greenhouse gas (GHG) emissions in any meaningful way, and significant questions raised about the probability of reaching an effective international emission reduction agreement. This is shifting the emphasis from GHG emissions abatement toward a more urgent focus on direct GHG removal from the atmosphere.

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Research into any pathway that offers the opportunity to divert atmospheric carbon into low risk sinks, sustainably and economically, deserves utmost priority. This research should establish the frameworks and methodologies required to create a robust evidence base needed to inform sustainability analyses and policy development. **20**

Although climate engineering has been discussed by scientists and politicians since the 1960s, the necessity of major geoengineering solutions has attracted serious research and debate since Crutzen put them firmly on the agenda through his editorial in *Climate Change* in 2006.<sup>1</sup> Since then, biochar has been added to the arsenal of geoengineering solutions by several authors.<sup>2-5</sup> Biochar is considered as a longwave geoengineering option for climate-change mitigation because it results in the removal of CO<sub>2</sub> from the atmosphere, hence increasing levels of longwave radiation leaving the planet.<sup>2</sup> A biochar system, where plants are grown, and subsequently (either directly or as a residue from another use) pyrolyzed to produce biochar, which is then applied to soil, is a carbon sink: CO<sub>2</sub> from the atmosphere is sequestered as carbohydrates in the growing plant and conversion of the plant biomass to biochar stabilizes this carbon. The stabilization of carbon in biochar delays its decomposition thus ensuring that the carbon remains locked away from the atmosphere for hundreds to thousands of years. Biochar could be stored in many terrestrial environments. Its application to agricultural and forestry soils is a likely outlet due to its demonstrated productivity and soil health benefits. **25**  
**30**  
**35**  
**40**

Biochar technology has been recognized as having potential to be implemented on a climate-changing scale.<sup>2-4,6,7</sup> The global potential for annual sequestration of atmospheric CO<sub>2</sub> via this method has been estimated at the billion-tonne scale (10<sup>9</sup> t yr<sup>-1</sup>) within 30 years.<sup>8</sup> The risk and reward profile associated with that course of action needs to be assessed and communicated to the global community as industry moves toward commercializing the technology. Political and public confidence in the technology must be built from a sound scientific basis for the technology to be quickly implemented on the immense scale required if it is to make a meaningful contribution to climate stabilization. Policy should be designed and implemented to ensure that biochar technology has a positive impact on the environment, with direct social and economic benefits. **45**  
**50**

The biochar concept, for the purpose of this investigation, has been divided into three key stages: biomass feedstock sourcing, conversion technology, and biochar product utilization. Analysis of the risk assessment strategies that can be applied to each of these stages is discussed with a focus on identifying the possible risks presented and reviewing management methods that may be effective at mitigating these risks. This discussion is intended to identify key considerations that should be included by researchers conducting life-cycle assessments (LCAs) of biochars, and industry participants who are conducting biochar project risk assessments. This article will initiate **55**  
**60**



65 discussion for policymakers who are seeking to develop appropriate stan-  
 dards, and certification schemes to oversee and direct the implementation of  
 biochar systems at the local and international levels. The aspects identified in  
 this discussion will provide guidance for legislative frameworks so that they  
 may provide effective coverage of biochar. It may also prove useful for those  
 70 designing accreditation requirements for carbon offset schemes (voluntary or  
 regulated) under which biochar offsets will be offered as a quality assured  
 product.

#### METHOD FOR RISK ASSESSMENT, MITIGATION, AND COMPARISON

75 A large investment (political, economic, and social) will be needed if the  
 biochar industry is to be implemented at the scale required for stabilizing  
 the climate. Public confidence in biochar as a solution will be integral to  
 driving this investment. This confidence will be secured, in part, through  
 regulation informed by comprehensive risk assessment.

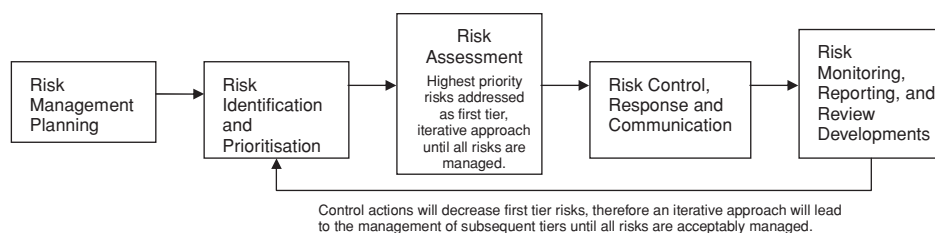
80 Methodologies for risk assessment are well established for existing in-  
 dustries such as the waste, chemical, energy, and water sectors. These risk-  
 assessment methodologies include not only environmental impact assess-  
 ments (EIA), which are required routinely for planning approvals, but also  
 cover social and economic risks. Hazards associated with biochar technology  
 must first be identified for their severity and probability to be quantified. The  
 85 scale of the risks they pose, and therefore the level of management and reg-  
 ulation required to mitigate these risks, can then be determined. Mitigation  
 of the risks identified is achieved through the introduction of a barrier that  
 prevents the hazard causing an incident of harm. The barrier may be direct,  
 such as the physical installation of air pollution control equipment or safety  
 90 guards, or indirect, such as regulation dictating eligible biomass sources.

However, any risk assessment cannot include the potentially infinite  
 scenarios and variables applicable. Educated judgments as to the likelihood  
 and severity of the hazards are required to identify the most critical risks to  
 be included.<sup>9</sup> The number and type of factors included in the investigation  
 95 has a strong influence on the outcomes.<sup>9</sup> Many regulators now promote a  
 tiered approach to risk assessment, as is demonstrated in Figure 1, which  
 allows for an initial screening and prioritization of risk, prior to undertaking  
 more detailed assessments.<sup>10</sup>

100 Risk assessment, and the associated mitigation actions, need to occur  
 on an ongoing and iterative basis through each phase of industry develop-  
 ment so that lessons are quickly learned and technology evolutions quickly  
 adopted (see Figure 1).

The LCA is being used to assess the environmental impacts of biochar  
 technology compared with alternate pathways.<sup>11</sup> There is broad agreement



**FIGURE 1.** Risk management process.

in the scientific community that LCA is one of the best methodologies for the evaluation of the environmental burdens associated with industrial processes. The international standards, ISO 14040 and 14044, define LCA as a compilation and evaluation of the inputs, outputs, and the potential environmental impacts of a product system throughout its life cycle. LCA can include a global warming impact assessment alone, or can be expanded to provide a broader study of environmental impacts.

The GHG balance is an essential factor in any risk assessment around biochar technology as one of the major objectives for implementation is to mitigate the risks associated with climate change. The GHG balances of biochar systems differ depending on the type of feedstock sourced, conversion technologies utilized, end-use technologies, system boundaries, and reference systems with which the biochar pathway is compared. GHG emissions arise from each stage in the supply chain and the degree to which these are offset by the sequestration of carbon vary from project to project (see Figure 2).

Risks posed by individual biochar projects vary. To demonstrate this, a positive and negative example of environmental, social, and economic impacts are provided in Table 1. The method used for this short example can be adopted for considering a very wide range of parameters, such as

Q3

**FIGURE 2.** Greenhouse gas balance, sources, and sinks.

**TABLE 1.** Example considerations and how they may vary among biochar systems

Area	Consideration	Contrasting cases	Resulting outcomes
Environmental	Biomass source	<ul style="list-style-type: none"> <li>• Waste from landfill</li> <li>• Purpose grown</li> </ul>	<ul style="list-style-type: none"> <li>• Improved land use</li> <li>• Reduction in landfill methane emissions</li> <li>• Resource recovery (decreased requirement for new materials, fossil and grown)</li> <li>• Possibility of contamination</li> <li>• Land use change, possible displacement of food or fiber crops or deforestation</li> <li>• Requirement for inputs (e.g., fertilizer, diesel)</li> <li>• Water use</li> <li>• Soil degradation (carbon stock change)</li> <li>• Regional development and employment</li> <li>• Diversification of farming revenues</li> <li>• Emission controlled to meet local regulatory requirements, preventing adverse impacts on the local environment</li> <li>• Energy production from syngas displaces fossil fuel use</li> </ul>
	Local air pollution	<ul style="list-style-type: none"> <li>• Technology engineered to capture syngas and with emissions controls</li> </ul>	<ul style="list-style-type: none"> <li>• Unacceptable decline in local air quality, which may lead to respiratory illness</li> </ul>
Social	Food security	<ul style="list-style-type: none"> <li>• Syngas and emissions released directly to local environment</li> <li>• Biochar feedstocks coproduced with food or fiber crops</li> </ul>	<ul style="list-style-type: none"> <li>• Release of potent GHGs</li> <li>• Profitability of crops is enhanced through the production of biochar from waste crop residues (see Figure 3)</li> </ul>
	Regional employment	<ul style="list-style-type: none"> <li>• Biochar feedstocks replace food or fibre crops</li> <li>• Rural distribution of biochar production facilities</li> </ul>	<ul style="list-style-type: none"> <li>• Food and products shortages, and price inflation</li> <li>• Jobs are created in regional areas, involving training and capability enhancement</li> <li>• Flow on services required in the community further enhances regional employment</li> <li>• Challenges of quality control across many systems and aggregation of products for marketing</li> </ul>

*(Continued on next page)*

**TABLE 1.** Example considerations and how they may vary among biochar systems (*Continued*)

Area	Consideration	Contrasting cases	Resulting outcomes
Economic	Carbon trading	<ul style="list-style-type: none"> <li>• Large-scale, automated biochar production facilities</li> <li>• Price put on carbon</li> <li>• No value for carbon</li> </ul>	<ul style="list-style-type: none"> <li>• Limited job creation centralized in urban areas</li> <li>• Economies of scale achieve higher conversion efficiencies and improved access to product markets</li> <li>• Biochar production facility revenue streams include incentives for mitigating GHG emissions, therefore making a profitable business case</li> <li>• Biochar business case relies on revenues from waste management, energy, and biochar production</li> </ul>
		• Biochar enhances crop production	<ul style="list-style-type: none"> <li>• Increased revenue streams for agricultural products</li> <li>• Increased adaption capability against climate change</li> <li>• Less land required to achieve same production levels</li> <li>• Decreased inputs required</li> <li>• Food security</li> </ul>
		• Biochar decreases crop production	<ul style="list-style-type: none"> <li>• Loss of income from agricultural products</li> <li>• More land required to achieve same production levels</li> <li>• Increased inputs required</li> <li>• Lack of food security</li> </ul>
	Agricultural productivity		

125 acidification, eutrophication, ozone depletion, land use, soil health, water quality, public health, and workplace safety.

The emerging biochar industry can learn from the precedents set by other comparable industries. For example, previously overlooked yet significant influences to the GHG balance have been identified through LCAs performed on biomass for energy (biofuels) systems. In this case, considerations such as the influence on soil carbon levels,<sup>12</sup> nitrous oxide emissions from soils,<sup>13</sup> and indirect land use change<sup>14</sup> have been raised. As the science improves, a continual review of previous assumptions is vital.

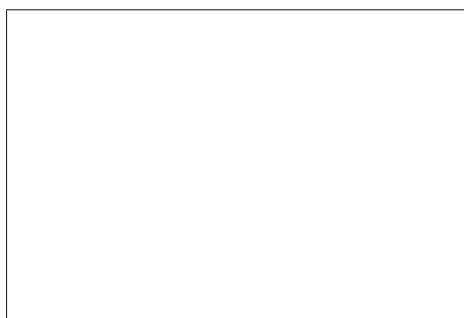
135 The urgent need for climate stabilization suggests that continual improvement is preferred over delayed perfection. However, it is essential in the early stages of the biochar industry that predominant risks are identified and managed so that the full potential can be quickly realized without subsequent unacceptable adverse effects from ill-managed systems.

## BIOMASS FEEDSTOCK SOURCING

### 140 Sustainability and Competing Uses

There is a risk that the biomass required for biochar production will not be sourced in a sustainable way, leading to negative environmental, social, and economic consequences. It is essential that the complete process chain of the biomass, including the production, harvest, transport, preprocessing required, and alternate uses, be considered to assess the true net benefit of the biochar pathway. Utilization of biomass for food, fuel, fiber, and fodder is fundamental to all economies and societies.<sup>15</sup> Its diversion into new uses can have dramatic direct and indirect effects that need to be accounted for. Risks are associated with diverting biomass into biochar technology from these human uses, as well as from essential ecosystem services it may perform, such as providing habitats. Alternate uses for the biomass are not all positive as they may also pose public health and environmental concerns, such as those identified for composting,<sup>16</sup> which may be prevented by the adoption of biochar technology. The wide variation in raw materials, multiplied by the variety of processes for its sourcing and harvesting, means that there is no single verdict on the sustainability of biochar feedstocks as a whole, but rather a highly complex picture, influenced by a number of parameters.

155 The topic of sustainability has been the cause of much debate for the broader biofuels industry, which has resulted in the development of guidelines and standards by the international community. Biochar stakeholders can look to build on criteria that have already been put forth by groups such as the Roundtable on Sustainable Biofuels (RSB), Roundtable on Sustainable Palm Oil (RSPO), Forest Stewardship Council (FSC), and the United Kingdom's Renewable Transport Fuel Obligation when seeking to implement feedstock sustainability guidelines.



**FIGURE 3.** Biochar pathway for food, fuel, and carbon sequestration.

Biochar production has significant sustainability advantages over conventional (first generation) biofuels, which require feedstocks such as grain and corn that directly compete with food or fodder uses. However, indirect land use competition could occur and should be assessed. Slow pyrolysis facilities can produce energy and biochar from very low-grade, even waste, biomass feedstocks.<sup>17</sup> By-products and wastes from agriculture, forestry, households, and biomass processing industries (including residuals from second-generation biofuels processing such as spent algae post oil recovery or separated lignin from lignocellulosic ethanol plants) are all suitable slow pyrolysis feedstocks. It has been previously demonstrated that processes that utilize by-products from other sectors are greatly rewarded in terms of reduced ecological footprint.<sup>18,19</sup>

Figure 3 demonstrates a proposed concept of sustainable coproduction of food, fuel, fiber, or fodder. Waste materials from the crop or process can be used for biochar production, after the necessary environmental services delivered by these materials, such as ground cover for erosion control, water management, and habitat have been met. For example, forests can be sustainably harvested, under the FSC guidelines or similar, to produce wood and paper products. The by-products of these processes, such as sawdust or paper sludge, can then be used to produce biochar to transform the carbon it contains from the short to long-term carbon cycle. The biochar can then be recycled back to the forest, recycling carbon and mineral nutrients, which provides a positive feedback loop to enhance the production of the next crop.

The diversion of biomass waste, which by definition has no beneficial reuse options, does not usually increase environmental pressures.<sup>19</sup> However, biomass sources such as forestry or agricultural residues are not strictly wastes because they provide essential environmental services. When developing an LCA to understand the environmental risk factors posed by biochar feedstock sourcing, it is recommended that the following factors be considered: habitat, erosion control, changing carbon and nutrient stocks, water management, and the potential that additional income makes the production

of the main commodity (e.g., timber) economically more attractive, leading to expansion of the land use.<sup>19</sup>

200 It is recommended that to mitigate the risks of unsustainable biomass use for biochar production, certification schemes operated by governing bodies need to administer a robust set of standards to ensure the sustainable use of biomass resources. However, reporting requirements must not limit the viability of the industry by imposing unnecessary barriers.

## 205 Feedstock Contamination

Pyrolysis feedstocks may contain chemical and biological pollutants that pose environmental or health risks. Municipal waste resources<sup>20–23</sup> are examples in which biomass resources exhibit contaminant risk. Heavy metals, for example those derived from copper-, chromium-, and arsenic-treated  
210 (CCA) timber, or present in some industrial and wastewater sludges, must be managed appropriately.<sup>23</sup> Moreover, biocide-treated biomass, radioactive material, and chlorinated or other chemically treated materials may not be suitable biochar feedstocks.

Chemical and biological contaminants contained in the original waste  
215 material have the potential to be altered by the thermal conversion process of slow pyrolysis. The biological sterilization of the material through pyrolysis gives it significant environmental advantages, compared with alternate treatments when biosecurity issues, such as pathogen and plant propagules, are of concern.<sup>24</sup>

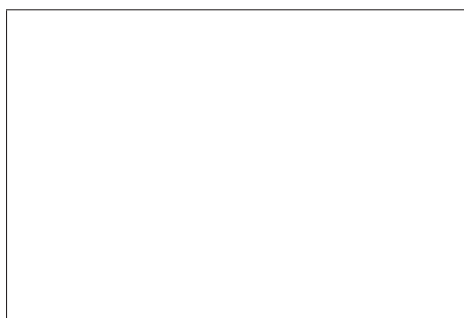
Heavy metal contaminants are concentrated into the biochar,<sup>25</sup> with the exception of low-temperature sublimating metals such as mercury and cadmium. These may be lost to the syngas stream, depending on the temperature profiles for the given technology. Composting has been demonstrated to be an effective way to reduce levels of organic pollutants, including pesticides,  
225 oils and solvents, printing ink, bleaching chemicals, mercaptans, sulfides, carbonates, hydroxides, and dyes,<sup>26</sup> via biodegradation, volatilization, and photolysis processes. Reductions in organic pollutants due to pyrolysis processing may also occur; however, no published data was found. Future research in this area is recommended.

230 To mitigate the risks associated with feedstock contamination it is recommended that sources of potential contaminants be identified and analysis procedures established as an industry standard.

## CONVERSION TECHNOLOGY

### Engineering Controls

235 The technical, environmental, health, and safety risks from biochar technology are not likely to approach the scale or complexity of the chemical production sector. The risk profile of biochar technology is more comparable to alternate waste and bioenergy technologies. The risks posed by industrial



**FIGURE 4.** Pacific pyrolysis' biochar production facility, NSW Australia.

biochar production facilities (see Figure 4) are managed by the process engineering principles<sup>17</sup> used in their design and operational optimization. The risks posed by elevated temperatures (hot surfaces and exhausts), mechanical moving parts, vehicle movements, and the generation of gases with significant explosion potential pose human workplace health and safety concerns. These can and should be addressed with engineering controls.

Examples of engineering risk tools that can be employed by the biochar industry include failure mode and effects analysis (FMEA), event tree analysis (ETA), hazard and operability (HAZOP), and hazard analysis critical control point (HACCP) studies. These methods have been developed and used widely in many major process industries including food, petrochemical, nuclear, energy, and waste and water treatment. These tools are designed to rigorously study the process system in its entirety and allow vulnerabilities to process failure to be assessed.<sup>27</sup> Engineering risk management tools can also be used to infer the key routes of environmental exposure, providing the system is properly represented, and can identify and prioritize risk management actions, including contingency planning to minimize harm.<sup>27</sup> Most engineering risk management processes include the identification of undesired events that pose health and safety or environmental risks, and quantify their severity and likelihood. The event may be the result of engineering failure of process equipment, fire and explosion occurrence, or contamination or emissions release. A mitigation strategy to guard against each event scenario is then developed. However, it should be noted that these methods are not infallible because potential hazards may fail to be identified in the process through lack of experience and expertise.<sup>28</sup>

Due to the large range of engineered pyrolysis systems available at present and in the future, it is beyond the scope of this investigation to identify all hazards associated with their construction, operation, and decommissioning. However, it is highly recommended that processing facilities are designed and constructed to applicable process and mechanical engineering standards, such as the ASTM International Standards, and that

270 risk-management tools, such as those mentioned previously, are utilized in  
 conjunction with appropriate expertise and third-party review.

### Regulatory Controls

Regulatory controls are a proven mechanism for risk mitigation of process industries. Technology being implemented, especially if it is at a commercial scale (i.e., not backyard applications which process typically <5 t biomass/day), will be required to meet the relevant local jurisdiction's planning, consenting, and licensing requirements. However, the public will only trust regulatory decisions if the decision-making process is credible and transparent.<sup>9</sup> A biochar project in many developed countries would need to meet their respective governmental EIA guidelines and other statutory regulations that identify particular issues of concern. Such issues will generally require mitigation, monitoring, and reporting. For example, the UK EIA procedure guidelines<sup>29</sup> specify the information needed for an environmental impact statement (EIS). These include (a) a description of the proposed development, comprising information about the size and design of the development; (b) data necessary to identify and assess the main effects that the development is likely to have on the environment; and (c) a description of the likely development on human beings, flora and fauna, soil, water, air, climate, the landscape, the interaction of any of the foregoing, material assets, and cultural heritage.<sup>29</sup> Where significant adverse effects are identified with respect to these environmental criteria, a description of the mitigation measures to avoid, reduce, or remedy the impact is required. This regulatory framework has ensured that the environmental credentials of all major industries are maintained and improved and it is anticipated to do the same for the emerging biochar industry.

Assurance challenges arise when developing biochar technologies fall outside of existing regulatory mechanisms. This may occur with small, mobile operations, which may fall below the threshold for coverage set by regulatory authorities, or with larger operations in countries in which environmental regulations are not legislated or enforced. In these cases, if carbon offsets are to be generated and traded in a quality-assured manner, operations are required to meet the accreditation requirements of the respective trading scheme. These are likely to include assurances of compliance with environmental protocols.

### 305 Energy Efficiency

The energy efficiency of the biochar production technology employed represents a risk to the environmental benefits achievable (especially GHG abatement). Energy efficiency is therefore a key consideration, especially when



applying the LCA and GHG balance methodologies, as poor efficiencies pose a risk to the GHG abatement achievable.

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Biochar technology may require some nonrenewable energy at several stages of the life cycle, which must be included in the LCA. Accurate calculation of the net GHG benefit of bioenergy production relies on the selection of the appropriate fossil reference system for the area in which the project is implemented.<sup>19,30</sup> Clearly, the more fossil fuel input required by a certain bioenergy system, the less energetically desirable it is<sup>19</sup> and the less GHG benefit it will provide. Fossil energy savings and GHG mitigation will be increased if the technology is vertically integrated to use process residues internally to run the biomass conversion plant.<sup>19</sup> This lowers the ecological impact, whereas economic viability may be significantly improved.<sup>18</sup>

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Biochar technology also produces energy products that can be used to displace fossil fuel use or meet growing energy demand.<sup>31,32</sup> The technology can producing more than one product through the coproduction of usable bioenergy in addition to biochar, instead of simply flaring the gases and oils produced from the process. This inevitably decreases the ecological pressure per unit of product, as the impact of providing the facility and raw material is split between more products.<sup>18</sup> The production of liquid biofuels usually requires more fossil energy inputs than the generation of electricity and heat from biomass.<sup>19</sup> This is likely to hold true for the energy products of pyrolysis, with bio-oil production<sup>31</sup> and upgrading or conversion of syngas to liquid fuels requiring greater fossil inputs, and therefore having less GHG mitigation potential, than use for heat or electricity directly.

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Technologies with broad feedstock specifications with respect to particle size distribution, chemical composition (ash content), and moisture content will be the most flexible. This will limit preprocessing requirements that can be energy—and therefore cost—and GHG intensive.

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It is recommended that MMV protocols be established for all energy inputs required by the technology for GHG accounting purposes. Biochar projects should source technologies that employ energy efficiency practices to mitigate the risk that energy requirements offset environmental gains from the biochar production.

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## Emissions

To quantify the net benefits of biochar technology the potential risks to the environment and human health from continuous stack emissions<sup>28,33</sup> need to be considered. Uncontrolled release of gases (smoke, syngas, producer gas) produced during pyrolysis in traditional kilns generates pollution and increases the burden of GHGs in the atmosphere.<sup>32,34,35</sup>

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Charcoal making via traditional means is renowned for the creation of air pollution.<sup>32,36,37</sup> Production techniques have therefore advanced from the early industrial processes to ensure regulatory requirements can be met.

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Dramatic improvements have been achieved in pollution control and energy efficiency through the adoption of controlled continuous kilns compared to batch kilns.<sup>32,37</sup>

New generation technology should be employed, which purifies these gases and efficiently uses them for bioenergy production and, hence, delivers the objectives outlined previously.<sup>17</sup> If gas cleanup is not a viable option (e.g., on very small-scale systems or where there is no useful application for the syngas), gases should be flared. This will convert all higher hydrocarbons, including methane, to CO<sub>2</sub>, thus reducing its global warming impact.

Thermal treatment of biomass represents an important option for (a) its conversion to energy and (b) waste management. The ongoing industrial use of thermal conversion technologies has been challenged with increasing emissions standards and regulations. This has resulted in the move from combustion toward pyrolysis and gasification systems that have improved emissions profiles.<sup>38</sup> Combustion occurs when biomass is heated in an oxygen-rich environment, whereas when biomass is heated with no oxygen or up to about one third the oxygen needed for efficient combustion, it pyrolyzes or gasifies, respectively. These reactions include the volatilization of the solid to a gas mixture of mainly carbon monoxide and hydrogen, which is collectively referred to as syngas. The syngas inherently burns cleaner and more efficiently than the solid biomass from which it was made, due to the more effective mixing of the gas stream with oxygen.<sup>39</sup> Lower operating temperatures and conditions favoring reduction reactions also improve the emissions profile compared with combustion systems.<sup>38</sup> Therefore, the emissions risk posed by the pyrolysis technology used for biochar production is considered lower than that posed by combustion technologies.

Although emissions are reduced by pyrolysis compared with combustion technologies, concerns remain over atmospheric emissions from the thermal treatment of biomass. Emissions vary with feedstocks and process conditions; however, those of concern may include acid gases (e.g., SO<sub>x</sub>, HCl, HF, NO<sub>x</sub>); volatile organic compounds (VOCs),<sup>40</sup> especially polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and the potential carcinogenic agents polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs); carbon monoxide (CO), heavy metals, and other noxious substances.<sup>38,41–43</sup> For example, PCDD/Fs emissions that exceed the regulatory requirements have been reported in the literature for a high temperature gasification process.<sup>44</sup> The previously listed air pollutants are commonly regulated under existing emissions standards, and all can be controlled in well-engineered biochar systems using existing emissions control technology. Emissions control measures add to the cost of the technology and therefore some economies of scale are likely to be required to make nonpolluting biochar production economically feasible.

If specific biochar technologies cannot demonstrate that they meet standard emissions limits, they are unlikely to be approved by regulators or

accepted by society. As several of these pollutants are expensive to measure and monitor, the requirement for reporting levels of these substances may limit the economic viability of smaller, low-tech versions of biochar technology. Governmental or philanthropic funding may play a role in demonstrating emissions profiles of low-tech biochar technologies (such as stoves commonly used in developing countries<sup>32</sup>). It is recommended that the emissions credentials of specific biochar production techniques should be understood before they are deployed at any scale to ensure they deliver a net benefit to the environment. This is especially true when deploying technology into more vulnerable rural communities in developing countries. The benefits to these areas are potentially the greatest; however, there are no resources to ensure air quality and other environmental parameters are maintained.

## BIOCHAR UTILIZATION

### Storage, Transport, and Handling

The precedent for the safe handling and transport of biochar has been well established by the charcoal industry. As with charcoal, biochar can be classified as a Class 4 Dangerous Good, as it is a flammable solid.<sup>45</sup> Legislation and regulations surround dangerous goods, which put people, property and the environment at risk if they are not handled appropriately. This is to ensure they are classified, packaged, labeled, and transported in a way that minimizes risk.

A materials safety data sheet (MSDS) describes the chemical and physical properties of a material and provides advice on safe handling and use of the material. The MSDS provides the necessary information to safely manage the risk from hazardous substance exposure. It is recommended that the biochar industry establish generic MSDS information for biochar materials, along with a health warning and hazardous information labels to guide customers on the safe handling of products. These may be similar to those required for compost and potting mix products by the Australian Standards AS3743 and AS4454.<sup>24,46</sup>

National health standards relating to chemical, organic, and pathogen containment provisions may apply to the movement of biochar products and their precursor feedstocks.

### Biochar as a Soil Amendment Product

The high carbon content of biochar produced via pyrolysis makes it suitable for a range of purposes that would sequester the carbon it contains. Examples include using biochar as a concrete aggregate or as a thermal insulation material. However, studies show that the greatest rewards are presented by

its use as a soil amendment, which enhances plant growth and nutrient use efficiency<sup>47–50</sup> and reduces nitrous oxide emissions<sup>51,52</sup>. On the other hand, application to soil may also present the greatest risk. There is no practical way to remove biochar from soil following application,<sup>53</sup> thus mitigating any risks associated with applying biochar to soils is particularly critical.

However, it should be noted that charcoal is a natural constituent of most soils.

Charcoal has been found to persist in almost all soils of the world<sup>54–56</sup> due to the occurrence of natural fires over history, and hence the application of biochar to soils cannot be considered alien to the natural soil ecosystem. There are also several examples in which the anthropogenic addition of large quantities of biochar to soils has occurred over long time frames. These include the *Terra Preta de Indio* of Brazil,<sup>57</sup> Plaggen soils of Europe,<sup>58</sup> and *Terra Preta Australis* in Australia.<sup>7</sup> These examples cover different climatic regions, soil types, and land management practices. The outcomes of improved soil quality for agriculture are universal across these studies, demonstrating that the risk of adverse side effects is low.

Charcoal has been used as a soil amendment for orchid growing mix and for growing turf grass for many decades. In Japan, a strong tradition in the use of charcoal as an authorized soil improver for horticultural and agricultural applications means that 15,000 t of carbonized material is annually applied to soil.<sup>59</sup> No reports of detrimental long-term side effects have been published to date from this broad range of applications. Further, scientifically rigorous long-term experiments are recommended to add to this knowledge and confirm the absence of negative side effects for modern biochar technologies.

An assessment of whether the biochar product is suitable for use as a soil additive and poses no environmental or economic (through loss of production) risks requires analysis on a case-by-case basis. The range of biochar properties, especially contaminant levels, mean that some are well suited to grow plants for human consumption, whereas others are only suitable for use in forestry applications. Where product is unsuitable for land application, for example due to heavy metal contamination, this may mean landfilling is the best outcome. In a landfill biochar still has the ability to retain C (and the heavy metals) for many years,<sup>60</sup> so the GHG mitigation potential remains intact.

Toxic compounds that are associated with thermal treatment products and those highlighted as concerns for soil amendments generally should be understood and controlled for biochar products. Compounds identified of possible concern include PAHs, PCDD/Fs,<sup>8,21,61</sup> heavy metals,<sup>21,62</sup> PCBs, chlorophenols (CPs), and chlorobenzenes (CBzs).<sup>21</sup> Limited data are available to assess the likelihood of these compounds being passed through or formed during biochar manufacture. It is recommended that verification of minimal risk be achieved through reporting of measured quantities for each feedstock

and process method. If it is found that the risk of these compounds is in fact low, and does not pose a significant risk, so ongoing measurement should not be required.

Standards such as Australian Standards for composts, soil conditioners and mulches,<sup>24</sup> potting mixes,<sup>46</sup> and soils for landscaping and garden use<sup>63</sup> can all provide guidance to biochar application. They provide a starting point to begin the consideration of how possible risks, such as toxic contaminants, can be measured, monitored, and controlled. Furthermore, many local environmental protection legislators provide guidance in this area for other products that are also applicable to biochar. For example, the Environmental Protection Authority of New South Wales, Australia, publishes *Environmental Guidelines for the Use and Disposal of Biosolids Products*, which limit application rate and location on the basis of the heavy metals and nitrogen content of biosolids and the existing levels in the soil to which it is to be applied.<sup>64</sup> The U.S. Environmental Protection Agency also provides a guide to the Federal Part 503 rule that governs the land application of biosolids,<sup>65</sup> including a risk assessment to evaluate and establish limits for a number of pollutants.<sup>66</sup> The risk assessment process took nearly 10 years to design and had extensive rigorous review and comment. It is recommended that the findings of this work be used as a starting point for establishing biochar guidelines so a significant amount of time and resources can be saved by the emerging biochar industry.

In some jurisdictions, guidelines have been enforced to limit agricultural and horticultural use of dioxin-contaminated land. For example, several federal states of Germany introduced laws which limit the cultivation of certain feedstuffs and foodstuffs if the dioxin contamination is above 40 pg TEQ g<sup>-1</sup> in the soil, and set a target in which that soil used for agricultural purposes should be reduced to below 5 pg TEQ g<sup>-1</sup>.<sup>67</sup>

Dioxins predominantly form at temperatures in excess of 1000 °C and require oxygen for their formation. Such process conditions are not typical for modern pyrolysis systems for biochar production. However, no published data were found to verify dioxin levels in biochar samples. For the purposes of this investigation, three biochar samples produced in the Pacific Pyrolysis continuous slow pyrolysis pilot plant 17 were analyzed by Dioxin Responsive Chemically Activated Luciferase expression (DR CALUX<sup>®</sup>), under an ISO 9001:2000 quality system, using a NATA-certified dioxin in sediments method (a method suitable for the analysis of soils and sediments). The samples tested were found to have dioxin levels below 5 pg TEQ g<sup>-1</sup> (see Table 2). Therefore, the addition of these biochars to soil would not result in the soil dioxin levels exceeding the target. Although dioxin levels in the biochars tested do not cause concern, this does not mean that all biochars will have low levels of dioxin, as the dioxin content is dependent on the feedstock and biochar production conditions. This is an area recommended for further scientific review.

**TABLE 2.** Biochar dioxin analysis

Biochar product	TEQ, dry weight (pg/g)
Agrichar™ biochar, paper sludge derived	2.4
Agrichar™ biochar, municipal greenwaste derived	4.2
Agrichar™ biochar, poultry litter derived	3.9

Concentrations of contaminants of concern should be considered in regard to their mobility, which may result in contamination of ground- and surface waters, and their availability, which may result in them being taken up into the food chain via crops.<sup>68</sup> The main factor determining heavy metal mobility in soil is pH,<sup>69</sup> hence the mobility should not only be determined by product chemical analysis, but rather should be assessed in the environmental context in which it is used. There is some evidence that biochar can lock up heavy metals in the carbon matrix,<sup>60</sup> and hence biochar production from heavy metal-contaminated feedstocks may present a management strategy to prevent their exposure to the environment.

Biochar products may pose a phyto- and ecotoxicity risk. Some plant species are sensitive to specific chemical elements, such as phosphorus (P), boron (B), magnesium (Mg), chloride (Cl), manganese (Mn), zinc (Zn), copper (Cu), and sodium (Na) at levels which are generally beneficial to most species.<sup>24,46</sup> Application rates at which biochars become phytotoxic therefore vary with target plant species; recommendations for the use of specific biochar products need to be developed. Germination test methods, such as those outlined in the Australian Standard for composts (AS4454) determine whether a product is sufficiently toxic to inhibit germination and the growth of roots. An Organization for Economic Co-Operation and Development (OECD) earthworm avoidance test method for ecotoxicity, applied to Agrichar™ biochars produced from papermill wastes<sup>50</sup> and poultry litter<sup>49</sup> demonstrated no negative impact of biochar on earthworms. It is recommended that these tests be adopted as a risk management tool to determine phytotoxicity and ecotoxicity before biochar products are applied in bulk to soils as a risk management tool.

Biochar addition to soil may provide a risk mitigation tool for the remediation of contaminated soils. Biochar has been demonstrated to decrease the risks posed by environmental contaminants that are already present in soils.<sup>70</sup>

It is recommended that the biochar industry establish guidelines outlining rigorous periodic analytical quality controls that correspond to evaluations of the components identified as posing a risk. A certification mechanism may also be implemented by the industry to provide consumers with confidence that such risks have been adequately mitigated and the product can be used without concern.



If the productivity benefits of biochar are not verified and are oversold to consumers, it poses a risk to its ongoing marketability. Ultimately, each biochar product's performance as a soil amendment should be demonstrated by independent third-party trials in the field. However, the large number of variables involved (e.g., biochar feedstock and processing, application rate, soil type, climate, crop) means that laboratory methods to identify key areas that pose a risk to productivity benefits are a more practical management strategy. Therefore, we recommend that accessible laboratory techniques that have been demonstrated by peer-reviewed trials be developed to test the likelihood of productivity benefits.

## CONCLUSIONS

The use of biochar for environmental management is a growing area of scientific and commercial interest. International cooperation, regulations, certification, and accreditation mechanisms must be utilized to ensure the mitigation of the potential environmental and social impacts caused by biochar production and use. A summary table of considerations identified throughout the discussion and suggested methods to manage them are provided in Table 3.

The key findings and recommendations identified by this investigation are the following:

- Sustainability guidelines implemented for biofuel raw materials production should be adopted for biochar production systems.
- Full LCA on a project-by-project basis should be adopted to ensure direct and indirect impacts are considered to determine net environmental outcomes.
- Biochar production technologies should be regulated under jurisdiction-specific industrial standards that presently enforce pollution limits on all industries. For example, emissions regulation may be imposed by the environment protection authorities or local governments.
- Biochar production technologies should utilize appropriate engineering risk assessment methodologies and engage the required expertise to ensure process risks are managed.
- Small-scale and mobile operations (and large-scale operations in unregulated environments) may not be controlled by existing environmental regulations and could, therefore, result in less than best practice production of biochar and adverse environmental and social impacts.
- Biochar production can cause detrimental impacts on GHG levels and local environmental conditions and, therefore, controls must be in place to prevent this.

**TABLE 3.** Summary of risk assessment considerations

Boundaries	Risk	Management strategy required for public assurance
Biomass sourcing	<ul style="list-style-type: none"> <li>• Influence surrounding flora and fauna</li> <li>• Net carbon stock change (including soil carbon)</li> <li>• Increased transport: emission and impact of vehicular movements on local infrastructure, community, and environment</li> <li>• Inadequate supply for alternate uses (e.g., reduced food production and ecological services)</li> <li>• Preprocessing requirements resulting in energy use and emissions</li> <li>• Increased water use</li> <li>• Increase in soil degradation</li> <li>• Land use change (e.g., Destruction of Forests)</li> <li>• Storage (especially methane and N<sub>2</sub>O production if allowed to decompose)</li> <li>• Increased soil emissions (especially N<sub>2</sub>O and CH<sub>4</sub>) for purpose grown biomass</li> <li>• Change in local employment</li> <li>• Health and safety of operators</li> <li>• Nutrient cycling away from resource base</li> <li>• Movement/cycling of contaminants (e.g., heavy metals)</li> </ul>	<ul style="list-style-type: none"> <li>• Monitoring and verification of LCA assumptions such as base line emissions levels, transport distances</li> <li>• Enforcement of sustainability guidelines for biomass resource</li> <li>• Measurement of contamination levels in feedstocks</li> <li>• Adherence to workplace health and safety regulations</li> <li>• Development and planning approvals required for technology installations</li> </ul>
Conversion technology	<ul style="list-style-type: none"> <li>• Low energy efficiency</li> <li>• Local air emissions</li> <li>• Water usage/contamination levels</li> <li>• Construction and maintenance emissions</li> <li>• Decommissioning (e.g., site contamination, recycling options)</li> <li>• Workplace health and safety (e.g., explosions risk, exposure limits, hot surfaces)</li> <li>• Visual intrusion</li> <li>• Employment</li> <li>• Previous land use of proposed project site</li> </ul>	<ul style="list-style-type: none"> <li>• Existing regulatory frameworks covering all industry sectors (e.g. planning approvals, work place health and safety legislation, air quality and emissions legislation, construction and operation to international standards etc)</li> <li>• Use of by-products (energy)</li> <li>• MMV of LCA assumptions such as emissions testing of biochar production facilities</li> <li>• Engineering controls applied to hazards identified through iterative application of risk assessment tools</li> </ul>

*(Continued on next page)*



**TABLE 3.** Summary of risk assessment considerations (*Continued*)

Boundaries	Risk	Management strategy required for public assurance
Biochar utilization	<ul style="list-style-type: none"> <li>• Biochar utilized for alternate uses (e.g. fuel) other than soil amendment</li> <li>• Increased transport emissions and impact on infrastructure</li> <li>• Postprocessing requirements resulting in energy use and emissions</li> <li>• Incorporation resulting in energy use and emissions</li> <li>• Carbon content and stability is low resulting in minimal GHG mitigation benefits</li> <li>• Present land management practices and changes with the inclusion of biochar use may include variation in inputs such as fuel requirements and biocide use</li> <li>• Toxicity and contaminants of agricultural land with contaminated product</li> <li>• Nitrous oxide emissions from soils</li> <li>• Workplace health and safety (e.g., inhalation exposure, ingestion, materials handling)</li> <li>• Fit for purpose (likely to induce positive or negative productivity outcomes in the system to which it is applied)</li> <li>• Changes in fertilizer use requirements</li> <li>• Changes in water use requirements</li> <li>• Net carbon stock change (including soil carbon) impacting GHG mitigation potential</li> </ul>	<ul style="list-style-type: none"> <li>• Existing regulatory frameworks covering transport and handling of hazardous goods</li> <li>• MMV of LCA assumptions such as transport distances, end use</li> <li>• Phytotoxicity and ecotoxicity testing</li> <li>• Testing for contaminant levels against existing standards for soil amendments and land application of biosolids</li> <li>• Product performance verification through laboratory characterization and independent third party field trials</li> <li>• Carbon turnover experiments along with chemical analysis to verify carbon stability</li> <li>• Accreditation of biochar under carbon offset and/or sustainability criteria</li> </ul>

- Each biochar production project will have a different GHG balance. Standard methods for MMV of key assumptions, such as biochar carbon contents, turnover rates, and influence on crop productivity and soil health parameters, should be developed by the industry. The MMV protocols required to ensure the GHG abatement predicted is achieved in practice will depend on the individual carbon offset accreditation bodies.
- Development of biochar MMV protocols acceptable to an emissions trading body is required to enable the technology implementation to be incentivized appropriately for the contribution it can make to reducing atmospheric GHG levels.
- Sound and well-informed risk management is critical to securing confidence in and establishing new technologies in a rapidly developing biochar marketplace.
- Public or private investment is required to ensure that all questions raised can continue to be addressed through targeted research and development.
- Processes for effective public engagement and consultation need to be part of any biochar implementation plan.
- The biochar industry should collaborate to create sustainability guidelines, product certification, generic MSDS information, generic health warning, and hazardous information labels.
- Sensitivity of the net GHG balance to variables should be investigated in detail to direct further research funding to the verification of the most material assumptions.
- Biochar projects resulting in negative outcomes will impact the public confidence in the solution and cause setbacks for all versions of the technology, even those that may comply with stringent environmental regulations.

To ensure the ongoing sustainability and viability of an emerging biochar industry, a fully informed and debated review of risks and rewards should be encouraged.

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## Chapter 4

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### *Terra Preta Australis: Reassessing the carbon storage capacity of temperate soils*

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## Terra Preta Australis: Reassessing the carbon storage capacity of temperate soils

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## ABSTRACT

Soils developed on the sites of Australian Aboriginal oven mounds along the Murray River in SE Australia, classified as Cumulic Anthrosols under the Australian Soil Classification, are shown to have traits similar to the *Terra Preta de Indio* of the Amazon basin. Seven such sites were characterised and compared with adjacent soils. The Cumulic Anthrosols contained significantly ( $p < 0.05$ ) more soil carbon (C), compared to adjacent non-Anthrosols. Solid-state  $^{13}\text{C}$  NMR spectroscopy showed that the C in the Cumulic Anthrosols was predominantly aromatic, especially at depth, confirming the presence of charcoal. Radiocarbon analysis carried out on charcoal collected from two of these sites showed that it was deposited  $650 \pm 30$  years BP at one site and  $1609 \pm 34$  years BP at the other site, demonstrating its recalcitrance in soil. The charcoal originated from plant material, as shown by SEM, and had high levels of Ca agglomeration on its surfaces. The Cumulic Anthrosols were shown to have altered nutrient status, with total N, P, K and Ca being significantly greater than in the adjacent soils throughout the profile. This was also reflected in the higher mean CEC of  $31.2 \text{ cmol } (+) \text{ kg}^{-1}$  and higher pH by 1.3 units, compared to the adjacent soils. Based on the similarity of these Cumulic Anthrosols with the *Terra Preta de Indio* of the Amazon, we suggest that these Cumulic Anthrosols can be classified as *Terra Preta Australis*. The existence of these soils demonstrates that Australian soils, in temperate climates, are capable of storing C in much higher quantities than has been previously recognised, and that this capability is founded on the unique stability and properties of charred organic matter. Furthermore, the addition of charcoal appears to have improved the physical and chemical properties of these soils. Together, this provides important support for the concept of soil amendment with “biochar”, the charred residue produced by pyrolysis of biomass, as a means for sequestering C and enhancing agricultural productivity.

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## 1. Introduction

The upper 100 cm of the world's soils represent an estimated 1200–1600 Gt C pool globally (Batjes, 1996; Eswaran et al., 2000; Post et al., 1982), which offers large sequestration potential (Cole et al., 1996; Lal et al., 2007) when considered in relation to the estimated  $270 \pm 30 \text{ Gt CO}_2\text{-C}$  emissions from fossil fuel combustion between 1850 and 2000 (IPCC, 2001). Increasing soil carbon (C) levels has benefits beyond climate change mitigation as it improves agricultural productivity and sustainability (Lal et al., 2007; Paustian et al., 1997). As these benefits relate directly to profitability, they have the potential to motivate land managers

to incorporate the practices of increasing soil C without the need for high C emissions offset prices.

The potential limit for C sequestration by soils is often assumed to be the C holding capacity of native, pre-cultivation soils (Lal et al., 2007; Paustian et al., 1997), which results in an estimated global potential of 40–60 Gt (Cole et al., 1996). It has been demonstrated, however, that incorporation of high levels of organic matter, and in particular chemically recalcitrant forms of organic matter, can result in greatly enhanced soil C levels (Sombroek, 1966; Sombroek et al., 1993). Notable examples are the *Terra Preta de Indio* (dark earths of the Amazon), the Plaggen soils of North-West Europe (Davidson et al., 2006; Pape, 1970; Sombroek et al., 1993) and the ancient agricultural soils of the Andes (Sandor and Eash, 1995). The achievement of high soil C levels that are stable over time in both these examples has been attributed to anthropogenic amendment with charred organic matter, which resists microbial breakdown (Glaser et al., 1998; Lehmann et al., 2003b; Sombroek, 1966).

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**Fig. 1.** Soil profile of *Terra Preta Australis* site TPA2, a predominantly sandy soil. The distinct colour difference observed is a hallmark of *Terra Preta* profiles. The trowel shown is 20 cm in height.

The *Terra Preta de Indio* soils have a clear anthropogenic origin involving the addition of charred organics, the remnants from earthen ovens used for cooking and firing pottery, to the surrounding soils (Glaser et al., 2001; Lehmann et al., 2003b; Sombroek et al., 1993). *Terra Preta* soils have garnered interest because of their anthropology, increased fertility over extended periods and demonstrated long-term soil C sequestration (Lehmann et al., 2003a). The enhanced fertility of *Terra Preta* in the Amazon has been explained by higher levels of soil organic matter (SOM), improved holding capacity of nutrients such as nitrogen, phosphorus, calcium and potassium, higher pH and higher moisture-holding capacity compared to the surrounding soils (Glaser et al., 2001; Lehmann et al., 2003a,b; Smith, 1980; Sombroek, 1966; Zech et al., 1990).

These soils demonstrate the potential benefits of adding charred organics to soils, both in terms of C sequestration and improving soil fertility, and have been directly linked to the idea of “biochar” amendment to soils. In this context, biochar is defined as charred organic matter produced specifically for this purpose. Although the *Terra Preta* soils provide the opportunity to investigate the long-term implications of biochar addition, the outcomes will almost certainly be influenced by soil type, climatic conditions and the anthropological process by which they are created. Therefore the clear benefits of biochar amendment in the *Terra Preta* soils of the Amazon will not necessarily occur in other regions. Hence there is great interest in finding examples where anthropological biochar addition has occurred in different soils and climates. The European Plaggen soil has been identified as an example of a Cumulic Anthroposol demonstrating *Terra Preta*-like characteristics (Pape, 1970). The highly fertile nutrient status of phosphorus and calcium in this soil has been attributed to carbonised (biochar) particles present due to anthropogenic activity (Davidson et al., 2006). Ancient agricultural terraces in the Colca Valley of Southern Peru have also been found to have more organic C and N, lower pH and enriched P compared to nearby uncultivated Mollisols (Sandor and Eash, 1995).

At the same time as the pre-Columbian Indians were using ovens in the Amazon, in Australia, the pre-European Aboriginals resident in nomadic camps above the flood zone of the Murray River were also using earthen ovens to cook food. The resulting charred organics and refuse were discarded, building up into mounds over generations (Beveridge, 1869; Coutts, 1976; Coutts et al., 1979; Spencer, 1918). To date, the relevance of these anthropogenic oven mounds, or kitchen middens, to long-term C sequestration and soil fertility has not been investigated.

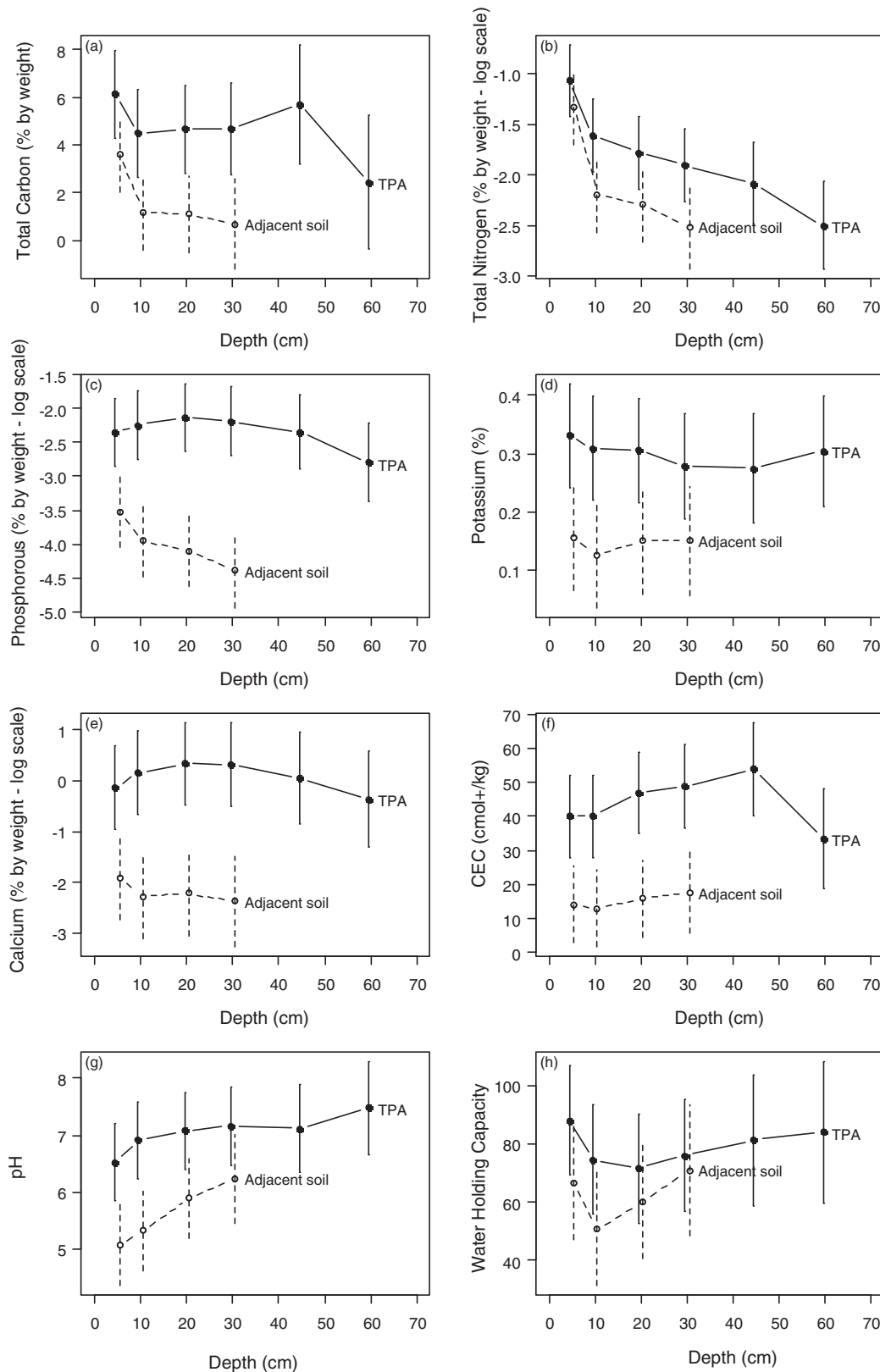
In this paper, these Cumulic Anthroposols are recognised as not simply oven mounds but as examples of Australian dark earth, for which we suggest the title *Terra Preta Australis* (TPA). We investigate these soils in terms of the impact that this anthropological activity has had on soil fertility and what C sequestration was achieved over the long-term. The findings of this investigation are considered in light of today’s pressing issues of climate change, food security and agricultural sustainability.

## 2. Methods

### 2.1. Classification

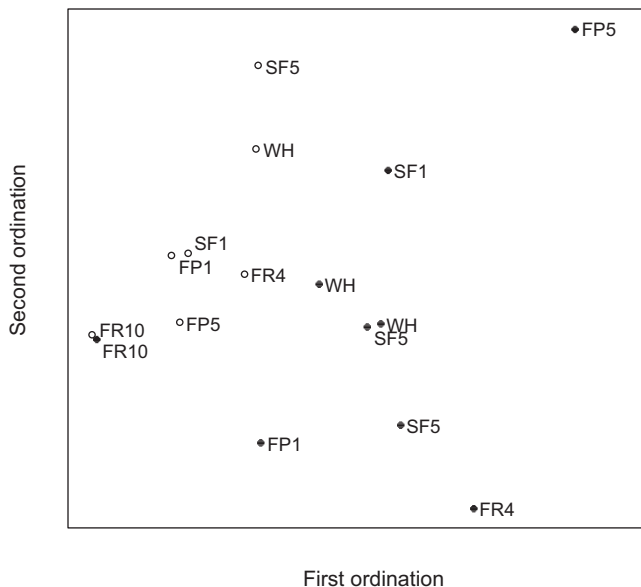
The soils investigated can be classified as Cumulic Anthroposols under the Australian Soil Classification (Isbell, 2002) or under the international framework for international soil correlation and communication as Anthrosoles (WRB, 2006). Anthrosoles are soils resulting from human activities which have led to a profound modification of the original soil horizons (Isbell, 2002). The suborder Cumulic refers to soils that have been formed by application of human-deposited material to a minimum depth of 0.3 m (Isbell, 2002).

*Terra Preta de Indio* soils have been formally classified as Anthrosoles (WRB, 2006).



**Fig. 2.** Total C (a), N (b), P (c), K (d), and Ca (e) contents of *Terra Preta Australis* soils compared with the adjacent soils. Cation exchange capacity (CEC) (f), pH (g) and gravimetric water holding capacity (mass of water divided by mass of soil) of *Terra Preta Australis* soils compared with adjacent soils. Vertical bars span the mean values plus or minus twice their standard error.





**Fig. 3.** Two dimensional ordination of the 16 (site) by 32 (trait) matrix of average 0–30 cm observations. Solid points indicate *Terra Preta Australis* sites while hollow points indicate the respective adjacent control sites. Points are labelled by location identification codes.

Despite possible suborder classification protocols specifically for *Terra Preta de Indio* (or Amazonian Dark Earths) being discussed in the literature (Kampf et al., 2003), no formal system has yet been agreed upon. Formal classification parameters could therefore not be applied to the Cumulic Anthrosols investigated to conclusively determine if the *Terra Preta* nomenclature could be applied. The *Terra Preta* sites in the Amazon occur on a variety of soil types (Smith, 1980), with various formation processes and local environments. This results in broad variability of soil properties of the *Terra Preta* examples (Eden et al., 1984), which makes definitive values for classification difficult.

The features used in the literature to identify *Terra Preta* soils include very thick, black or brown surface layers; evidence of anthropogenic influence; higher chemical fertility (high levels of organic C, calcium (Ca), magnesium (Mg), phosphorous (P) and microelements); and black C, charcoal or biochar content (Kampf et al., 2003). These features are identified by contrasting with the usually highly weathered and nutrient-poor surrounding soils (Eden et al., 1984; Lehmann et al., 2003b; Sombroek, 1966). Determination of these features was the focus of this investigation. The results are discussed with regard to these *Terra Preta* soil features, using comparative examples from the literature where possible, in order to justify the classification of the Cumulic Anthrosol as *Terra Preta Australis*.

## 2.2. Sites and soil sampling

In an expedition in 2007, we discovered and mapped thirty oven mounds (Cumulic Anthrosols) in the Murray River area around the New South Wales–Victoria border. All sites were in close proximity to the flood line of the river. The region where the *Terra Preta Australis* sites were identified is predominantly rural with a temperate climate consisting of average maximum daily temperatures of 21–24 °C and an average annual rainfall of between 400 and 500 mm, which falls predominantly over the winter months (BOM, 2009).

A total of 30 Cumulic Anthrosol sites were identified and mapped. Seven of these sites, along with their adjacent soils were sampled more intensively. Two of the sites contained two distinct

middens, which were sampled separately. Comparison soils were identified adjacent to the Cumulic Anthrosol sites, with sampling points typically separated by 20–30 m (see supplementary information) a much closer proximity than typically used in Amazonian *Terra Preta* studies (Glaser et al., 2001). Therefore, 16 soil cores were taken in total.

The sites were distributed across a range of soil types and land uses. Adjacent sites to be used as controls were selected in very close proximity to ensure consistency in parent soil type and land use history. It should be noted, however, that due to the Cumulic nature of the Anthrosols they are often raised above the native soil profile in mounds. This should be taken into consideration when comparing soil profile depths with the controls.

A pit was manually dug at each site and three segments were taken horizontally from each depth increment and bulked. Samples of the soil profile were taken in 5 and 10 cm increments to a depth of up to 60 cm. For comparison, samples from the adjacent soils near the Cumulic Anthrosol sites were taken at the same depths. At adjacent sites, the maximum depth of the pits was 30 cm due to a very hard B horizon. Soils were stored in plastic bags in portable ice-boxes until they were returned to the laboratory for analysis. The Cumulic Anthrosol sites were all located in close proximity to the high flood line of the river. Sites were visually distinguished in the environment by raised mounds, dark soils and, in some cases, altered natural vegetation.

## 2.3. Soil chemical analysis

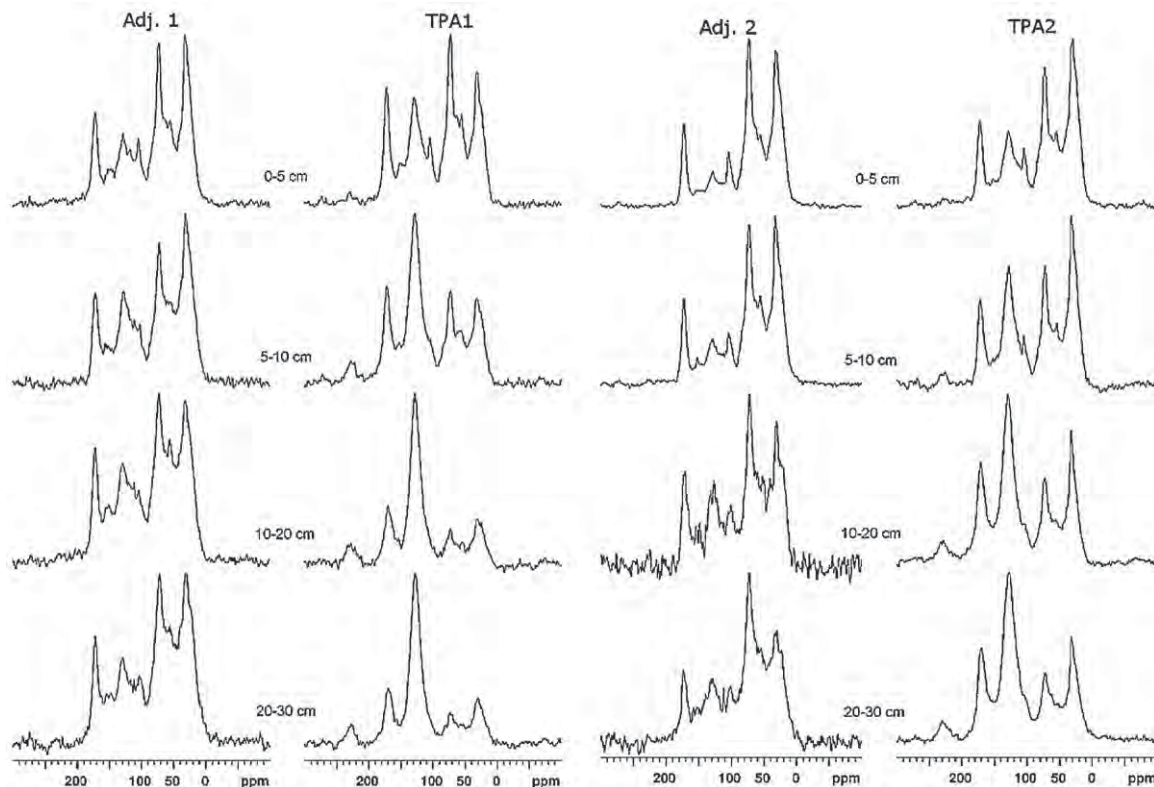
All soil chemical analyses were undertaken in a NATA (National Association of Testing Authorities, Australia) facility accredited to ISO 17025. A sub-sample of each homogenised bulked soil sample was air dried at 40 °C and passed through a 2 mm sieve. Total C and N were measured by Dumas combustion using an Elementar vario MAX CN analyser, at 900 °C, with an oxygen flow rate of 125 ml/min to ensure complete combustion of stable charcoal C. The pH was measured in 0.01 M CaCl<sub>2</sub> (5:1 soil:solution ratio) according to method 4B2 (Rayment and Higginson, 1992). Cation-exchange capacity (CEC) was assessed using exchange into 1 M NH<sub>4</sub>OAc, as described in method 15E1 (Rayment and Higginson, 1992). Acid digest for metal analysis was conducted according to USEPA method 3050B. The extract was analysed according to USEPA method 6010 with inductively coupled plasma atomic emission spectrometry.

Water-holding capacity was measured for all *Terra Preta Australis* sites for each soil depth sampled. The gravimetric water holding capacity of soils was determined using the method of Alef and Nannipieri (1998). Gravimetric water holding capacity is the mass of water divided by the mass of soil and, hence, is given as a dimensionless unit.

## 2.4. Statistical analysis

The soil analysis supplied measurements of 32 traits on 16 cores comprising the *Terra Preta Australis* and control cores at seven sites with two sites providing two distinct *Terra Preta Australis* cores and one control core. These results were analysed statistically as follows.

An ordination of the data was conducted in order to give an overview of differences between cores with respect to all of the traits. The average of each trait over the 0–30 cm segments was taken as representative of each core. The average traits were then centered and scaled to have mean zero and standard deviation of one. Euclidean distance between all pairs of cores was calculated and stored as a distance matrix. A two-dimensional ordination of



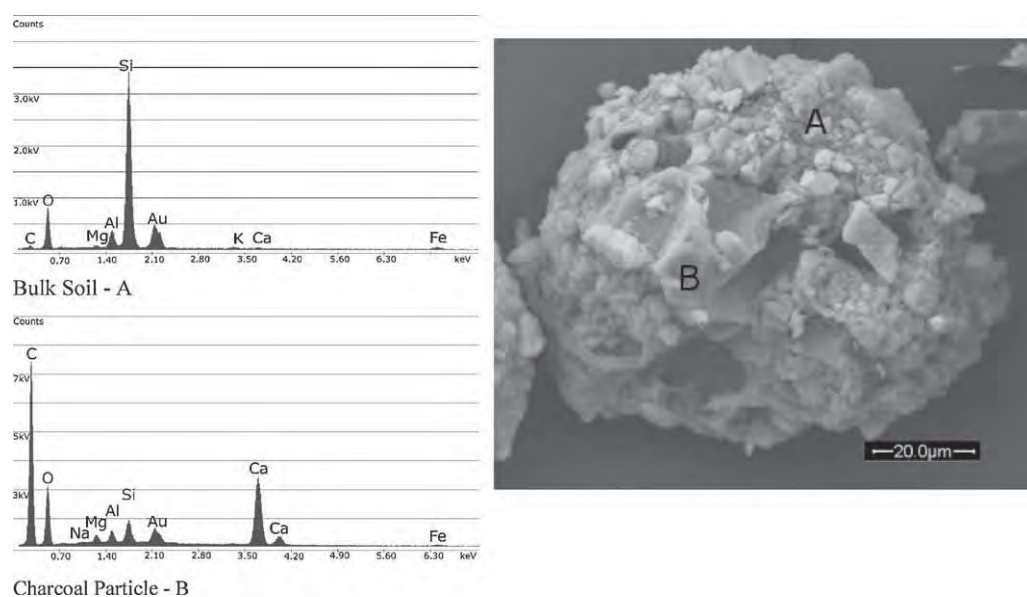
**Fig. 4.** Solid-state  $^{13}\text{C}$  CP NMR spectra of the HF-treated soils from the soil profile of a clay *Terra Preta Australis* site (TPA1) and its comparative adjacent site (Adj.1) and of a sandy *Terra Preta Australis* site (TPA2) and its comparative adjacent site (Adj.2).

the distance matrix was constructed using a multi-dimensional scaling algorithm described in Venables and Ripley (2002) and presented graphically to illustrate a general tendency for the *Terra Preta Australis* samples to be distinct from the control samples with respect to all of the traits.

Univariate analyses for a subset of the traits were conducted in order to describe specific differences between *Terra Preta Australis* and control soils for the qualities of interest. Each trait was fitted

to a mixed linear model, which included fixed terms for *Terra Preta Australis* soil or control, depth and their interaction. Variability due to sites and cores within sites was included as random effects. Some of the responses were transformed to a natural logarithm scale to stabilize tendencies for variance to increase with the size of the observations.

Estimates of the mean values for each soil type and depth were obtained from the models along with measures of variance. Sta-



**Fig. 5.** SEM image of a *Terra Preta Australis* soil particle from the 20 to 30 cm profile of TPA1 with corresponding EDS spectra. There is a close association of the charcoal C (B), recognizable by the distinct cellular structures, and the surrounding mineral content (A). The high calcium content amalgamated in the charcoal is a common feature in the *Terra Preta Australis* samples.



tistical inferences were made by comparing differences between control and *Terra Preta Australis* average traits to an estimated least significant difference at a 5% critical level.

Statistical analyses were conducted on the soil analysis results in the R software environment (R Development Core Team, 2009). The ordination was achieved by software in the MASS package (Venables and Ripley, 2002) and the mixed models were fitted through use of the asreml package (Butler et al., 2009).

## 2.5. NMR

Solid-state  $^{13}\text{C}$  NMR spectroscopy was used to characterize the soil C and determine the contribution of charcoal or biochar to the organic C pool. The soils were HF-treated prior to NMR analysis (Skjemstad et al., 1994). Solid-state  $^{13}\text{C}$  cross polarization (CP) NMR spectra were acquired with magic angle spinning (MAS) at a  $^{13}\text{C}$  frequency of 50.3 MHz on a Varian Unity200 spectrometer. Samples were packed in a 7 mm diameter cylindrical zirconia rotor with Kel-F end-caps and spun at  $5000 \pm 100$  Hz in a Doty Scientific MAS probe. A 1-ms contact time and a 1-s recycle delay were used, and 4000 transients were collected for each spectrum. Free induction decays were acquired with a sweep width of 40 kHz; 1216 data points were collected over an acquisition time of 15 ms. All spectra were zero-filled to 8192 data points and processed with a 50 Hz Lorentzian line broadening and a 0.005 s Gaussian broadening. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm. Spin counting was carried out using the method of (Smernik and Oades, 2000a; Smernik and Oades, 2000b).

## 2.6. SEM and EDS

Small soil aggregates from the 20 to 30 cm soil layer of *Terra Preta Australis* soils were oven-dried and mounted on Al stubs and coated with gold for energy dispersive X-ray spectrometry (EDX) and scanning electron microscopy (SEM) observation using an FEI Quanta 200 environmental scanning electron microscope (ESEM). The beam energy used was 20 kV.

## 2.7. Dating

The radiocarbon age of the charcoal in the soil samples from two of the *Terra Preta Australis* sites was determined from  $^{14}\text{C}$  measurement by accelerator-based mass spectrometry (AMS) by the University of Waikato Radiocarbon Dating Laboratory. Macroscopic charcoal samples from the 20 to 30 cm layer were physically cleaned, washed in hot 1 M HCl, rinsed and treated with multiple hot 1 M NaOH washes. The NaOH insoluble fraction was treated with hot 1 M HCl, filtered, rinsed and dried before the measurement was taken.

# 3. Results and discussion

## 3.1. Terra Preta Australis site descriptions

The *Terra Preta Australis* sites were identifiable as raised mounds with distinctly darker soil colouration. Sites were identified in native forests that are utilised for forestry and in cleared areas used for grazing. Glaser et al. (2000) describe the identification of *Terra Preta* in the Amazon by deep (40–80 cm) black A horizons which include charcoal particles, which is consistent with the identification of these Cumulic Anthrosols. The occurrence of ceramics also used as an identifier in the Amazon was not found in these sites, as Australian Aboriginals did not produce pottery. However the anthropogenic creation of these soils, a defining characteristic

of *Terra Preta*, has been well documented in the literature (Coutts et al., 1976).

Fig. 1 shows stark visual differences between the *Terra Preta Australis* site and the adjacent soil, reminiscent of those presented by Sombroek et al. (2002) and Glaser et al. (2001) from the Amazon. Mapping of the sites revealed that they consistently bordered the high flood zone of the river, an anthropological feature consistent with the Amazonian *Terra Preta* sites (Eden et al., 1984). Several sites show signs of disturbance, including intersection by roads, levelling for agriculture, rabbit warrens and excavation. A local land manager reported cases of excavation for the purpose of exporting the soils to local gardens, as is anecdotally reported to occur with the *Terra Preta* soils of the Amazon.

The *Terra Preta Australis* sites ranged in area from approximately 100 m<sup>2</sup> up to 1000 m<sup>2</sup>. The areas of the sites recorded are small in comparison to the Amazonian *Terra Preta*, whose areas average 20 ha (McCann et al., 2001; Smith, 1980; Zech et al., 1990) and include very large areas of 350 ha (Smith, 1999). This suggests that the nomadic Australian Aboriginal population, who did not establish agricultural plots, did not spread oven refuse materials across fields as the pre-Columbian Indians did. Also, the quantity of charred organic material produced by the Australian Aboriginals was small, consistent with the moderate use of ovens by the small populations compared to the pre-Columbians who used ovens extensively not only for cooking food, but also for firing pottery.

## 3.2. Comparison of soil properties between Terra Preta Australis and adjacent soil

The *Terra Preta Australis* soil samples from seven individual sites were compared to those of their respective adjacent comparison sites using the statistical methods described. Despite the large variation in distance, soil type, ages and concentrations of black C or biochar in the soils, clear and statistically significant trends could be observed. It should be remembered when comparing the soil profile results that due to the Cumulic nature of the Anthrosols the level of the native parent soil is likely to be lower than the top of the Anthrosol.

The average total C content was higher in the *Terra Preta Australis* soils than in the adjacent soils (Fig. 2a). The mean value of total C by weight in the 20–30 cm soil depth for the *Terra Preta Australis* soils was 4.7% compared to 0.7% for the adjacent control soils. The average increase of the total C mean values across the four soil segments making up 0–30 cm, was 3.35% (33.5 g kg<sup>-1</sup>). Soil bulk densities were not measured in the field to allow increases on an equivalent soil mass basis to be calculated, however due to the Cumulic nature of the anthrosol such values would not necessarily add to the accuracy of calculating net soil C stocks.

The nutrient status of the *Terra Preta Australis* soils and the adjacent controls were compared. The total nitrogen (Fig. 2b), phosphorus (Fig. 2c), potassium (Fig. 2d) and calcium (Fig. 2e) contents were all significantly higher in the *Terra Preta Australis* soils. Total nitrogen decreased down the soil profile with mean values decreasing from 0.27 to 0.08% and 0.35 to 0.15% by weight in the 0–5 cm layer to the 20–30 cm layer for the control soil and *Terra Preta Australis* soils, respectively. Phosphorous levels remained elevated down the *Terra Preta Australis* profile to a depth of 60 cm. In the 20–30 cm soil layer, the mean phosphorous content was almost 10 times higher in the *Terra Preta Australis* soils than the control soils. Potassium content in the *Terra Preta Australis* soils was consistently higher down the soil profile to 60 cm. In the 20–30 cm soil layer, the mean potassium content was almost twice that of the control: 0.28% compared with 0.15%. The mean weight percentage of calcium in the control soil was only 6.8% of that found for the *Terra Preta Australis* soils (0.093% and 1.363%, respectively).

Soil chemistry traits were also significantly changed through the historical accumulation of charcoal into these sites. Significantly higher CEC (Fig. 2f) and pH (Fig. 2g) were found in *Terra Preta Australis* compared with the adjacent soils. In the 20–30 cm soil layer, the mean CEC value of the *Terra Preta Australis* was found to be  $48.8 \text{ cmol (+) kg}^{-1}$  compared with only  $17.6 \text{ cmol (+) kg}^{-1}$  for the adjacent soils. A greater difference in the mean pH values was observed higher in the soil profile; the *Terra Preta Australis* soils were 1.3 pH units more alkaline than the controls on average for the four soil profile segments between 0 and 30 cm.

The improved nutrient status, higher pH and CEC of the *Terra Preta Australis* soils represent improved soil chemistry for agricultural productivity due to the anthropogenic alteration of the native soil hundreds of years prior to analysis. These trends are all consistent with *Terra Preta* soils. For example, the *Terra Preta de Indio* soils characterised by Glaser et al. (2000) showed in the 0–10 cm profile an increase in pH of 1.6 units and a CEC increase of  $13.3 \text{ cmol kg}^{-1}$  compared to the adjacent oxisol. In comparison, the *Terra Preta Australis* mean increase for pH and CEC were 1.3 units and  $31.2 \text{ cmol kg}^{-1}$  respectively. The increase of pH of *Terra Preta* sites recorded by Smith (1980) was attributed by Eden et al. (1984) to a relatively high concentration of exchangeable calcium. The predominance of calcium in the Cumulic Anthrosols investigated compared to the parent soils was also apparent, with significantly higher total and exchangeable Ca measured in the soil analysis and predominant Ca peaks in the EDS spectra. These soil chemical characteristics therefore align well with recognised *Terra Preta* features.

The water-holding capacity of the upper profile (0–20 cm) of the *Terra Preta Australis* soils was higher compared with the adjacent soils (Fig. 2h), especially in the upper soil horizons. It should be noted that although across the sites a significant increase in WHC was observed as a trend of the mean results, some individual sites exhibited no variation in WHC when compared to their adjacent site.

Water scarcity is a global issue threatening the sustainability of agricultural food production (FAO, 2010). The ability of biochar amendments to improve soil water-holding capacity could present a valuable climate change mitigation tool and enhance the sustainability of commercial agriculture in temperate climate regions which are adversely impacted by water stress conditions. The improved soil water interactions of the *Terra Preta Australis* is a finding supported by the literature on the Amazonian *Terra Preta* soils (Lehmann et al., 2003b), and the ability of charcoal (as a solid fuel source) to retain water in its structure has also been investigated in detail (Burrage, 1933). Hartt in 1885 (cited in Lehmann et al., 2003a,b) reported greener vegetation in the dry season on the *Terra Preta de Indio* sites. Newly prepared biochar has also been demonstrated to influence soil water holding characteristics (Chan et al., 2007).

The averaged values of all 32 traits of the *Terra Preta Australis* sites and their respective adjacent control sites at each soil depth can be found in the supplementary information. A graphical display of the ordination of the complete set is given in Fig. 3. As with the Amazonian *Terra Preta*, the anthropologically altered soils investigated have well defined boundaries with highly contrasting adjacent soils (Lehmann et al., 2003b). The ordination in Fig. 3 shows clear separation between the *Terra Preta Australis* and control sites at all locations except FR10 where little difference was found. The spread of the adjacent soils traits also indicates that the sites were spread across a range of soil types with varying properties. This indicates that the influence of the anthropological addition of charcoal from earthen ovens influences the properties of different soils with a statistically significant trend despite the variation in parent soil characteristics.

### 3.3. Identification and characterization of charcoal-rich organic matter in *Terra Preta Australis* soils

#### 3.3.1. NMR

Solid-state  $^{13}\text{C}$  NMR analysis was carried out on two *Terra Preta Australis* profiles and their adjacent control soil profiles. The solid-state  $^{13}\text{C}$  cross polarization (CP) NMR spectra are shown in Fig. 4. The main peak of interest is the aromatic signal centered at  $\sim 130 \text{ ppm}$ , which includes the aromatic structures of charcoal, as well as those of other soil organic matter components, especially lignin. Comparing the surface (0–5 cm) samples, it is clear that in both cases, the aromatic signal is stronger for *Terra Preta Australis* soil than its respective control soil. With increasing depth, the aromatic signal becomes increasingly dominant for the *Terra Preta Australis* soils. On the other hand, the  $^{13}\text{C}$  NMR spectra of the control soils vary little with depth. The control soils also contain a small peak at  $\sim 150 \text{ ppm}$ . This can be attributed to O-substituted aromatic C that is typical of lignin and indicates that some of the signal at  $\sim 130 \text{ ppm}$  for the control soils is due to lignin. For the *Terra Preta Australis* soils, the peak at  $\sim 150 \text{ ppm}$  is very small, especially for the strongly aromatic deeper soils, indicating that virtually all of the signal at  $\sim 130 \text{ ppm}$  can be attributed to charcoal.

Although the NMR spectra unambiguously show that the *Terra Preta Australis* soils contain more charcoal, especially at depth, than their respective adjacent soils, it is not possible to precisely quantify the charcoal contents of the soils directly from these spectra. It is quite simple to measure the proportion of aromatic signal (defined as signal occurring in the range 165–110 ppm) in the spectra by integration, but this cannot be equated to the proportion of charcoal C in the soil, primarily because (i) the required pre-treatment with hydrofluoric acid (HF) results in the loss of some C from the soils and (ii) not all C types are detected with equal efficiency by  $^{13}\text{C}$  CP NMR.

Table 1 confirms the trends in aromatic signal identified above through inspection of the spectra themselves (Fig. 4). At all depths, and for both pairs of profiles, there is a greater proportion of aromatic signal for the *Terra Preta Australis* than the respective control soil (Table 1). This is especially true for the deeper increments, with aromatic signal reaching a maximum of 65% for the TPA1 profile and 51% for the TPA2 profile.

Table 1 also shows that C recovery on HF-treatment was generally higher for the *Terra Preta Australis* soils than the adjacent control soils, especially at depth. This indicates that charcoal is concentrated relative to non-charcoal soil organic matter during HF-treatment for these deeper soils. Table 1 shows that NMR observability, as determined by spin counting (Smernik and Oades, 2000a,b), is consistently lower for the *Terra Preta Australis* soils, especially at depth. This is consistent with the widely-reported under-detection of charcoal-like aromatic C when the CP technique is used (e.g., Keeler and Maciel, 2003; Smernik and Oades, 2000a,b), which can be attributed to the presence of C atoms remote from hydrogen (Smernik et al., 2002a) and organic free radicals (Smernik et al., 2002b). The NMR observability values for the deeper (below 10 cm) *Terra Preta Australis* soil increments (17–27%) lie within the range of values reported for biochar C of 3–40% (McBeath and Smernik, 2009).

The two effects discussed above tend to cancel each other out, since HF-treatment concentrates the charcoal component and NMR observability underestimates the charcoal contribution to the spectra. However, the observability effect is the stronger, so it is that likely charcoal represents a greater proportion of total C than indicated by the aromatic C proportions shown in Table 1.

The NMR results verify that the dark colour and increased C content of the soil is predominantly caused by the presence of highly



**Table 1**

Results of solid-state  $^{13}\text{C}$  NMR analysis of the HF-treated soils from the soil profile of a clay *Terra Preta Australis* site (TPA1) and its comparative adjacent site (Adj.1) and of a sandy *Terra Preta Australis* site (TPA2) and its comparative adjacent site (Adj.2).

	% Aromatic signal <sup>a</sup>	C recovery on HF-treatment <sup>b</sup>	NMR observability <sup>c</sup>
TPA1 0–5 cm	30	76	40
TPA1 5–10 cm	49	75	33
TPA1 10–20 cm	65	81	17
TPA1 20–30 cm	64	71	22
Adj. 1 0–5 cm	23	66	56
Adj. 1 5–10 cm	24	67	43
Adj. 1 10–20 cm	27	54	54
Adj. 1 20–30 cm	21	53	40
TPA2 0–5 cm	25	88	58
TPA2 5–10 cm	32	99	34
TPA2 10–20 cm	50	80	27
TPA2 20–30 cm	51	86	26
Adj.2 0–5 cm	13	101	82
Adj.2 5–10 cm	16	48	60
Adj.2 10–20 cm	22	55	30
Adj.2 20–30 cm	22	47	59

<sup>a</sup> Proportion of signal in 165–110 ppm chemical shift range relative to total integrated signal (300–0 ppm).

<sup>b</sup> Determined as (mass of HF-treated residue  $\times$  C content of HF-treated residue)/(mass of whole soil  $\times$  C content of whole soil)  $\times$  100

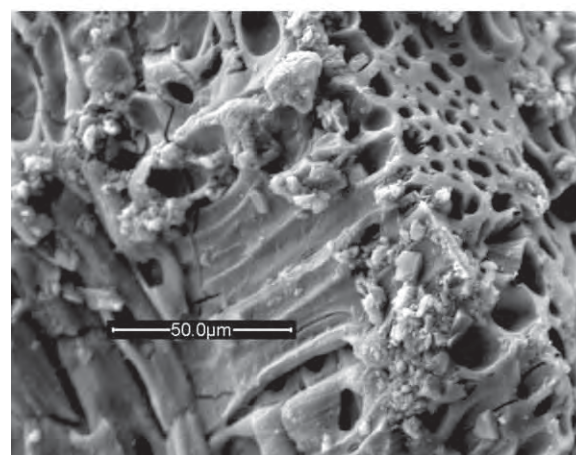
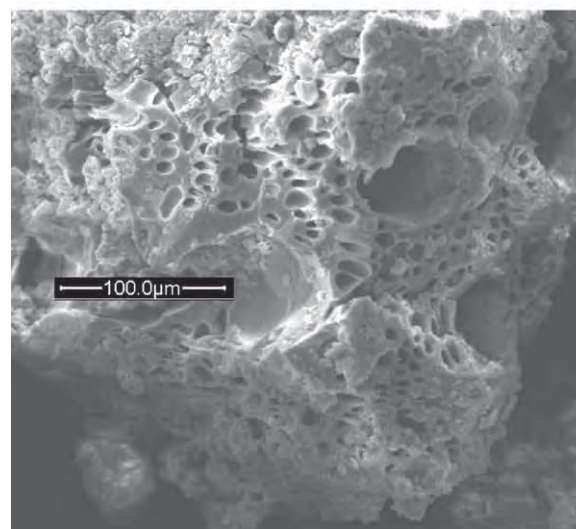
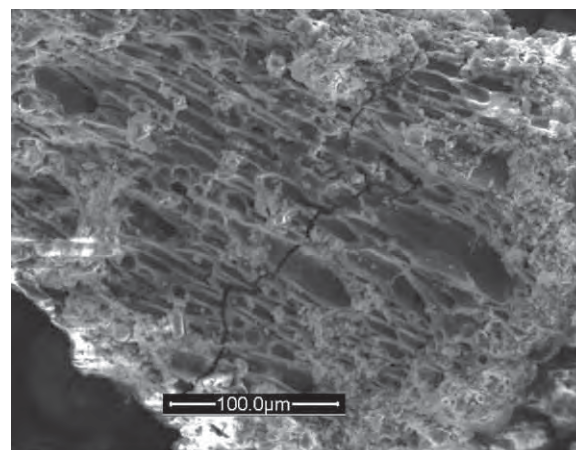
<sup>c</sup> Determined as (mg of C in HF-treated soil sample analysed  $\times$  total NMR signal for HF-treated soil sample analysed)/(mg of C in glycine standard analysed  $\times$  total NMR signal for glycine sample analysed)  $\times$  100. For both sample and glycine, total NMR signal was corrected for  $T_{1\rho}$  relaxation losses as described in Smernik and Oades (2000a,b).

aromatic charcoal C. As has been concluded in investigations of the *Terra Preta de Indio* soils, the primary cause for the differences observed between the *Terra Preta Australis* soils and the native adjacent soils is proposed to be the anthropological addition of large quantities of organic C in highly aromatic forms produced as a by-product of cooking in earthen ovens.

Increased organic C content, a hallmark in *Terra Preta* classification, was observed in the NMR analysis and quantitatively supported by the soil analysis results. The *Terra Preta de Indio* soils characterised by Glaser et al. (2000) showed C increases of  $23.5 \text{ g kg}^{-1}$  in the 0–10 cm depth and  $15.7 \text{ g kg}^{-1}$  in the 30–40 cm depth compared to the adjacent oxisol. The mean increase in total C value of the *Terra Preta Australis* sites exceeds these with a mean increase of  $33.5 \text{ g kg}^{-1}$ . The substantially higher C content measured provides justification of the *Terra Preta* classification for these soils. The intensity of the C application may be greater for the Australian examples due to the process by which the earthen ovens were emptied onto one mound for successive seasons, resulting in a large quantity of charred organics being deposited on the one concentrated location.

### 3.3.2. SEM

Particles of organic origin were identified by their distinct biological cell structure (Figs. 5 and 6) and EDS spectra with a dominant C peak (Fig. 5). The O:C ratios of the particles were found to be around 0.45, higher than what may be expected of black C or biochar ( $<0.25$ ) (Glaser et al., 2000) but significantly lower than uncarbonised cellulose (0.83) (Stoffyn-Egli et al., 1997). This may indicate surface oxidation over time. The solid-state  $^{13}\text{C}$  NMR spectra (Fig. 4) are also consistent with this, since the aromatic-rich deep increments (10–20 cm and 20–30 cm) of the *Terra Preta Australis* soils contain strong carbonyl peaks at  $\sim 170$  ppm. Similar peaks have previously been identified as carboxylic acid groups on partially-oxidized charcoal structures in soils (Smernik et al., 2000).



**Fig. 6.** SEM images of charcoal particles in the 20–30 cm profile of *Terra Preta Australis* soil. Representative images typical of particles observed in both TPA1 and TPA2 samples are provided.

### 3.3.3. Dating

The NMR results confirm that the high soil C levels found in the *Terra Preta Australis* soil analysis are predominantly charcoal based. The anthropology of the sites indicates that this charcoal was added to the soils through the practice of nomadic Aboriginals emptying earthen ovens. The radiocarbon age of charcoal isolated from *Terra Preta Australis* mound TPA1, a high clay, agricultural

grazing field site was  $650 \pm 30$  years BP, whereas the radiocarbon age of charcoal from TPA2, a sandy site on the border of a heavily timbered area in close proximity to the river, was  $1609 \pm 34$  years BP. It should be noted that the charcoal additions to this soil according to the anthropology are likely to have occurred over many years. Therefore, the dates of deposit may be considerably older, or younger than the radiocarbon age measured by this method.

The dating of the *Terra Preta Australis* is consistent with the anthropology of the pre-European habitation of Aboriginals in this location (Coutts and Witter, 1977). These results are supported by radiocarbon dating of Australian oven mounds by an anthropological survey in the 1970s, further North-West along the Murray River, which placed them between 600 and 3500 years BP (Coutts and Witter, 1977). The biochar black C therefore has been demonstrated to be persistent in these Australian soils in this climatic region over hundreds to thousands of years. This is an important finding for both global C balance calculations and greenhouse gas abatement studies of biochar projects, as it provides support for the theory that biochar is an effective pathway for C sequestration as the material sustains C in this environment over a long time frame.

The results of the radiocarbon dating of the *Terra Preta Australis* sites are contemporary with the *Terra Preta* examples in the Amazon which have reported ages ranging between 500 and 2500 years old (Glaser et al., 2001; Lehmann et al., 2003b; Saldarriaga and West, 1986). Radiocarbon dating of *Terra Preta* sites in the Amazon valley have provided not only evidence of their pre-Columbian origins but also of the long-term stability of black C in this soil environment (Glaser et al., 2001).

#### 3.4. Implications of these findings for biochar amendment of Australian soils

When investigating C sequestration potential, the upper limit of beneficial biochar incorporation is of interest. This is how much can be sequestered in the soil before adverse impacts to soil health occur. Increases in organic C of more than 4% were measured in soil profiles of several sites with markedly improved soil chemistry for agriculture. The upper limit of beneficial biochar incorporation can therefore be assumed to be well in excess of this value for the temperate climate soils examined.

If a 4% increase in soil C, a level observed possible in *Terra Preta Australis* sites discovered, was achieved through the application of biochar to all of Australia's 42 million ha of cropped soils (DEWHA, 2007) to a 30 cm depth, 7.5 Gt of solid C or 27 Gt of  $\text{CO}_2\text{-e}$  would be sequestered. This calculation assumes an average soil bulk density of  $1.5 \text{ g cm}^{-3}$  for all of Australia's cropping land, and takes cropping land to be the sum of dry land and irrigated agriculture, as described by the Australia Government Natural Resources Audit for Land Use (DEWHA, 2007).

Australia's net greenhouse gas emissions across all sectors totalled 576 Mt  $\text{CO}_2\text{-e}$  in 2006, under the accounting provisions applying to Australia's Kyoto emissions target (DCC, 2008), hence 27 Gt represents 48 years of Australia emissions at this level (DCC, 2008). This sequestration potential, however, would likely meet sustainability, economic, and logistical constraints before it was achieved in practice. However, the extensive management of soils through agricultural practices means they can be quickly and effectively engaged in C sequestration efforts, given the appropriate technologies, compared with other sinks such as oceans that offer little existing infrastructure.

Biochar could also be applied to forestry and rangeland soils, or sequestered in ocean sediments and deeper geological formations. The *Terra Preta Australis* sites therefore provide evidence that the sequestration potential of biochar application would become lim-

ited by sustainable biomass supply and production methods rather than soil C holding capacity, which we have demonstrated to be extensive.

It should be noted that greenhouse gas emissions will also be generated by the production of biochar, which will offset some of the gains made through sequestration. Full life-cycle assessment methods should be used to determine the net sequestration achieved with all factors considered. The source of feedstock used for biochar production will have a significant impact on the net greenhouse gas balance and effects of diversion of organics from alternate uses and land-use change should all be considered. Although mostly causing a net carbon sequestration, some life cycle assessments in the literature have been shown to result in a net greenhouse gas emission due to land-use change (Roberts et al., 2010). The maximum sustainable technical potential of biochar to mitigate climate change considering the complete lifecycle has been estimated at around 1.8 Gt  $\text{CO}_2\text{-e}$  (Woelf et al., 2010).

The *Terra Preta Australis* soils have been altered both physically and chemically compared to the adjacent soils, and have remained relatively undisturbed since their formation. It is important to note that the addition of fresh biochar to soils alone may not result in the outcomes observed if the physical impacts are not also replicated. Some of the benefits observed may take hundreds of years to develop. The process of charcoal aging in the soil environment has been documented in the literature (Cheng et al., 2008; Liang et al., 2006). The discovery of *Terra Preta Australis* allows for further investigation of the process of charcoal aging so that it might be related to the timeframes and impacts of biochar applied to Australian, temperate, agricultural soils.

The addition of freshly made biochars to soil and their impact on soil traits and productivity is an area of growing research interest. Increases in total soil carbon levels achieved by the application of biochar obviously will vary with the application rate and carbon content of the biochar. A 4% increase is total soil C, however, in theory could be achieved via a single application of biochar. Increases in soil C with biochar addition may be compounded over time by the further stabilization of non-biochar carbon on the biochar surfaces (Van Zwieten et al., 2010).

These findings demonstrate that Australian agricultural soils are suitable precursors of *Terra Preta* formation and that C and fertility levels are not necessarily limited to upper limits of the native soil levels.

#### 4. Conclusions

Cumulative Anthroposols exist in Australia and exhibit all the features typical of *Terra Preta* soils in the Amazon, with the exception of geographical location. Therefore, informal classification of these soils as *Terra Preta Australis* is justified. These *Terra Preta Australis* soils have been created via anthropological addition of charred organics (biochar) to soil hundreds of years ago. The *Terra Preta Australis* exist in a temperate climate with low rainfall.

The formation of *Terra Preta Australis* has resulted in significant changes to soil chemical characteristics, making them potentially more productive agricultural soils. Australian agricultural soils are suitable precursors of *Terra Preta* formation. Through the application of biochar, temperate climate soils have the potential to sequester large quantities of C, while improving chemistry and structure for increased agricultural viability in a changing climate. It should be noted, however, that these chemical and physical improvements may take hundreds of years to develop. Nonetheless, the characterisation of *Terra Preta Australis* will accelerate our understanding of biochar's potential in the Australian environment and in other soils in temperate regions. The knowledge of how



to improve these soil traits provides the opportunity to enhance the sustainability of agriculture and hence enhance ongoing food security.

C sequestration calculations based on the soil C levels achieved by the *Terra Preta Australis* examples indicate that biochar could represent an important global sink for atmospheric C, which could be anthropogenically managed on the immense scale required to reduce atmospheric C levels. The sustainable sourcing of biomass and the logistics of production, rather than the capacity of soils to beneficially hold biochar, limits their sequestration potential. Full life-cycle analysis of biomass harvesting and production needs to be considered to quantify the net greenhouse gas outcome, however the addition of biochar to soils could make a positive contribution to managing atmospheric greenhouse gas levels and hence decrease the risk of climatic change.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.agee.2010.11.020.

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**Supplementary Information Figure 1: The person in the background is standing on what can be seen as the raised oven mound or *Terra Preta Australis* site. The hole in the foreground is where the adjacent soil profile was sampled. Inset A is the *Terra Preta Australis* profile, to be compared with inset B of the adjacent soil. As can be seen from the placement of the trowel (20cm height), the adjacent soil was very hard only allowing for a comparatively shallow profile to be dug.**



## Chapter 5

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### *Biochar: A co-product to bioenergy from slow-pyrolysis technology*

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## Chapter 8

### Biochar: A co-product to bioenergy from slow-pyrolysis technology

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#### Abstract

Well engineered, slow-pyrolysis technology, optimized for the production of bioenergy and biochar from sustainable feedstocks, could deliver significant environmental and economic advantages to industry. Utilization of biochar products as a soil amendment could contribute to ongoing food security and agricultural productivity. Biochar production and sequestration can result in the net removal of greenhouse gases from the atmosphere, making the technology a potentially valuable tool for climate change mitigation. It is essential that the emerging industry is well regulated and that quality assurance and sustainability mechanisms are adopted. This will optimize the net benefit of the technology.

Biochar products produced from different industries will vary greatly in characteristics. Equally, the drivers for different industries to adopt slow pyrolysis technology will vary. Significant advantages provided by the technology across multiple industries may result in extensive adoption. The development of a biochar market is required, with the uncertainty in biochar price and market size, being a major contributor to lack of confidence in the business case for the technology. Markets for biochar as a product are diverse ranging from broad acre agriculture to niche applications such as roof gardens where its unique properties give it significant competitive advantages over competing alternatives.

## Introduction

International interest in the adoption of modern slow pyrolysis technology for the production of biochar products and bioenergy is growing. Solid, carbon rich biochar can be a co-product of pyrolysis and gasification technologies, which have traditionally had a focus on energy generation. Optimisation of the technology for sustainable and economic biochar production however has recently garnered significant and escalating investment. This is due to a mounting body of scientific literature demonstrating its potential application as a valuable soil amendment, which not only enhances soil health and productivity but stores carbon in soil (Lehmann and Joseph, 2009). Carbon storage in the terrestrial sink of agricultural soils via biochar could present a low-risk solution that sustainably reduces atmospheric loads of greenhouse gases (Downie et al., in press).



**Figure 1: Biochar produced from a modern slow pyrolysis plant, operated by PacPyro, from greenwaste as a soil amendment and means to sequester carbon over the long term.**

When seeking to apply the technology to achieve atmospheric greenhouse gas stabilisation and soil health for ongoing environmental sustainability, all aspects of the technology must be considered to ensure sustainability gains in one area are not undermined by consequences in another. This kind of thinking is driving the development of a new generation of pyrolysis technologies that deliver higher standards of process efficiency, reductions in emissions of pollutants, and improved public health and safety outcomes than is possible from traditional charcoal production technologies.

Another appeal of modern slow-pyrolysis technologies is that some have been engineered to process very low-grade waste organics (Pacific Pyrolysis Pty Ltd, 2010). That is, organic materials that have: high ash and moisture content; soil, stone and other contamination; large particle size distributions; and few options for beneficial reuse. This enables modern slow-pyrolysis technologies to fit within the definition of a second-generation bioenergy solution, as it does not rely on food-based feedstocks or high-grade forestry products (IEA, 2010). Significant sustainability and food security benefits can be achieved with the use of such technologies, as they do not compete for valuable resources, but provide resource

recovery of waste materials (Cherubini *et al.*, 2009). Managing wastes, that by definition are underutilised and may present an environmental risk, not only contributes to the sustainability credentials of pyrolysis technology but also provides economic advantages. Low-grade feedstocks are typically low-cost and often have significant management costs, hence providing a revenue stream (or cost saving) to a pyrolysis project providing an organic waste management service.

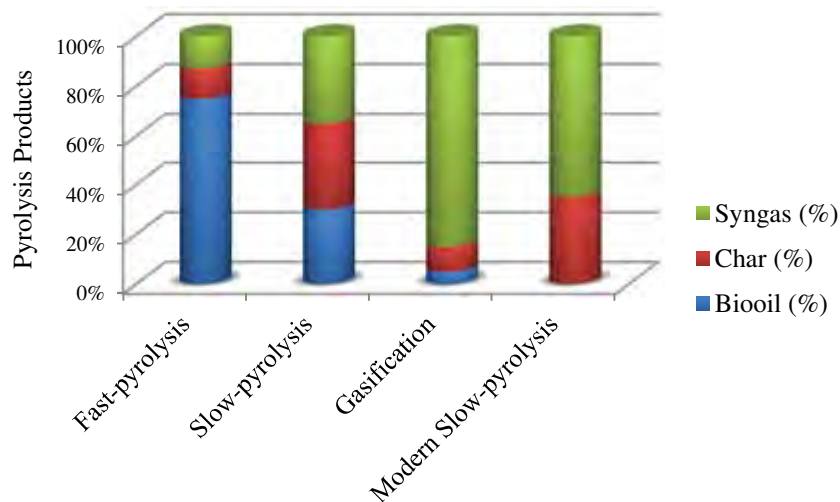
Along with revenue for waste services, slow pyrolysis technology may generate revenue through the production of bioenergy, biochar and environmental offsets. The technology can be applied at a scale that is large enough to get the economies-of-scale required to make a commercial business case, yet small enough that the distributed nature of organic feedstocks does not limit viability.

When slow-pyrolysis technology is utilised for bioenergy and biochar production the following benefits can be achieved:

- Generating renewable, distributed energy, improving energy security;
- Mitigating greenhouse gases and sequestering carbon;
- Recycling nutrients back to agricultural land while increasing soil carbon levels;
- Increasing the sustainability of agricultural production through enhancing soil health, hence improving food security;
- Improving land use outcomes through minimizing waste going to land-fill; and
- Ensuring environmental quality (air, water and soil) and human health through strict environmental and operational standards.

## Technology Overview

Pyrolysis technology relates to the heating of organic or fossil sources of solid carbon in a very low oxygen environment to temperatures over 400° C. The resulting thermal decomposition yields solid char, liquid bio-oils and tars, and gaseous syngas. The reaction conditions can be engineered to change the product ratios and properties (Bridgwater, 2007; Di Blasi, 2008) as illustrated in Figure 2. Pyrolysis technologies that optimise for bio-oil production facilitate fast heating rates, from ambient to highest heating temperature in seconds, and are therefore described as fast pyrolysis. Utilisation of fast pyrolysis for biochar and bio-oil production has been the subject of a recent investigation (Laird *et al.*, 2009). The focus of this chapter however is on slow pyrolysis technology, which via more steady heating rates, from ambient to highest heating temperature in minutes to hours, optimises for the production of syngas and biochar. In modern systems designed for commercial biochar production, such as that operated by Pacific Pyrolysis Pty Ltd (see Figure 3). Bio-oil produced is cracked to syngas to circumvent the necessity to market or dispose of a bio-oil (Downie *et al.*, 2007).



**Figure 2: Thermal conversion technology product splits. Fast and slow pyrolysis, gasification product data (Bridgwater, 2007), modern slow-pyrolysis data (Downie *et al.*, 2007)**

The utilisation of slow pyrolysis for the production of charcoal is one of the oldest industries known to society (FAO, 1983). Traditional systems vent all volatiles directly to the atmosphere and have very limited process controls. This results in environmentally damaging air pollution and risks to human health and safety (Namaalwa *et al.*, 2007; Adam, 2009; Brown, 2009; Downie *et al.*, in press). Modern slow pyrolysis technology developers need to conform to the relevant regulatory and economic requirements. This means that high environmental standards need to be met and losses of potentially valuable products to the atmosphere eliminated.

Characteristics targeted by developers of modern slow pyrolysis technologies for the economical and sustainable production of biochar include (Bridgwater, 2007; Brown, 2009; Laird *et al.*, 2009; Pacific Pyrolysis Pty Ltd, 2010):

- Energy Efficiency – continuous feed rather than batch processing, exothermic operation without air infiltration (i.e. pyrolysis conditions rather than gasification/combustion), waste heat recovery and recycling, utilisation of insulation, lagging and refractory;
- Reduced Pollution – air emissions managed (i.e. no smoke, low NO<sub>x</sub> burners, low organic pollutants such as dioxins etc);
- Improved biochar yields and quality – slow pyrolysis rather than gasification or fast pyrolysis (see Figure 2), process control to ensure consistent product quality;
- Operability – decreased labour requirement (i.e. automated materials handling, continuous operation etc), steady state operation resulting in control of product quality and quantity, high workplace health and safety standards;
- Feedstock flexibility – allowing broader range of low-cost feedstocks to be processed;

- Scalability – sufficient size to reach the required economies-of-scale, whilst small enough to not be limited by biomass availability.

Adequate precautions need to be taken to ensure that environmental standards are upheld. For example, technology should be designed to prevent formation of toxic compounds such as PAH's and dioxins. There is extensive literature on the reaction conditions conducive to the formation of PAH's (Baek *et al.*, 1991; Mastral and Callean, 2000; Richter and Howard, 2000) and dioxins (Gullett *et al.*, 1992; Lavric *et al.*, 2005; Kulkarni *et al.*, 2008; McKay, 2002), which can be referred to. It should be noted that these are usually in reference to more commonly employed thermal-conversion technologies such as gasifiers and incinerators; however this knowledge can be adopted for pyrolysis reactor design.

### **Current Status of the Technology**

Although charcoal production is one of the oldest industries the adoption of modern slow pyrolysis technologies, optimised for biochar and bioenergy production, is in the early stages of commercialisation (Brown, 2009; Laird *et al.*, 2009). Adoption of the technology relies on building a convincing business case to be demonstrated (Bryant and Downie, 2007). Although each application of the technology will have project specific differences, the technology business case is built around the following framework.

### **Revenue streams**

The following revenue streams may be available to a biochar production business:

- Biochar sales;
- Energy sales such as electricity or thermal energy generated from liquid, solid or gas products;
- Environmental offsets such as policy driven fiscal incentives for greenhouse gas emissions abatement, renewable energy generation, waste reduction, etc; and
- Organics waste management charges (perhaps offsetting landfill tipping fees).

Revenue streams may alternatively be cost-savings compared with business-as-usual operation. For example, energy generated may be used internally (embedded) by the industry operations and hence not generate a revenue stream from sales, but a cost savings due to decreased retail energy requirements.

All revenue streams may not be available to all projects. For example, there may be no market for the energy, and/or the project may have to pay for feedstock making it a cost rather than a revenue stream. If however, one of the remaining revenue streams is very profitable a reduction in the number of revenue streams may not necessarily result in an unviable project (Bryant and Downie, 2007).

Some revenue streams are more economically certifiable than others in the project (and industry) development phase. That is, they represent a more reliable and lower risk source of income to the project. For example, at the time of writing

there is no existing market for biochar demonstrated on a commercial scale. Therefore the level of demand and market price for this new product is debatable (the value of biochar products is discussed further in Biochar as a Soil Amendment). Energy on the other hand is a commoditised product with a long price and demand history. Energy sales are therefore considered a more economically certifiable or bankable form of revenue when developing a business case for a proposed biochar production facility.

### **Operating costs**

The following operating costs may be incurred by a biochar production business:

- Management, administration, monitoring and reporting;
- Operations staff;
- Maintenance, service agreements and sustaining capital;
- Debt servicing;
- Insurance;
- Transport of feedstocks and products;
- Consumables; and
- Energy requirements (start-up, shut-down, and sustaining).

The magnitude of the project operating costs varies greatly depending on the location of the project and the regulatory regime it is subjected to. For example, in a developed country the cost of human resources is likely to be one of, if not the, most significant contributor to operating costs. However in a developing country these resources come at a significantly lower cost. Likewise in developing countries the level of administration, monitoring and reporting required to meet government requirements could also be less and therefore represent a decreased operating cost.

### **Capital costs**

The following items are likely to contribute to the capital cost of establishing a modern slow-pyrolysis facility for biochar production:

- Site preparation and civil works such as buildings, roads, fences, etc;
- Feedstock harvesting and pre-processing equipment. This may include plant items such as; dewatering of sludges; grinders, shredders or mills for size reduction; screens or sieves for size selection; conveyors and/or screws for on-site transfer; pads, bays, buckets and bins for storage; trucks and front end loaders for transport;
- Feedstock drying equipment (may be incorporated into the pyrolysis kiln design);
- Pyrolysis kiln;
- Biochar conditioning, blending, handling and packaging;
- Syngas cleaning, cooling and flaring equipment;
- Energy conversion technology. This may include a gas engine, turbine, boiler etc. If electricity is produced, grid connection and metering is required. If bio-oil is produced, condensing, handling and packaging equipment is required.
- Piping and instrumentation;



- Control systems;
- Emissions control;
- Ancillary services such as water, power, telephone, etc.; and
- Safety systems and controls.

Additional items typically added to the capital cost include:

- Project management;
- Procurement;
- Installation and commissioning;
- Technology license or development costs;
- Project structuring and contracting;
- Project development;
- Planning approvals and environmental consents; and
- Financing.

The capacity factor of the project, or the number of hours the project is operating compared to periods of shut-down or de-rated operation, can also have a large impact on the business case. Capacity factors can be impacted by; technology specific reliability and maintenance requirements, processing configuration (batch versus continuous), integration with other industries (only producing feedstock or requiring energy for limited periods) or limitations imposed by planning and consents. For example the project may run 24 hours a day, 7 days a week, or 8 hours a day, 5 days a week. If the quantity and value of the products produced per hour is the same, the greatly reduced production hours will result in a far greater burden per unit produced to payback the capital and fixed operating costs.

Uncertainty surrounding the business case is high due to the lack of any verified commercial biochar production business being in operation. Although the technology has been successfully demonstrated on a pilot-scale (Downie *et al.*, 2007) (see Figure 3), the technology faces the challenging hurdle faced by all new technologies and that is attracting the higher-risk investment required for the initial, commercial-scale demonstration projects. In typical commercialisation pathways, this investment is made either by governments to enable the new industry or by an industry for which the opportunity presents an exceptional rate-of-return which warrants the risk to be taken on the new technology approach (Ernst and Young, 2010). Once demonstrated, the rate-of-return required by projects utilising the technology is expected to decrease in line with the decreased risk profile.



**Figure 3: Pacific Pyrolysis Pty Ltd's slow-pyrolysis demonstration facility at Somersby, Australia. Production facility for Agrichar™ biochar and bio-electricity from syngas.**

### **Opportunities for Industry**

Adoption of slow-pyrolysis technology may eventually occur within stand-alone businesses whose core business is the production of biochar. It is likely however that the first projects will be driven by the advantages gained through integration with existing industry, which makes the technology more economically viable in the short-term. Case studies have been developed to explore how some major existing industries may utilise pyrolysis technology to overcome some of the challenges they face. Each industry examined in the case studies has a unique organics resource to manage. Resource recovery, energy security, greenhouse gas savings and economic outcomes for each industry are discussed using a comparison between adoption of a slow-pyrolysis solution and business-as-usual.

### **Pulp and Paper**

Worldwide, about 300 million metric tons of paper and paperboard are produced each year. About 2-4% (dry weight) of paper sludge is produced as a by-product of the paper making process (Phillips *et al.*, 1997). The managed disposal of paper sludge is a significant challenge to the pulp and paper industry globally. The sludges produced by the paper industry can be divided into several categories: the waste paper sludge coming from the production of virgin wood fibre, called primary sludge; the waste paper sludge produced by removing inks from post-consumer fibre, called de-inking paper sludge; the activated sludge from the secondary systems, called secondary sludge; and combined waste paper and activated sludge, called combined sludge (Boni *et al.*, 2004).

In the United Kingdom, paper mills produce a total of 250000 dry tonnes of waste sludge per year (Phillips *et al.*, 1997). This is most typically dewatered to about 30% dry matter and sent to a commercial landfill at considerable cost (Phillips *et al.*, 1997). Slow-pyrolysis technology offers one of few options to traditional landfill, and presents significant advantages over alternatives such as land spreading, or incineration.

There are several advantages to be gained from producing biochar from paper sludge for land application, compared with using the sludge directly as has been proposed by some authors (Bellamy *et al.*, 1995; Beyer *et al.*, 1997; Phillips *et al.*, 1997). The sludge derived biochar has improved physical characteristics, such as increased surface areas, and is more friable than the stodgy sludge. The carbon, carbonates and nutrient contained in the sludges are concentrated in the biochar while the product itself is more readily transportable to markets due to being greatly reduced in volume and mass. Caution however should be exercised with flammability of the product. Testing against the Dangerous Goods, class 4, for combustible solids is recommended to ensure appropriate transporting controls are in place where needed.

Benefits of slow-pyrolysis for the Paper and Pulp Industry:

- Increased resource recovery of waste sludges;
- Decreased need for landfill;
- Value adding of paper sludge to marketable biochar product;
- Cheaper transport due to decreased mass and volume of product;
- Concentration of carbon and carbonates into biochar;
- Odor and pathogen elimination;
- Decreased greenhouse gases from landfill and direct land application; and
- Stabilization of carbon for sequestration.

One of the challenges of processing sludges through thermochemical processes, such as pyrolysis, is the high moisture content which imposes a large energy burden to evaporate the water. This challenge can be overcome via blending the sludge with a higher calorific value and/or dryer organic material, such as waste wood and bark that are also commonly found at pulp mills. Alternatively waste heat from existing boilers already in operation at the mill can be utilized to dry the material.

Biochar produced from paper sludge has been demonstrated to increase productivity in an acidic ferrosol, but had little influence in an alkaline calcarosol (Van Zwieten *et al.*, 2010c). Further research is still required before the benefits across a wide range of soil types and crops are determined. This will allow cost-benefit analysis to be undertaken for farmers utilising the product.

The high content of carbonates in the sludge material, due to the use of  $\text{CaCO}_3$  as a whitening agent in the paper making process, means that their use on acidic

soils for pH control is beneficial (Boni *et al.*, 2004; Van Zwieten *et al.*, 2010c). Direct paper sludge application for acid-mine drainage treatment and in the removal of heavy metals in solution has been proposed (Boni *et al.*, 2004). These functions may be enhanced in the biochar derived from paper sludges due to their increased surface areas and adsorptive properties (Downie *et al.*, 2009) compared with the unprocessed sludge.

The greatest uptake of paper sludge derived biochar is to be expected when consumers have commercial quality and environmental assurances related to the product. Possible contaminants in the paper sludge should be assessed for each project application according to the processes used in production. Biochar qualities from each paper sludge source and pyrolysis process should also be reviewed to ensure all risks identified are managed (Downie *et al.*, in press). Analysis of a primary sludge from an Italian mill suggest that the sludge does not represent a major threat for the environment in terms of heavy metal release (Boni *et al.*, 2004). If chlorine is used to whiten the paper this could be a potential source of dioxins and furans (Boni *et al.*, 2004), which should be monitored in sludge derived products to be applied to the environment.

The net production of greenhouse gases of slow-pyrolysis compared to business-as-usual management of paper sludges needs to be assessed on a case-by-case basis. However the outcome is likely to be positively influenced by the improved resource recovery of the sludge from landfill where a portion of the carbon would be released to the atmosphere as the potent greenhouse gas methane. The stabilisation of the carbon into the biochar and the flow-on benefits of biochar application to soil, as discussed in Greenhouse Gas Outcomes, all contribute to a significantly enhanced greenhouse gas outcome compared to the standard practice for managing paper sludges. It is unlikely, due to paper sludges being very wet, that any energy will remain for export after energy is utilised for internal drying. If however, significant external energy sources from fossil fuels are required to allow the thermal conversion process to progress with this very wet feedstock then any greenhouse gas advantages may be undermined. The energy efficiency of the specific slow-pyrolysis technology will need to be assessed through a complete life cycle assessment to ensure optimised environmental gains are realised in practice.

### **Municipal Organic Wastes**

The United Nations *2008 Revision of World Population Prospects* estimates the world population, which stood at 6.8 billion in 2009, is projected to reach 9 billion in 2050 (UN, 2009). Most of the additional people expected by 2050 will be concentrated in developing countries, whose population is projected to rise from 5.6 billion in 2009 to 7.9 billion in 2050. This high growth in the rate of urbanisation and development will drive significant increases in demand for energy production while generating ever-expanding volume of centralised organic waste in urban centres. Organic wastes typically from urban centres are from parks and gardens, food waste, and wastewater solids from sewage treatment plants. The increasing dissociation of this organic waste resource from farming production areas significantly challenges the ongoing sustainability of rural crop production that relies on the effective cycling of carbon and nutrients (Asomani-Boateng, 2007). Urban centres are also challenged with the lack of appropriate area for land filling wastes, with the transporting of wet, bulky and often odorous waste to landfills increasing in costs and social pressure.



**Figure 4: Processing of urban, source separated, green waste to reduce volume for land-filling.**

Slow-pyrolysis technology applied to municipal organic wastes may help in addressing these challenges experienced currently in urban centres that are expected to be exacerbated by the predicted growth in urban populations. The environmental and economic benefits of utilising urban waste water sludges in thermal conversion processes has been demonstrated in the literature (Poulsen and Hansen, 2003; Cartmell *et al.*, 2005). Slow-pyrolysis processing of organic wastes could provide not only a renewable source of electricity; it also fills in the missing link between soil carbon, nutrient cycling and urban food consumption through the production of biochar. The nutrients and carbon contained in the organic wastes are concentrated into a greatly reduced mass and volume of biochar that is therefore more cost effectively transported back to agricultural land.

The pyrolysis process effectively sterilises the wastes so that biosecurity risk (human health, animal disease risk, plant pathogen, plant propagule etc) is greatly diminished. It should be noted however that there is potential for contamination in waste streams and therefore an evaluation, monitoring and verification plan should be adopted to ensure the risk of applying contaminated biochar to land is mitigated (Downie *et al.*, in press).

**Benefits for Local Governments of urban centers:**

- Job creation;
- Renewable energy production;
- Increased resource recovery of waste organics;
- Decreased need for landfill;
- Value adding of wastes to marketable product;
- Decreased mass and volume of product – less to transport;
- Concentration of carbon and nutrients into biochar;
- Odor reduction;
- Improved biosecurity through pathogen destruction;
- Decreased greenhouse gases from landfill;
- Carbon offsets generated to contribute to achieving targets;
- Stabilization of carbon for sequestration;
- Enhanced energy security; and

The production of biochar also presents some opportunities unique to urban uses. For example, the incorporation of gardens into the landscape of urban building development provides many environmental and social benefits. The concept of retrofitting existing roof areas with gardens, known as “green roofs”, is becoming increasingly popular. One of the challenges of this practice is that existing roofs have load ratings that greatly limit the amount of heavy soil and water that they can support. Biochar has been demonstrated to have a low bulk density (Downie *et al.*, 2009) and good water holding capacity (Chan *et al.*, 2007) which potentially make it an ideal substrate for soil mixes which need to be light weight and retain moisture. Another advantage of biochar for this application is that it is recalcitrant and therefore breaks down slowly in the environment. This means that it will need to be replaced a lot less frequently than other low-bulk density substrates that are made from more labile carbon components. This becomes important when access to roof areas for bulk goods is difficult.

The use of slow-pyrolysis for producing thermal energy, in the form of high pressure hot water, from urban waste organics for district heating also presents a unique resource recovery opportunity. Local governments overseeing the delivery of both waste management and district heating services to the community are in position to implement such projects without the need for complicated counterparty agreements.

### **Intensive Agriculture**

The intensification of agriculture is resulting in large stocks of high nutrient waste accumulating in localized areas (Sims *et al.*, 2005). Industries include; cattle feedlots, dairy cattle on hard-stands, piggeries and poultry. This presents challenges of eutrophication, nutrient cycling, biosecurity and disposal. Waste materials including; poultry litter (manure and bedding), deep litter piggery bedding, and mechanically managed beef feedlot manures could be utilized in a slow-pyrolysis process to produce energy and a high nutrient biochar. It should be noted that very wet wastes such as dairy slurry, manures washed out with water, are not likely to be suitable for pyrolysis technology as the energy required to drive off moisture in the thermal process would require significant external energy sources. These materials could however be utilized in biological conversion processes such as anaerobic digestion to enhance resource recovery.

In some regions where intensive agriculture is practiced, the drivers for improved management of livestock wastes are compelling due to:

- nutrient saturation of surrounding land which prevents further land spreading;
- the bulky and wet nature of the material making it uneconomical to transport to broader markets;
- regulatory requirements for biosecurity, where manures are not allowed to be transported and/or used on food crops due to public health risk;
- expansion being limited by regulators due to lack of sustainable waste management; and
- social pressures to control and limit odors.



This risk is acutely managed in Europe where animal waste is routinely incinerated. However in many regions there is no viable alternative in use other than land spreading, as landfill and incineration are expensive or have legislative barriers due to emissions and odor concerns. Slow pyrolysis technology may offer the industry and regulators the opportunity to address this gap in the market and provide a viable means for mitigating public health risk, whilst providing effective recovery of this valuable resource.

Benefits of slow-pyrolysis for intensive livestock production:

- Regional development and employment opportunities;
- Distributed energy security, which is essential to regional industries who experience frequent brown-outs through lack of capacity, which adversely effects productivity;
- Renewable energy production;
- Diversifying farm revenues;
- Ability to demonstrate waste management plans to regulators who may then allow continued operation or expansion;
- Resource recovery of carbon and nutrients;
- Decreased mass and volume of product – less to transport;
- Odor reduction;
- Improved biosecurity through pathogen destruction;
- Stabilization of carbon for sequestration;
- Enhanced food security;
- Offsetting of greenhouse gas emissions.

Operators in this sector in developed countries already invest in large capital items of plant to optimize their processes. Slow-pyrolysis technology could be targeted at large beef feedlot operations or poultry producers, who manage enough waste to achieve the economies of scale required for a viable project. In many cases these operations are vertically integrated in that they also grow the grain for the livestock and have meat processing and packing facilities. Hence they have an internal requirement for the biochar and energy produced. Waste heat from the process could also contribute to space heating animal sheds in cooler climates, adsorption chillers in warmer climates, and for processing such as steam flaking of grain, which increases its digestibility for livestock.

The agricultural sector is a large greenhouse gas emitter, predominantly through livestock. The large emissions liability may be able to be offset partly through the integration of pyrolysis facilities into their operations. The greenhouse gas savings demonstrated from soils with biochar applied (Singh *et al.*, 2010b; van Zwieten *et al.*, 2010d) may be particularly relevant to soils which have been saturated with nutrient via the historic application of high rates of animal manures.

### **Biochar Product Qualities and Marketing**

Biochar characteristics are highly dependent on the feedstock from which they were made and the processing conditions under which they were made (Downie *et al.*, 2009). Biochar quality control will be critical in establishing a valuable and re-



liable market for the product. Consumers are likely to be sensitive to the following biochar attributes:

- Homogeneity (consistent, and repeatable);
- Visual Appeal (packaging, contamination, color);
- Odours;
- Handling (convenient, low risk, economical);
- Availability (quantities and seasonality);
- Measurable productivity benefits; and of course
- Price.

Standards for biochar products may be adopted to ensure that quality products are available on the market and that consumers are able to easily identify what they are purchasing (Glover, 2009).

As there are no commercial biochar production facilities established at the time of writing the ability to marketing significant quantities of the product has not yet been tested. Despite the demand for biochar building on the back of increasing levels of research being published, along with media attention about its verified benefits, the lack of supply has meant that no market has been demonstrated at any significant scale. Therefore the use of the product by consumers has been limited and hence their response to the products benefits and usability are unable to be gauged. If and when supply is established, according to standard market economics, the initial quantities of product are likely to attract a premium. Once the backlog of demand is exhausted, however, a more stable, commodity type market will be established.

The quantities and price points of the product required to satisfy this market are difficult to estimate. However there is a large range of target markets where biochar could be applied:

- Potting mixes and home garden landscaping,
- market gardens,
- public parks and gardens,
- playing fields,
- turf industry,
- horticulture and viticulture,
- hydroponics,
- cropping,
- intensive pasture,
- land remediation and mine site rehabilitation,
- planted forestry,
- urban landscaping,
- green roofs,
- industrial applications such as effluent clean-up.

Each of the potential markets identified has a different cost-benefit outcome from increased productivity. This will influence the price each primary producer or customer can afford to pay for the biochar product that provides the benefit. Therefore it is likely that markets for biochar will be initially developed for high value uses. The exception may be where government incentives such as C offsets may make biochar available for lower value applications, or where biochar production is subsidized by another revenue stream, such as electricity sales, and no

high value applications for the biochar product exist in close vicinity to the production facility.

### Biochar as a Soil Amendment

Biochar is attracting increasing scientific, political and industry attention for its potential benefits as a soil amendment. Issues such as food security, declining soil fertility, climate change adaptation and profitability are all drivers for implementing new technologies or new farming systems. Application of biochar to soil has been shown to have effects ranging from very positive, through to neutral and even negative impacts for crop production. It is therefore essential that the mechanisms for action of biochar in soil be understood before it is applied.

The application of biochar to soil can influence a wide range of soil constraints including low pH and high available Al (Van Zwieten *et al.*, 2010a), soil structure and nutrient availability (Chan *et al.*, 2007) bioavailability of organic (Yu *et al.*, 2009) and inorganic contaminants (Hua *et al.*, 2009), cation exchange capacity (CEC) and nutrient retention (Major *et al.*, 2009; Singh *et al.*, 2010a), and organic matter decline (Lehmann and Rondon, 2006). Biochars have a highly porous structure with surface areas sometimes exceeding 1000m<sup>2</sup>/g (Downie *et al.*, 2009). Like activated charcoal, they adsorb organics, nutrients and gases, and are likely to provide habitats for bacteria, actinomycetes and fungi (Thies and Rillig, 2009). Increases in water holding capacity following biochar application to soil have been well established (Pietikainen *et al.*, 2000; Busscher W. *et al.*, 2010), and this may influence crop production, soil microbial populations and population flux during wetting/ drying cycles.

Soil constraints where biochar may provide benefits to productivity include:

- Low pH and high Al availability;
- Low CEC and nutrient holding capacity;
- Low water holding capacity, poor infiltration;
- Poor soil aeration, root development;
- Hard setting soils;
- Residual herbicide or heavy metal phytotoxicity; and
- Presence of certain soil borne diseases.

In some cases, biochar application to soil may influence nutrient availability and nutrient use efficiency (Van Zwieten *et al.*, 2010d). The application of a low nutrient biochar derived from timber increased the retention of N in soil and uptake of N into crop biomass (Steiner *et al.*, 2008). Lehmann *et al.*, (2003) showed that biochar reduced leaching of NH<sub>4</sub><sup>+</sup>, maintaining it in the surface soil where it is available for plant uptake. Similarly, the application of charcoal derived from bamboo into a sludge composting system was shown to provide significant increases in N retention in the compost (Hua *et al.*, 2009). Increased fertility of soil resulting from biochar application is likely to increase crop vigor, and thus may enhance disease tolerance.

Biochar is also likely to influence a range of soil physical properties. For example, Chan *et al.*, 2007 and Busscher *et al* 2010 demonstrated significant declines in soil tensile strength following addition of biochar derived from green waste or pecan shells. These declines in soil tensile strength may allow for better crop root penetration (especially during dry periods), and will also reduce costs associated with soil preparation (such as tillage).

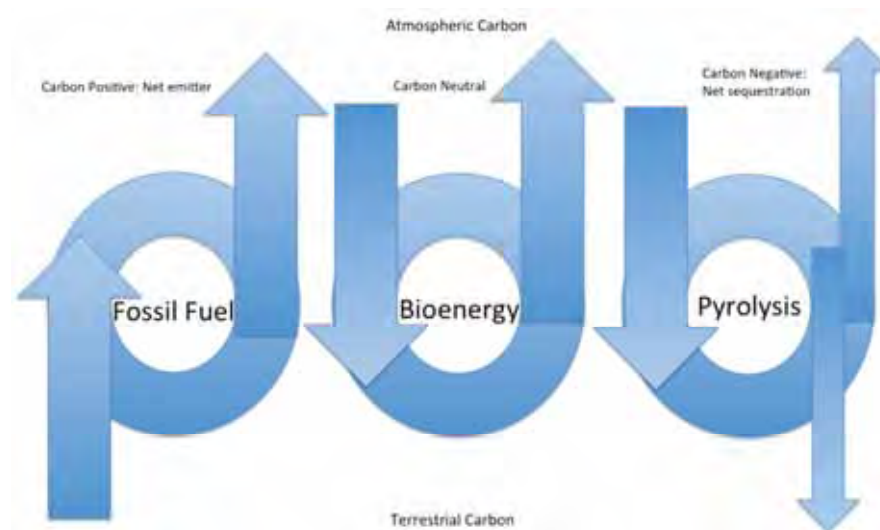
Biochar has been shown to increase biological N<sub>2</sub> fixation (BNF) of *Phaseolus vulgaris* (Rondon *et al.*, 2007), largely due to greater availability of plant micronutrients following biochar application. By increasing potential for BNF, and increasing N use efficiency, lower rates of synthetic N fertilizers may be acceptable for maintaining productivity. Synthetic N fertilizers have a significant C footprint, with over 4t CO<sub>2</sub> emission required per t N fertilizer produced (Wood and Cowie, 2004).

Although there is a paucity of published data on the effects of biochar on soil-borne pathogens, evidence is mounting that control of certain pathogens may be possible. The addition of biochar (0.32, 1.60 and 3.20 % (w/w)) to asparagus soils infested with *Fusarium* root rot pathogens increased asparagus plant weights and reduced *Fusarium* root rot disease (Elmer *et al.*, 2010). Further, Matsubara *et al* (2002) (cited in (Thies and Rillig, 2009)) have shown that biochar inoculated with mycorrhizal fungi are effective in reducing *Fusarium* root rot disease in asparagus. A study of bacterial wilt suppression in tomatoes found that biochar derived from municipal organic waste reduced the incidence of disease in *Ralstonia solanacearum* infested soil (Nerome *et al.*, 2005). The mechanism of disease suppression was attributed to the presence of calcium compounds, as well as improvements in the physical, chemical and biological characteristics of the soil. Likewise, Ogawa (2009) describes the use of biochars and biochar amended composts in reducing bacterial and fungal soil borne diseases.

The economic value of biochar as an agricultural commodity is largely untested. Although the benefit of biochar in many systems has been described to increase crop yield, the cost-benefit ratio of applying the technology has not been completed. Van Zwieten *et al.*, (2010b) discusses several mechanisms for valuing biochar as a commodity. Simply, it could be valued based on its nutrient or liming value, replacing commodities such as fertilizer or lime, alternatively, it could be valued according to benefits to productivity or projected productivity. A recent study (Blackwell *et al.*, 2010) using biochar derived from *Eucalyptus* banded at a low rate of 1t/ha was shown to have a breakeven valuation of around Aus\$170 per tonne of biochar in broadacre wheat, assuming yield benefits for 12 years. In the cost benefit outcome described by Van Zwieten *et al* (2010b), biochar derived from poultry litter waste was valued at \$300 per tonne, based on performance enhancement of 3 crops following the single application of biochar. Clearly, the economic value of biochar will depend on its properties, but will also be driven by supply and demand, inherent value of the target enterprise, and demonstrated benefits.

## Greenhouse Gas Outcomes

Slow pyrolysis technology has the potential to deliver renewable energy, and biochar products whilst exhibiting a carbon negative greenhouse gas balance (Mathews, 2007; Gaunt and Cowie, 2009). The carbon sequestration achieved by the high carbon biochar product results in a net removal of carbon dioxide from the atmosphere. If organics are not used as fuel they decompose relatively quickly in the natural environment, releasing the carbon as CO<sub>2</sub> back to the atmosphere. Production of biochar from these organics removes this material from the short-term carbon cycle, into the long-term carbon cycle. Biochar is far more stable in the environment when compared to the original organics and prevents the release of the carbon in its structures.



**Figure 5: Comparison of carbon balances: fossil fuel, bioenergy, and slow-pyrolysis for bioenergy and biochar.**

When compared to typical bioenergy GHG balances, where all of the carbon in the fuel source (biomass organics) is released through the energy cycle as greenhouse gases, in pyrolysis a portion of the carbon is stabilised as the biochar product. The co-production of biochar along with renewable energy results in a significant net removal of GHGs from the atmosphere via this pathway. It should be noted however that not all biochar technologies are necessarily carbon negative as carbon leakage and poor combustion systems can have a significant negative impact on the carbon lifecycle analysis (Downie *et al.*, in press). It is essential that modelling, monitoring and auditing of the system is carried out to verify carbon offsets generated.

Key pathways to GHG mitigation via production and use of biochar include:

- Renewable energy generation (displacing fossil fuel);
- Bio-sequestration (stabilizing organic carbon as biochar and storing it in terrestrial sinks);
- Stabilization of labile soil organic carbon onto biochar surfaces;
- Reduced agriculture emissions (from reduced; nitrous oxide from soil, fuel use, fertiliser use, and improved water use efficiency);
- Decreased emissions from waste biomass (including avoided methane generation from landfills and compost production); and
- Increased agricultural productivity (increased biomass yields taking up more atmospheric carbon, less land area required for food production).

The sequestration of carbon via biochar and mitigation of GHGs are offset by various steps along the biochar production lifecycle. These aspects might include:

- Use of fossil fuels for harvesting, transporting, and processing;
- Fugitive emission from feedstock degradation being stored or pre-processed;
- Emissions from the processing plant, such as uncombusted syngas;
- Land use change, for example biomass requirements provide a market for more purpose grown organics which may result in deforestation (Cherubini *et al.*, 2009).

Technology considerations that should be optimised to ensure carbon negative balances are achieved:

- Energy efficiency of processes;
- Emissions control, including utilisation of syngas;
- Limited distances for feedstock collection and product distribution;
- Alternate higher uses of organics is fully considered, e.g. waste organics are sourced over purpose grown feedstocks.

The contribution biochar can make in maintaining soils for agricultural production during climate variability may prove a vital tool for adaptation.

## Conclusions and Future Outlook

Well engineered, slow-pyrolysis technology, optimized for the production of bioenergy and biochar from sustainable feedstocks, could deliver significant environmental and economical advantages to industry. The increasing focus by soil and plant scientists on the utilization of biochar in production systems is leading to a body of evidence surround how biochar products can beneficially be used as a soil amendment that will continue to support a justification for a marketable price for the product. Several companies, such as Pacific Pyrolysis in Australia, are working towards commercializing new technology for the production of biochar along with bioenergy from low-grade organics. Establishing one or more commercial-scale production facilities dedicated to demonstrating the technical, environmental and economic outcomes of the business will be an essential next step for the emerging industry.

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## Chapter 6

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### *Approaches to Greenhouse Gas Accounting Methods for Biomass Carbon*

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# Approaches to Greenhouse Gas Accounting Methods for Biomass Carbon

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## Abstract

This investigation examines different approaches for the GHG flux accounting of activities that influence biomass C cycling. Alternative approaches are examined that a) account for all emissions including biogenic CO<sub>2</sub> cycling – the biogenic method; b) account for the quantity of C that is moved to and maintained in the non-atmospheric pool – the stock method; and c) assume that the net balance of C taken up by biomass is neutral over the short-term C cycle and hence there is no requirement to include this C in the calculation – the simplified method. This investigation demonstrates the inaccuracies in both emissions forecasting and abatement calculations that result from the use of the simplified method, which is commonly accepted for use in various methods guidelines. It has been found that the stock method is the most accurate and appropriate approach for use in calculating GHG inventories, however shortcomings of this approach emerge when applied to abatement projects, as it does not account for the increase in biogenic CO<sub>2</sub> emissions that are generated when non-CO<sub>2</sub> GHG emissions in the business-as-usual case are offset. Therefore the biogenic method or a modified version of the stock method should be used to accurately estimate GHG emissions abatement achieved by a project. This investigation uses both the derivation of methodology equations from first principles according to each approach and worked examples to explore the fundamental differences in the alternative approaches examined. Worked examples are developed for three project scenarios including; landfill, combustion and slow-pyrolysis (biochar) of biomass.

**Keywords:** biomass, greenhouse gases, carbon sequestration, carbon accounting methods, landfill, combustion, biochar.

## Highlights:

- Different approaches can be taken to account for the GHG emissions from biomass
- Simplification of GHG accounting methods is useful however can lead to inaccuracies
- Approaches used currently are often inadequate for practices that store carbon
- Accounting methods for emissions forecasting can be inadequate for abatement accounting



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46 **Definition of Terms**

47  $E_{biogenic}$  = emissions forecast of GHG to the atmosphere via the biogenic method [kg CO<sub>2</sub>-  
48 e/kg(dry) organics].

49  $E_{stock}$  = emissions forecast of GHG to the atmosphere via the stock method [kg CO<sub>2</sub>-e/kg(dry)  
50 organics].

51  $E_{simplified}$  = emissions forecast of GHG to the atmosphere via the simplified method [kg CO<sub>2</sub>-  
52 e/kg(dry) organics].

53  $E_{i,j,k}$  = emissions forecast of GHGs i,j,k released to atmosphere from the portion of organics  
54 decomposed to gas [kg CO<sub>2</sub>-e/kg(dry) organics].

55  $i = CO_2$

56  $j = CH_4$

57  $k = NO_2$

58  $m$  = mass of organic material at the start of the process [kg (dry)].

59  $occ$  = organic carbon content of organic material at the start of the process [kg/kg].

60  $d$  = mass fraction of  $occ$  that decomposes to gas as part of the short term carbon cycle  
61 [kg/kg]. [kg/kg].

62  $a_{i,j,k}$  = mass fraction of GHG component i,j,k in emissions released to atmosphere from the  
63 decomposition of organic material [kg/kg].

64  $M_{i,j,k}$  = molar mass of GHG component i,j,k [kg/kmol].

65  $M_c$  = molar mass of carbon = 12 [kg/kmol].

66  $WP_{i,j,k}$  = Greenhouse warming potential of GHG component i,j,k.

67  $C_i$  = C stabilised by moving carbon from the short to the long-term carbon cycle [kg CO<sub>2</sub>-  
68 e/kg(dry) organics].

69  $s$  = mass fraction of  $occ$  that is stabilised from the short to the long term carbon [kg/kg].

70  $A_{method}$  = emissions abatement calculated using a particular approaches method (biogenic,  
71 stock, simplified) [kg CO<sub>2</sub>-e/kg(dry) organics].

72  $E_{BAU}$  = emissions forecast for the business-as-usual activity [kg CO<sub>2</sub>-e/kg(dry) organics].

73  $E_{project}$  = emissions forecast for the project activity [kg CO<sub>2</sub>-e/kg(dry) organics].

74  $\delta_{a/b}$  = absolute difference in emissions forecast between approach methods a and b [kg CO<sub>2</sub>-  
75 e/kg(dry) organics].

76  $E_{a,b}$  = emissions forecast calculated using approach method a and b [kg CO<sub>2</sub>-e/kg(dry)  
77 organics].

78  $\Delta_{a/b}$  = difference in emissions abatement calculated between approach methods a and b  
79 [kg CO<sub>2</sub>-e/kg(dry) organics].

80  $A_{a,b}$  = absolute emissions abatement calculated using approach method a and b [kg CO<sub>2</sub>-  
81 e/kg(dry) organics].

82  $BAU$  = Business-as-usual emission forecast.

83  $Project$  = Project emission forecast.

84  $r_{j,k}$  = mass fraction of GHG component j,k in landfill gas converted to carbon dioxide by  
85 landfill management [kg/kg].

86  $f_{j,k}$  = mass fraction of GHG component  $j,k$  in landfill gas produced by landfill [kg/kg].  
 87  $m_W$  = mass of organic waste [kg (dry)].  
 88  $\gamma$  = biochar yield [kg biochar/kg biomass] (dry basis).  
 89  $A_{stock(modified)}$  = emissions abatement forecast of GHG to the atmosphere via the stock  
 90 method amended for accurate representation of abatement projects [kg CO<sub>2</sub>-e/kg(dry)  
 91 organics].  
 92  $B_i$  = emissions forecast of CO<sub>2</sub>-e of non-GHG's in the BAU that have been abated in the  
 93 project and released as CO<sub>2</sub> [kg CO<sub>2</sub>-e/kg(dry) organics].

## 94 1 Introduction

### 95 1.1 Inventories and Abatement

96 Internationally, the threat of climate change due to elevated levels of greenhouse gases  
 97 (GHG) in the atmosphere has led to a desire to both understand the flux of GHG between  
 98 carbon pools and the abatement of anthropogenic GHG emissions achieved by changing  
 99 practices.

100 A GHG inventory, that sums emissions and removals can be compiled on a range of  
 101 scales, from a household, project, organisation, to a country. Countries that are parties to  
 102 the United Nations Framework Convention on Climate Change (UNFCCC) report  
 103 annually on their GHG inventories. Increasingly corporations are including GHG  
 104 inventories of their operations in annual reports and are required by regulation to  
 105 report their inventory to governments.

106 GHG flux estimation methodologies are applied to calculate the net emissions of  
 107 activities so that they can be appropriately incentivised or discouraged. To determine  
 108 the mitigation value of abatement activities the emissions are compared with the  
 109 "business-as-usual" baseline. Calculations according to agreed methodologies are used  
 110 under voluntary or compliance emissions trading schemes, where abatement projects or  
 111 activities need to be accredited, measured, monitored and verified to determine the  
 112 number of offset credits generated.

### 113 1.2 Biomass Carbon Cycling

114 The short-term carbon (C) cycle includes the uptake of CO<sub>2</sub> from the atmosphere by  
 115 photosynthetic organisms that convert it to organic C molecules in solid state. The  
 116 growth, death and degradation of these C reservoirs, or the cycling of atmospheric C  
 117 being taken up and re-released via biomass, occurs in a time scale that is highly  
 118 dependent on the life cycle and habit of the plant, ranging from days to centuries. This  
 119 is, however, a short-term cycle relative to the formation of fossil C structures such as  
 120 coal and oil that takes millennia.

121 Pathways exist for stabilising biomass C in long-term terrestrial reservoirs via directing  
 122 short-term cycling biomass C into a longer-term C pool, such as occurs for coal and oil.  
 123 One such pathway is through the formation of charcoal [1-4]. The highly aromatic  
 124 chemical structure of the carbon in charcoal means that it is dense and recalcitrant to  
 125 environmental degradation, similar to fossil coal. The growing of biomass and  
 126 converting it to charcoal, or biochar, has been recognised as a stable sink for  
 127 atmospheric C [1, 4].

Another potential pathway for stabilising biomass C is the burial of wood, to protect it from decomposition [5], this may be achieved in a landfill under some environmental conditions.

There is extensive literature covering the GHG accounting methods for the majority of emission sources required to account for projects that seek to achieve GHG abatement via the management and use of biomass. However, there is insufficient guidance available, both in the peer-reviewed scientific literature and in accredited methodologies that are adopted by various schemes, for project proponents wishing to account for the reduction of global warming impacts achieved via stabilising biogenic C from the short to longer-term C pools. The absence of agreed methods for accounting for this 'negative' emission source can result in at best; the inconsistent use of methods between different GHG accounts, and at worst; the omission of these sometimes significant emission sources causing an organisation or countries GHG accounts to be unnecessarily inaccurate.

### 1.3 Limitations of Existing Approaches to Biomass Carbon Accounting

Approaches and methods for the GHG accounting of the C stored in wood products have been the focus of several studies and hence they have been incorporated into some inventories [6]. For the first commitment period of the Kyoto Protocol (2008–2012), C stock changes of harvested wood products (HWP) were ignored, and forest harvesting was treated as an instantaneous emission of carbon dioxide [7]. However, it is expected that in the next commitment period of the UNFCCC, the C stock changes resulting from HWP may be taken into account in the National GHG Inventories [7].

Current inventory reporting and accounting frameworks recognise the benefits of sequestering C in forest biomass, but do not typically recognise the benefit of delaying emissions through transferring biomass C from the rapidly cycling pool to slow-cycling forms. Methods to account for delayed decomposition when biomass is used for biochar production or preserved in landfill for example are yet to be incorporated into IPCC guidelines. It should be noted that these pathways do not result in the removal of GHG directly from the atmosphere, but lateral movement in the biomass pool of C from a short-term reservoir to a long-term reservoir, hence delaying biogenic C emissions and decreases atmospheric GHG concentrations.

Activities that impact on the cycling of biomass C, such as the generation of energy from biomass, can be carbon neutral over the short-term cycle, as the C emitted from the biomass pool is balanced by the uptake of C by other plants in the pool. This is why, for example, under the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, CO<sub>2</sub> released from the combustion of biomass fuels is excluded from the calculation of net emissions.

Methodologies that estimate the amount of biomass C in landfills released as the potent GHG methane are widely in use. Methane is generated by the decay of biomass in the landfill and reflects waste disposal activity over many decades. The quantity of methane generated from solid waste disposal is typically estimated using a C mass balance approach, with increasingly sophisticated decay models applied [8].

For the same reasons that CO<sub>2</sub> released from using biomass as fuels is excluded from national inventory reports, typically no term is included in equations for calculating landfill GHG emission for biomass C either released (as CO<sub>2</sub>) or stored [9, 10].

GHG accounting of biochar production systems is a relatively new field in the literature. For the purpose of investigating the abatement achieved by biochar production systems,

176 typically a mass balance approach including a term for the removal of C that is  
177 subsequently stabilised as biochar has been used [11-13]. Incorporation of methods for  
178 biochar GHG balance accounting into inventory or offsetting mechanisms is yet to be  
179 seen.

## 180 1.4 Alternative Approaches Investigated

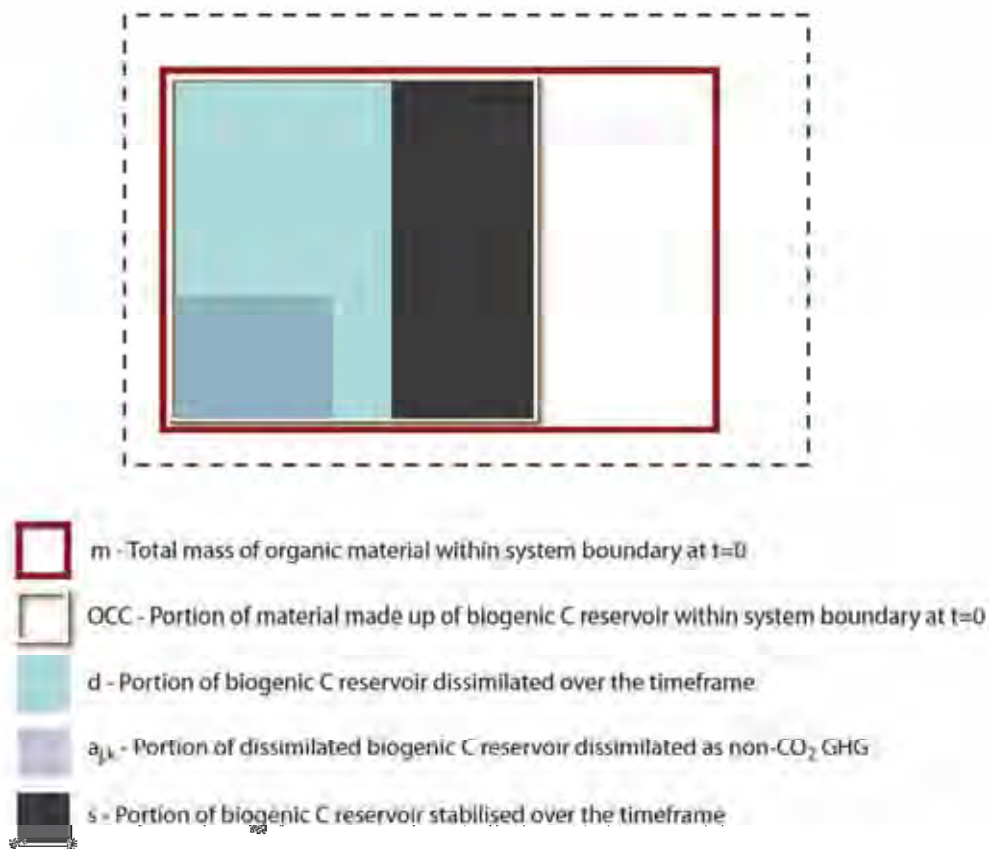
181 Different approaches to GHG accounting result in differing degrees of simplification of  
182 the GHG fluxes considered in the system to aid in the task of measurement, monitoring  
183 and verification. To examine the implications of simplifying assumptions, and to  
184 determine an appropriate level of simplification for different purposes, this paper  
185 assesses three alternative approaches to accounting for emissions in biomass  
186 management: (1) the biogenic method, that includes all C fluxes including biogenic CO<sub>2</sub>  
187 emissions, even though they may be neutral over the time-frame; (2) the stock method,  
188 that recognises biomass C that is moved to a long-term C cycle but not releases and  
189 removals of biogenic C; and (3) the simplified method, which assumes that the net  
190 biogenic CO<sub>2</sub> flux is neutral over the time-frame and hence does not need to be included  
191 in the calculation. The simplified method being the approach commonly found in  
192 accredited methodologies applied by existing schemes.

193 The purpose of this investigation is to examine the alternative approaches to calculating  
194 the net GHG emissions from processes that manage and use biomass along with the  
195 mathematical representations, or methods, of each approach. Three project scenarios  
196 are developed involving biomass C cycling to examine how the equations for each  
197 approach are applied. The applicability and accuracy of each of these approaches is then  
198 discussed and recommendations are made as to the most appropriate approach for both  
199 inventory and abatement activity accounting.

## 200 2 Investigation Methods

### 201 2.1 Conceptual framework

202 The conceptual framework used for estimating emissions and removals of GHG for the  
203 purpose of this investigation has been limited to a system boundary around only the  
204 processes that result in C emissions from a known starting mass of biomass C, as shown  
205 in Figure 1. Indirect emissions sources, such as use of fossil fuels to process the biomass  
206 have been excluded to simplify the equations. It should be noted that this is an  
207 examination of only one small aspect of the project lifecycle and a more comprehensive  
208 GHG lifecycle assessment must include all emissions sources. Care has been taken to  
209 ensure that in calculating the abatement achieved, the base case and the project case are  
210 comparable, that is, they deliver the same services.



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**Figure 1. System boundary**

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The investigation has been limited to within a single inventory and does not include approaches for accounting for C stocks that move laterally out of the system boundary [6, 14-17].

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A mass balance method based on the *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories* [18] and the *Good Practice Guidance and Uncertainty Management in Nation Greenhouse Gas Inventories* [19] 'tier 1' method has been used to calculate emissions of GHG. The *2006 IPCC Guidelines for National Greenhouse Gas Inventories* [8] strongly discourage the use of the mass balance method and provide a Tier 1 version of the first-order decay (FOD) method instead. It is acknowledged that the FOD method used in the IPCC 2006 Guidelines produces a time-dependent profile that better matches the actual pattern of emissions over time; however the mass balance approach is sufficient for exploring the differences in methods investigated by this paper. Decay models should be applied to the equations developed for accounting over a range of timeframes, however this is beyond the scope of this investigation.

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For the purpose of this investigation, it is assumed that the biomass C is already accounted for as a C pool in the inventory and hence no C uptake term had been included.

## 2.2 Proposed GHG Emissions forecasting calculation approaches

The first emissions forecasting approach accounts for all emissions fluxes to and from the atmosphere from the system boundary, including the biogenic CO<sub>2</sub> emissions in the short-term carbon cycle. This approach, expressed as Eq. 1 and shown graphically in Figure 2, is referred to in this investigation as the biogenic method.

### Eq. 1: Biogenic Method

$$E_{biogenic} = E_i + E_{j,k}$$

$$= \underbrace{\left[ m \times occ \times d \times a_i \times \frac{M_i}{M_C} \times WP_i \right]}_{CO_2\_GHGs\_from\_organic\_decomposition} + \underbrace{\left[ m \times occ \times d \times \sum_{j,k} \left( a_{j,k} \times \frac{M_{j,k}}{M_C} \times WP_{j,k} \right) \right]}_{non\_CO_2\_GHGs\_from\_organic\_decomposition}$$

and where by the conservation of mass principle,

### Eq. 1.a:

$$a_i = 1 - \sum_{j,k} (a_{j,k})$$

must always be true for any given gas composition.

The second approach accounts for the net change in atmospheric GHG levels by directly calculating the quantity of C that has been moved from the short-term carbon cycle into the long-term carbon cycle, this is, into a long-lived reservoir. This approach has been used by some biochar GHG balance assessments in the literature [11-13]. This approach, expressed as Eq. 2 and shown graphically in Figure 2, will be referred to in this investigation as the stock method. This approach gives a credit for delayed emissions, calculated as the proportion of C that is retained in the long-lived pool. It uses a C stock approach for the pool and does not include the calculation of biogenic CO<sub>2</sub> emissions as they are assumed to be neutral over the timeframe.

### Eq. 2: Stock Method

$$E_{stock} = E_{j,k} - C_i$$

$$= \underbrace{\left[ m \times occ \times d \times \sum_{j,k} \left( a_{j,k} \times \frac{M_{j,k}}{M_C} \times WP_{j,k} \right) \right]}_{non\_CO_2\_GHGs\_from\_organic\_decomposition} - \underbrace{\left[ m \times occ \times s \times \frac{M_i}{M_C} \times WP_i \right]}_{C\_stabilised}$$

and where by the conservation of mass principle,

### Eq 2.a:

$$1 = d + s$$

must always be true for any given conversion process.

A comparison with current IPCC methods that are applied routinely to calculate emissions inventories on a project scale, for example to calculate the liability of a landfill operator, have been included in this investigation. Adoption of these equations can be seen in various national guidelines, including, for example, the Australian National Carbon Offset Standard methods for biomass in landfill [20] where no term for the



263 biogenic CO<sub>2</sub> released is included in the equations as it is assumed to be neutral over the  
 264 timeframe due to the short-term biomass C cycle.

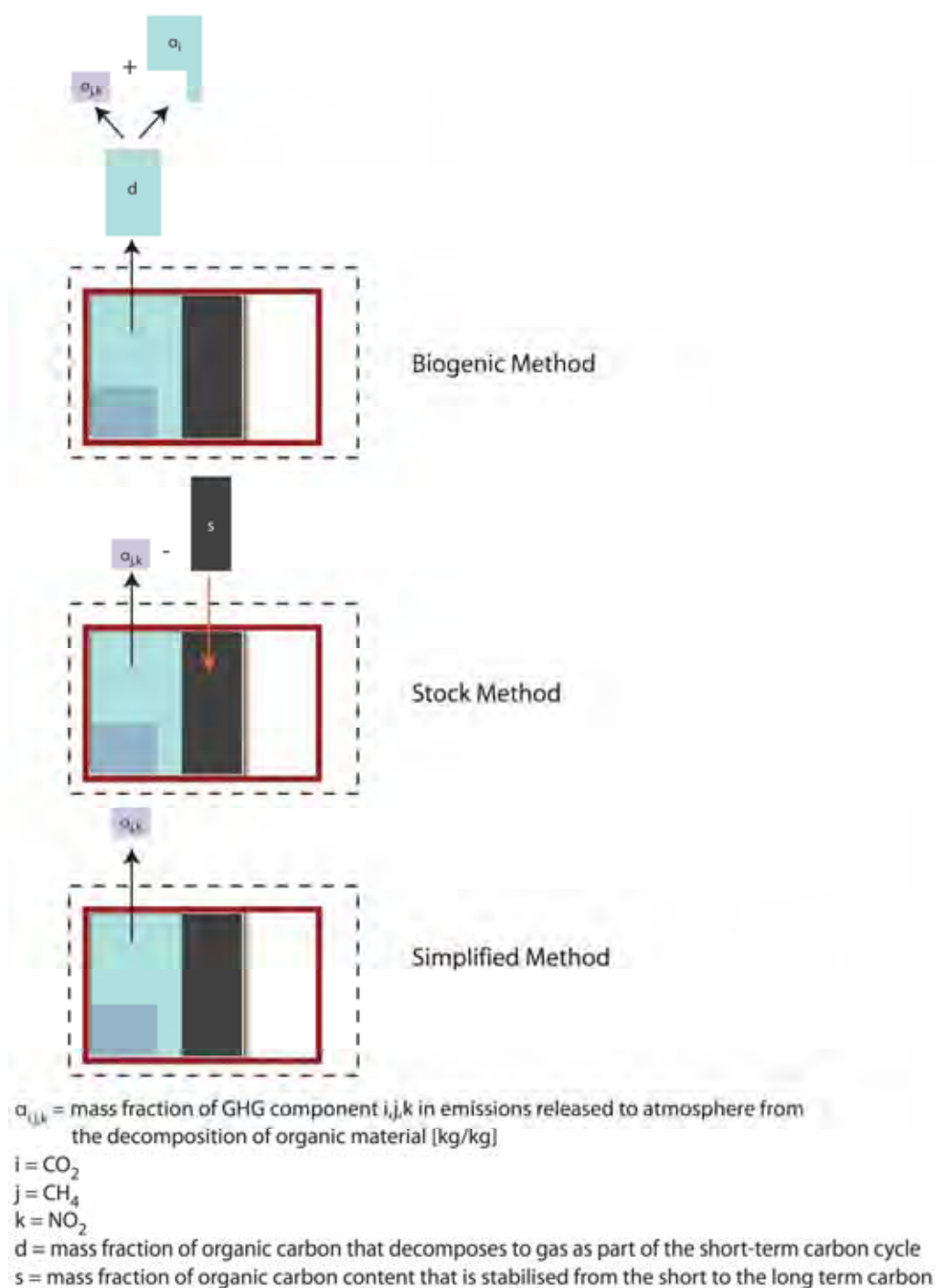
265 This approach, expressed as Eq. 3 and shown graphically in Figure 2, will be referred to  
 266 in this investigation as the simplified method.

267 **Eq. 3: Simplified Method**

$$E_{simplified} = E_{j,k}$$

$$= \left[ \underbrace{m \times occ \times d \times \sum_{j,k} \left( a_{j,k} \times \frac{M_{j,k}}{M_C} \times WP_{j,k} \right)}_{non\_CO_2\_GHGs\_from\_organic\_decomposition} \right]$$

268

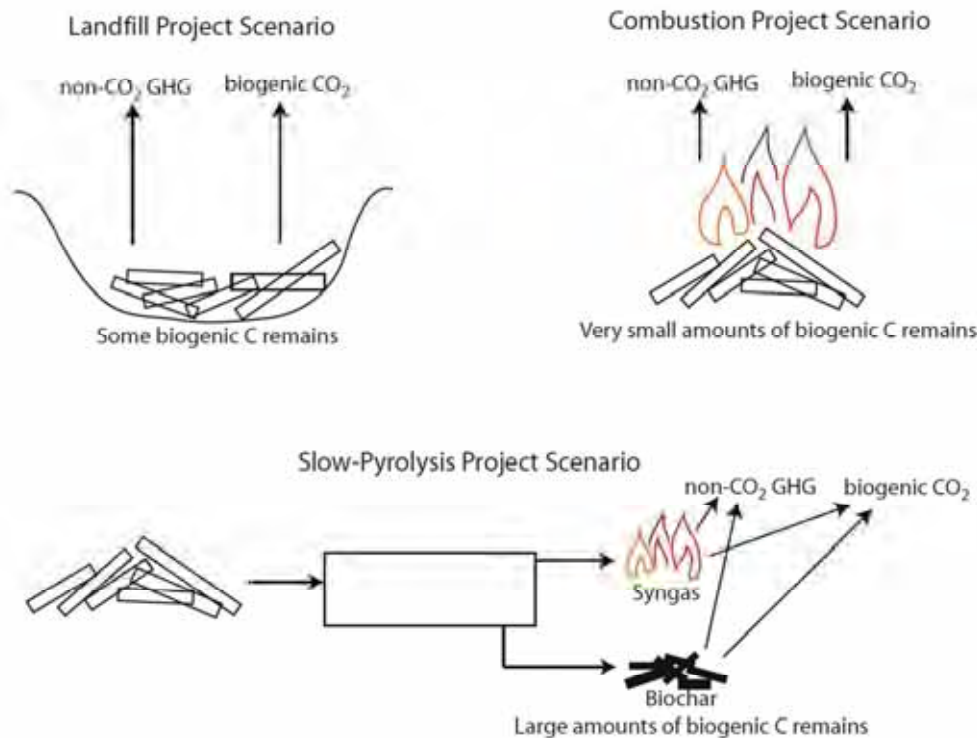


**Figure 2. Pictorial representation of the three GHG accounting approaches investigated**

### 2.3 Project Scenarios

The three approaches under consideration have been applied to three scenarios for managing waste organics, such as wheat straw, animal manures or forestry residue. The waste organics are assumed to be either landfilled, combusted, or pyrolysed via a slow-

pyrolysis process for biochar production. A pictorial representation of the project scenarios is provided in Figure 3.



277

278 **Figure 3. Representation of the project scenarios used to examine the atmospheric fluxes**  
 279 **of GHG from biomass. a) Landfill; b) combustion; and c) slow-pyrolysis (biochar).**

## 280 2.4 GHG Emissions Inventory and Abatement Calculations

281 To assess the proposed GHG accounting approaches, a method has been developed for  
 282 each and this has been used to calculate the GHG emissions forecast for each project  
 283 scenario. The emissions forecast calculation estimates the values to be reported in an  
 284 inventory.

285

286 The GHG abatement achieved by implementing a project is calculated by comparing the  
 287 project emissions with a reference, or business-as-usual (BAU), emission forecast (Eq.  
 288 4).

### 289 Eq. 4: GHG Emissions Abatement

290 
$$A_{method} = E_{BAU} - E_{Project}$$

291 Several cases, using the proposed project scenarios, have been developed to examine the  
 292 abatement achieved by the different GHG accounting approaches. The abatement cases  
 293 are outlined in Table 2. For example, in Case 1, waste organics are diverted from a BAU  
 294 practice of landfill to a slow-pyrolysis project. A key to the numbering of equations used  
 295 in provide in Table 2.

296 **Table 1: Scenarios used to illustrate differences in GHG accounting approach methods for**  
 297 **abatement projects.**

	Business-as-usual	Project
Case 1	Waste organics to landfill	Waste organics to slow-pyrolysis
Case 2	Waste organics combusted	Waste organics to slow-pyrolysis
Case 3	Waste organics to landfill	Waste organics combusted

298 **Table 2: Key to Equation Numbering**

	Biogenic Method 1	Stock Method 2	Simplified Method 3
Landfill - 0.1	1.1	2.1	3.1
Slow-pyrolysis – 0.2	1.2	2.2	3.2
Combustion – 0.3	1.3	2.3	3.3

299

## 300 2.5 Comparing GHG Accounting Approaches

301 The GHG emissions levels estimated for each project scenario and abatement case are  
 302 different for each approach due to the different elements that are included in the  
 303 method calculations (Eq. 1 - Eq. 3). The emissions forecast and abatement calculated via  
 304 each of the approaches has been compared to determine a) what the fundamental  
 305 differences in the equations are and b) which approach gives the most accurate method  
 306 for prediction of both the emissions forecast and subsequent abatement achieved when  
 307 comparing different project scenarios. Eq. 5 has been applied to compare emissions  
 308 forecasts and Eq. 6 has been applied to compare emissions abatement.

309 **Eq. 5: Comparison of emissions forecast by different accounting approaches**

$$310 \delta_{a/b} = (E_a - E_b)$$

311 **Eq. 6: Comparison of emissions abatement by different accounting approaches**

$$312 \Delta_{a/b} = (A_a - A_b)$$

$$313 = \left[ \underbrace{(E_a)_{BAU} - (E_a)_{project}}_{abatement\_by\_method\_a} \right] - \left[ \underbrace{(E_b)_{BAU} - (E_b)_{project}}_{abatement\_by\_method\_b} \right]$$

## 314 2.6 Variables and Assumptions

315 A numerical comparison of the three project scenarios and abatement cases listed in  
 316 Table 1 has been made using worked examples.

317 The basic assumptions used for each variable in the worked examples are shown below  
 318 in Table 3. As was done by Pingoud and Wagner [10], our objective is to demonstrate  
 319 which of the approaches provides a method that is mathematically a more exact and  
 320 elegant solution using the provided assumptions, rather than to question the  
 321 assumptions themselves, which are rough estimates of indicative values only.

322 **Table 3: Definition of Terms and Assumptions applied in these examples based on waste**  
323 **organics**

Term	Qty	Unit	Description
$m_W$	1	[kg (dry)]	Mass of organic waste material
$occ_W$	0.50	[kg/kg (dry)]	Organic carbon content of waste organics
$d_W$	0.50	[kg/kg]	Mass fraction of $occ_W$ that dissimilates in landfill as part of the short term carbon cycle (< 100 years)
$s_W$	0.50	[kg/kg]	Mass fraction of $occ_W$ stabilised in landfill as part of the long term carbon cycle (> 100 years)
$f_j$	0.55	[kg/kg]	Mass fraction of methane in landfill gas produced by the landfill
$f_k$	0.00	[kg/kg]	Mass fraction of other non-CO <sub>2</sub> GHGs in landfill gas produced by the landfill
$r_j$	0.10	[kg/kg]	Mass fraction of methane in landfill gas converted to carbon dioxide by landfill management
$u_i$	0.999	[kg/kg]	Mass fraction of CO <sub>2</sub> in syngas emissions released to atmosphere
$u_j$	0.001	[kg/kg]	Mass fraction of methane in syngas emissions released to atmosphere
$u_k$	0.000	[kg/kg]	Mass fraction of other non-CO <sub>2</sub> GHGs in syngas emissions released to atmosphere
$\gamma_{BC}$	0.38	[kg/kg]	Biochar yield (dry basis)
$occ_{BC}$	0.80	[kg C/kg]	Biochar organic carbon content
$d_{BC}$	0.09	[kg/kg]	Mass fraction of $occ_{BC}$ dissimilated from biochar in <100 years
$s_{BC}$	0.91	[kg C/kg C]	Mass fraction of biochar $occ_{BC}$ stabilised from the short to long term carbon cycle (remaining after 100 years)
$y_i$	0.997	[kg/kg]	Mass fraction of CO <sub>2</sub> in biochar decomposition gas released to atmosphere
$y_j$	0.003	[kg/kg]	Mass fraction of methane in biochar decomposition gas released to atmosphere
$y_k$	0.000	[kg/kg]	Mass fraction of other non-CO <sub>2</sub> GHGs in biochar decomposition gas released to atmosphere
$d_C$	0.995	[kg/kg]	Mass fraction of $occ_W$ that is thermally decomposed to gas (combustion emissions) during combustion
$s_C$	0.005	[kg/kg]	Mass fraction of $occ_W$ stabilised in combustion residue from the short to the long term carbon cycle (remaining after 100 years)
$v_i$	0.999	[kg/kg]	Mass fraction of CO <sub>2</sub> in combustion emissions released to atmosphere
$v_j$	0.001	[kg/kg]	Mass fraction of methane in combustion emissions released to atmosphere
$v_k$	0.000	[kg/kg]	Mass fraction of other non-CO <sub>2</sub> GHGs in combustion emissions released to atmosphere
$M_i$	44	[kg/kmol]	Molecular mass of carbon dioxide
$M_c$	12	[kg/kmol]	Molecular mass of carbon
$M_j$	16	[kg/kmol]	Molecular mass of methane
$WP_i$	1	-	Global warming potential of carbon dioxide
$WP_j$	21	-	Global warming potential of methane

324

325 It should be noted that the term  $a_{j,k}$  used in Eq 1, 2 and 3, has been substituted for  $z_{j,k}$  for  
326 landfill gases,  $u_{j,k}$  for syngas,  $y_{j,k}$  for biochar, and  $v_{j,k}$  for the combustion scenario. It  
327 should be noted that the values assumed for  $u_{j,k}$  and  $v_{j,k}$  have been exaggerated in order to  
328 demonstrate the differences between the calculation methods for each approach; typical  
329 values are likely to be much lower, making these emission sources immaterial to the  
330 overall emissions forecast.

### 3 Results

The equations constituting the methods developed for each of the approaches for each of the project scenarios have been presented below. A summary of the results are presented in the Tables below and a full description of the worked examples is presented in the supplementary information.

#### 3.1 Biogenic Carbon Method

##### 3.1.1 Landfill Emissions

The GHG emission forecast for landfilling of organic waste using the biogenic method can be calculated by applying Eq. 1 as follows:

**Eq 1.1. a: Landfill GHG emissions forecast by the biogenic method**

$$E_{biogenic}(landfill) = \underbrace{\left[ m_W \times occ_W \times d_W \times z_i \times \frac{M_i}{M_C} \times WP_i \right]}_{CO_2\_from\_landfill} + \underbrace{\left[ m_W \times occ_W \times d_W \times \sum_{j,k} \left( z_j \times \frac{M_j}{M_C} \times WP_j \right) \right]}_{non\_CO_2\_GHGs\_from\_landfill}$$

$z_{i,j,k}$  in Eq 1.1. a can be calculated by substitution of the followings terms that differentiate between GHG production in landfill, and the subsequent release to atmosphere of each compound, which may be reduced by landfill management practices, such as oxidation of methane to  $CO_2$  in the landfill cap.

**Eq 1.1.b: Substitution of terms to include landfill management practices**

$$z_{j,k} = f_{j,k} \times (1 - r_{j,k})$$

and,

$$z_i = (1 - f_{j,k}) + f_{j,k} \times r_{j,k}$$

##### 3.1.2 Slow-pyrolysis Emissions

The GHG emission forecast for a slow-pyrolysis plant using the biogenic method can be calculated by applying Eq. 1 as follows:

**Eq 1.2. a: Slow-pyrolysis GHG emissions forecast by the biogenic method**

$$E_{biogenic}(pyrolysis) = \underbrace{\left[ m_S \times occ_S \times u_i \times \frac{M_i}{M_C} \times WP_i \right]}_{CO_2\_from\_syngas} + \underbrace{\left[ m_S \times occ_S \times \sum_{j,k} \left( u_j \times \frac{M_j}{M_C} \times WP_j \right) \right]}_{non\_CO_2\_GHGs\_from\_syngas} + \underbrace{\left[ m_{BC} \times occ_{BC} \times d_{BC} \times y_i \times \frac{M_i}{M_C} \times WP_i \right]}_{CO_2\_from\_biochar\_decomposition} + \underbrace{\left[ m_{BC} \times occ_{BC} \times d_{BC} \times \sum_{j,k} \left( y_j \times \frac{M_j}{M_C} \times WP_j \right) \right]}_{non\_CO_2\_GHGs\_from\_biochar\_decomposition}$$

$m_{BC}$  in Eq 1.2. a can be defined in terms of the biochar yield as follows:



357 **Eq 1.2. b: Definition of  $m_{BC}$**

358 
$$m_{BC} = m_W \times \gamma_{BC}$$

359 This substitution is made to define the GHG emissions in terms of the biochar yield,  
360 which is commonly used and measured by biochar producers.

361 The term  $(m_S \times occ_S)$  in Eq 1.2. a can then be defined in terms of the organic waste and  
362 biochar by the conservation of C as being:

363 **Eq 1.2. c: Substitution of syngas terms for solid phase terms**

364 
$$\left( \underbrace{m_S \times occ_S}_{\text{carbon\_in\_syngas}} \right) = \left( \underbrace{m_W \times occ_W}_{\text{carbon\_in\_organic\_waste}} \right) - \left( \underbrace{m_{BC} \times occ_{BC}}_{\text{carbon\_in\_biochar}} \right)$$

365 This equation allows the GHG emissions forecast to be calculated in terms of easily  
366 quantified variables i.e. solid phase material entering and leaving the slow-pyrolysis  
367 process, rather than having to quantify the volume and composition of gas flows.

### 368 3.1.3 Combustion Emissions

369 The GHG emission forecast for combustion using the biogenic method can be calculated  
370 by applying Eq. 1 as follows:

371 **Eq 1.3. a: Combustion GHG emission forecast by the biogenic method**

372 
$$E_{biogenic}(combustion) = \underbrace{\left[ m_W \times occ_W \times d_c \times v_i \times \frac{M_i}{M_C} \times WP_i \right]}_{CO_2\_from\_combustion} + \underbrace{\left[ m_W \times occ_W \times d_c \times \sum_{j,k} \left( v_j \times \frac{M_j}{M_C} \times WP_j \right) \right]}_{non\_CO_2\_GHGs\_from\_combustion}$$

## 373 3.2 Stock Method

### 374 3.2.1 Landfill Emissions

375 The GHG emission forecast for landfilling of organic waste using the stock method can  
376 be calculated by applying Eq. 2 as follows:

377 **Eq 2.1. a: Landfill GHG emissions forecast by stock method**

378 
$$E_{stock}(Landfill) = \underbrace{\left[ m_W \times occ_W \times d_W \times \sum_{j,k} \left( z_j \times \frac{M_j}{M_C} \times WP_j \right) \right]}_{non\_CO_2\_GHGs\_from\_landfill} - \underbrace{\left[ m_W \times occ_W \times s_W \times \frac{M_i}{M_C} \times WP_i \right]}_{C\_stabilised\_in\_landfill}$$

### 379 3.2.2 Slow-pyrolysis Emissions

380 The GHG emission forecast for a slow-pyrolysis plant using the stock method can be  
381 calculated by applying Eq. 2 as follows:

382 **Eq 2.2. a: Slow- Pyrolysis GHG emissions forecast by stock method**

$$E_{stock}(Pyrolysis) = \underbrace{\left[ m_S \times occ_S \times \sum_{j,k} \left( u_j \times \frac{M_j}{M_C} \times WP_j \right) \right]}_{non\_CO_2\_GHGs\_from\_syngas} + \underbrace{\left[ m_{BC} \times occ_{BC} \times d_{BC} \times \sum_{j,k} \left( y_j \times \frac{M_j}{M_C} \times WP_j \right) \right]}_{non\_CO_2\_GHGs\_from\_biochar\_decomposition} - \underbrace{\left[ m_{BC} \times occ_{BC} \times s_{BC} \times \frac{M_i}{M_C} \times WP_i \right]}_{C\_stabilised\_in\_biochar}$$

384 **3.2.3 Combustion Emissions**

385 The GHG emission forecast for combustion using the stock method can be calculated by  
386 applying Eq. 2 as follows:

387 **Eq 2.3. a: Combustion GHG emissions forecast by the stock method**

$$E_{stock}(Combustion) = \underbrace{\left[ m_W \times occ_W \times d_C \times \sum_{j,k} \left( v_j \times \frac{M_j}{M_C} \times WP_j \right) \right]}_{non\_CO_2\_GHGs\_from\_combustion} - \underbrace{\left[ m_W \times occ_W \times s_C \times \frac{M_i}{M_C} \times WP_i \right]}_{C\_stabilised\_in\_combustion\_residue}$$

389 **3.3 Simplified Method**

390 **3.3.1 Landfill Emissions**

391 The GHG emission forecast for landfilling of organic waste using the simplified method  
392 can be calculated applying Eq. 3 as follows:

393 **Eq 3.1. a: Landfill GHG emissions forecast by the simplified method**

$$E_{simplified}(Landfill) = \underbrace{\left[ m_W \times occ_W \times d_W \times \sum_{j,k} \left( z_j \times \frac{M_j}{M_C} \times WP_j \right) \right]}_{non\_CO_2\_GHGs\_from\_landfill}$$

395 **3.3.2 Slow-pyrolysis Emissions**

396 The GHG emission forecast for a slow-pyrolysis plant using the simplified method can be  
397 calculated by applying Eq. 3 as follows:

398 **Eq 3.2. a: Slow-pyrolysis GHG emissions forecast by simplified method**

$$E_{simplified}(Pyrolysis) = \underbrace{\left[ m_S \times occ_S \times \sum_{j,k} \left( u_j \times \frac{M_j}{M_C} \times WP_j \right) \right]}_{non\_CO_2\_GHGs\_from\_syngas} + \underbrace{\left[ m_{BC} \times occ_{BC} \times d_{BC} \times \sum_{j,k} \left( y_j \times \frac{M_j}{M_C} \times WP_j \right) \right]}_{non\_CO_2\_GHGs\_from\_biochar\_decomposition}$$

400 **3.3.3 Combustion Emissions**

401 The GHG emission forecast for combustion using the simplified method can be  
402 calculated by applying Eq. 3 as follows:

Eq 3.3. a: Combustion GHG emission forecast by the simplified method

$$E_{simplified}(Combustion) = \underbrace{\left[ m_W \times occ_W \times d_c \times \sum_{j,k} \left( v_j \times \frac{M_j}{M_C} \times WP_j \right) \right]}_{non\_CO_2\_GHGs\_from\_combustion}$$

### 3.4 Emissions Forecast Summary

The emissions forecast of each project scenario, using each of the GHG accounting approaches is summarised in Tables 4 to 7 below. Full worked examples are provided in the supplementary materials.

**Table 4: Landfill GHG emissions forecast. All units in kg CO<sub>2</sub>-e/kg (dry organics).**

#### Biogenic Method

= CO <sub>2</sub> from landfill	$E_i$	0.463
+ Non-CO <sub>2</sub> GHG from landfill	$E_{j,k}$	3.465
<b>Total emissions forecast from landfill</b>	<b><math>E_{biogenic} (landfill)</math></b>	<b>3.928</b>

#### Stock Method

= Non-CO <sub>2</sub> GHG from landfill	$E_{j,k}$	3.465
- CO <sub>2</sub> -e C stabilised in landfill	$C_i$	0.917
<b>Total emissions forecast from landfill</b>	<b><math>E_{stock} (landfill)</math></b>	<b>2.548</b>

#### Simplified Method

= Non-CO <sub>2</sub> GHG from Landfill	$E_{j,k}$	3.465
<b>Total emissions forecast from landfill</b>	<b><math>E_{simplified} (landfill)</math></b>	<b>3.465</b>

**Table 5: Slow-pyrolysis GHG emissions forecast. All units in kg CO<sub>2</sub>-e/kg (dry organics).**

#### Biogenic Method

= CO <sub>2</sub> from syngas	$E_i (syngas)$	0.718
+ non-CO <sub>2</sub> GHG from syngas	$E_{j,k}(syngas)$	0.005
+ CO <sub>2</sub> from decomposition of biochar	$E_i (biochar)$	0.100
+ non-CO <sub>2</sub> GHG from decomposition of biochar	$E_{j,k}(biochar)$	0.002
<b>Total emissions forecast from pyrolysis</b>	<b><math>E_{biogenic} (pyrolysis)</math></b>	<b>0.825</b>

#### Stock Method

= non-CO <sub>2</sub> GHG from syngas	$E_{j,k}(syngas)$	0.005
+ non-CO <sub>2</sub> GHG from decomposition of biochar	$E_{j,k}(biochar)$	0.002
- CO <sub>2</sub> -e C stabilised in biochar	$C_i$	1.014
<b>Total emissions forecast from pyrolysis</b>	<b><math>E_{stock} (pyrolysis)</math></b>	<b>-1.007</b>

#### Simplified Method

= non-CO <sub>2</sub> GHG from syngas	$E_{j,k}(syngas)$	0.005
+ non-CO <sub>2</sub> GHG from decomposition of biochar	$E_{j,k}(biochar)$	0.002
<b>Total emissions forecast from pyrolysis</b>	<b><math>E_{simplified} (pyrolysis)</math></b>	<b>0.007</b>

413 **Table 6: Combustion GHG emissions forecast. All units in kg CO<sub>2</sub>-e/kg (dry organics).**

<b>Biogenic Method</b>		
= CO <sub>2</sub> from combustion	$E_i$	1.822
+ non-CO <sub>2</sub> GHG from combustion	$E_{j,k}$	0.014
<b>Total emissions forecast from combustion</b>	<b><math>E_{biogenic} (combustion)</math></b>	<b>1.836</b>
<b>Stock Method</b>		
= non-CO <sub>2</sub> GHG from combustion	$E_{j,k}$	0.014
- CO <sub>2</sub> -e C stabilised in combustion residue	$C_i$	0.009
<b>Total emissions forecast from combustion</b>	<b><math>E_{stock} (combustion)</math></b>	<b>0.005</b>
<b>Simplified Method</b>		
= non-CO <sub>2</sub> GHG from combustion	$E_{j,k}$	0.014
<b>Total emissions forecast from combustion</b>	<b><math>E_{simplified} (combustion)</math></b>	<b>0.014</b>

414

415 **Table 7: Total emissions forecast summary for all project scenarios using methods**  
416 **developed for each approach. All units in kg CO<sub>2</sub>-e/kg (dry organics).**

	$E_{biogenic}$	$E_{stock}$	$E_{simplified}$
Landfill	3.928	2.548	3.465
Slow-pyrolysis	0.825	-1.007	0.007
Combustion	1.836	0.005	0.014

### 417 3.5 Abatement Summary

418 The emissions abatement for each of the three cases outlined in Table 8 has been  
419 calculated for each method using Eq. 4. A summary of the results can be found in Table 8  
420 below:

421 **Table 8: GHG emission abatement for all project scenarios using the methods developed**  
422 **for each approach. All units in kg CO<sub>2</sub>-e/kg (dry organics).**

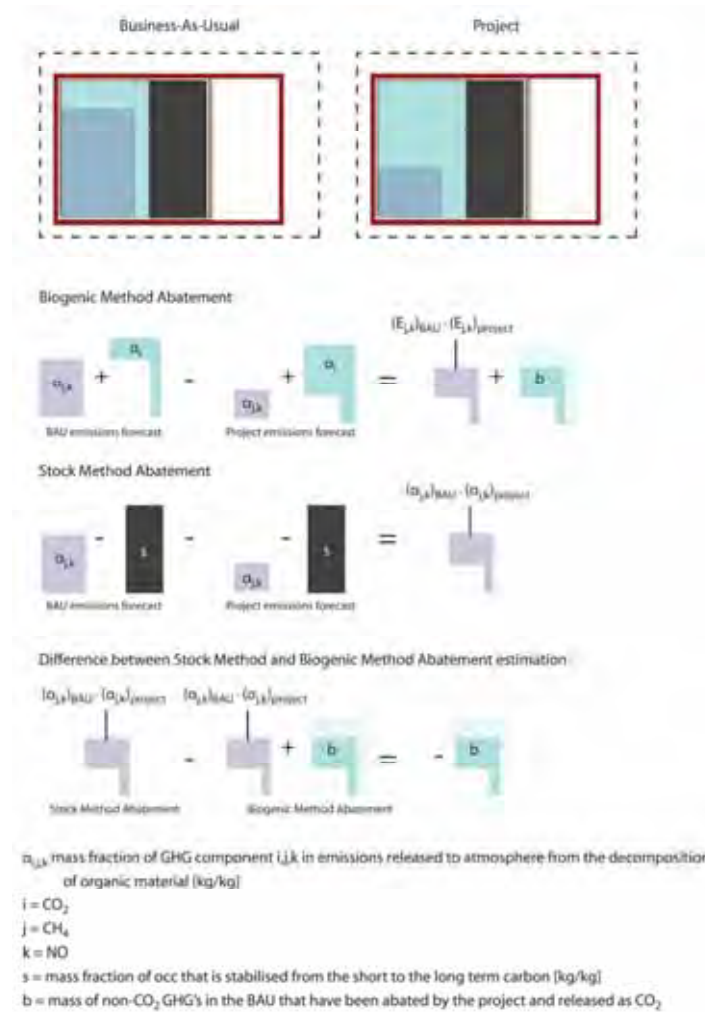
	<b>BAU</b>	<b>Project</b>	$A_{biogenic}$	$A_{stock}$	$A_{simplified}$
Case 1:	Landfill	Slow-pyrolysis	3.103	3.555	3.458
Case 2:	Combustion	Slow-pyrolysis	1.011	1.012	0.007
Case 3:	Landfill	Combustion	2.092	2.543	3.451

423

424

### 425 3.6 Comparing Approaches for Emissions Forecast

426 It can be seen from Table 7 that each approaches method results in a different forecast  
427 of the quantity of GHG's emitted. In this section the fundamental difference between the  
428 approaches are defined by applying Eq. 5. The differences are also described visually in  
429 Figure 4. This analysis assists in understanding which of the approaches provides the  
430 most appropriate representation of the GHG emissions flux of the activity for accounting  
431 purposes.



432

433 **Figure 4. Visual representation of the difference in approaches methods for emissions**  
 434 **forecasting**

435 The mathematical derivation of the differences in the equations between the methods is  
 436 provided in full in the supplementary information, and a summary of the findings is  
 437 included below.

438 The difference in emissions forecast ( $\delta_{a/b}$ ) between the simplified method and the  
 439 biogenic method is due to the emissions from carbon dioxide released to atmosphere  
 440 from the decomposition of organics being included in the biogenic method but not in the  
 441 simplified method.

442 
$$\delta_{biogenic / simplified} = (E_i)_{biogenic}$$

443 The difference in emissions forecast ( $\delta_{a/b}$ ) between the simplified method and stock  
 444 method is due to the inclusion of the  $CO_2$ -e of C stabilised by moving from the short to  
 445 the long-term C cycle emission in the stock method but not the simplified method.

446 
$$\delta_{simplified / stock} = (C_i)_{stock}$$

447 The difference in emissions forecast ( $\delta_{a/b}$ ) between the biogenic method and the stock  
 448 method is equal to the CO<sub>2</sub> emissions from the decomposing organic C fraction plus the  
 449 amount of CO<sub>2</sub>-e stored in the stabilised fraction.

$$450 \delta_{biogenic/stock} = (E_i)_{biogenic} + (C_i)_{stock}$$

### 451 3.7 Comparing Approaches for Emissions Abatement

452 The differences in the approaches in terms of accounting for GHG abatement have been  
 453 investigated. The mathematical derivation of the differences in the equations between  
 454 the approaches methods is provided in full in the supplementary information, and a  
 455 summary of the findings are described below:

456 The difference in emissions abatement ( $\Delta_{a/b}$ ) calculated by the biogenic method and the  
 457 simplified method is equal to the difference in biogenic CO<sub>2</sub> emissions between the BAU  
 458 and project.

459 **Eq 6.a:**

$$460 \Delta_{biogenic/simplified} = \frac{\left[ (E_i)_{BAU} - (E_i)_{Project} \right]}{\text{difference\_in\_biogenic\_emission\_between\_BAU\_and\_project}}$$

461 The difference in emissions abatement ( $\Delta_{a/b}$ ) as calculated by the stock and simplified  
 462 method is equal to the difference in C stabilised between the BAU and project.

463 **Eq 6.b:**

$$464 \Delta_{simplified/stock} = \frac{\left[ (C_i)_{BAU} - (C_i)_{Project} \right]}{\text{difference\_in\_C\_stabilised\_between\_BAU\_and\_project}}$$

465 The difference in emissions abatement ( $\Delta_{a/b}$ ) as calculated by the biogenic and stock  
 466 method is equal to the difference in the C released as CO<sub>2</sub> plus the C stabilised between  
 467 the BAU and project.

468 **Eq 6.c:**

$$469 \Delta_{biogenic/stock} = \underbrace{\left[ (E_i)_{BAU} - (E_i)_{Project} \right]}_{\text{biogenic\_method}} + \underbrace{\left[ (C_i)_{BAU} - (C_i)_{Project} \right]}_{\text{stock\_method}}$$

470 Further substitution of equation 6.c with terms, as fully derived in the supplementary  
 471 information, yields the following equation:

472 **Eq 6.d:**

$$473 \Delta_{biogenic/stock} = \left[ \underbrace{\left( d_{BAU} \times a_{i,BAU} - d_{Project} \times a_{i,Project} \right)}_{\text{difference\_in\_proportion\_of\_C\_emitted}} + \underbrace{\left( s_{BAU} - s_{Project} \right)}_{\text{difference\_in\_proportion\_of\_C\_stabilised}} \right] \times m \times occ \times \frac{M_i}{M_c} \times WP_i$$

474 and given that,

475 **Eq 2.a:**

$$476 1 = d + s$$

477 and that,

478 **Eq. 1.a:**

$$479 \quad a_i = 1 - \sum_{j,k} (a_{j,k})$$

480 further substitution demonstrates that the difference in emissions abatement can be  
481 expressed as;

482 **Eq 6.e:**

$$483 \quad \Delta_{biogenic / stock} = \left[ \frac{(d_{Project} \times \sum_{j,k} a_{j,k,Project} - d_{BAU} \times \sum_{j,k} a_{j,k,BAU})}{\text{difference\_in\_proportion\_of\_non-CO}_2\_GHG\_emissions\_between\_Project\_and\_BAU}} \right] \times m \times occ \times \frac{M_i}{M_c} \times WP_i$$

## 484 **4 Discussion and Conclusions**

### 485 **4.1 Emissions forecasts for inventories**

486 The biogenic emissions method will give the largest emission forecast of all the methods  
487 examined. It can be seen from Eq. 5.a that it is larger than the simplified method by the  
488 quantity of CO<sub>2</sub> released. Eq. 5.d demonstrates that the biogenic method emissions  
489 forecast will be larger than the stock method by the amount of CO<sub>2</sub> emissions from the  
490 decomposing organic carbon fraction minus the amount of CO<sub>2</sub>-e stored in the stabilised  
491 fraction. The biogenic method, is only valid if the initial removal by the growing plant is  
492 also accounted for in the inventory. The biogenic method however is corrected if a term  
493 that deducts the C taken up in the biomass is added to the equation (rather than  
494 assuming the C is already in the inventory). This would, in effect, make it the inverse of  
495 the stock method. The challenge however with the biogenic method arises when setting  
496 system boundaries consistently between various activities within an inventory. As this  
497 requires the determination of if the C pool has already been added to the inventory. For  
498 example, when the biomass was grown or a product was produced from it, the C in the  
499 biomass may have already been added to the inventory. This will add significantly to the  
500 accounting task compared to the simplified method, especially for biomass with complex  
501 lifecycles and multiple uses.

502 The stock method will estimate the lowest emissions forecast, except where there is no  
503 biogenic C retained in the reservoir over the timeframe, in which case, as expressed by  
504 Eq. 5.b, the result will be the same as the simplified method. For emissions inventories  
505 the stock method provides a more accurate reflection of the true contribution to GHG  
506 emissions of the project than the simplified method as it acknowledges the contribution  
507 from building the pool of stable carbon, which reduces GHG concentrations in the  
508 atmosphere. This accounting method may be more easily applied than a method based  
509 on expanding the biogenic method to include removals.

510 The stock method is the most accurate method to forecast the net change in atmospheric  
511 GHG for activities that involve biomass C. The biogenic method overestimates the  
512 emissions because it does not deduct from the emissions forecast the C that was initially  
513 drawn down from the atmosphere into the organic material (biomass) via  
514 photosynthesis. The simplified method also overestimates the emissions, because it  
515 does not deduct from the emissions forecast the C that is moved from the short to the  
516 long-term C cycle via stable reservoirs.



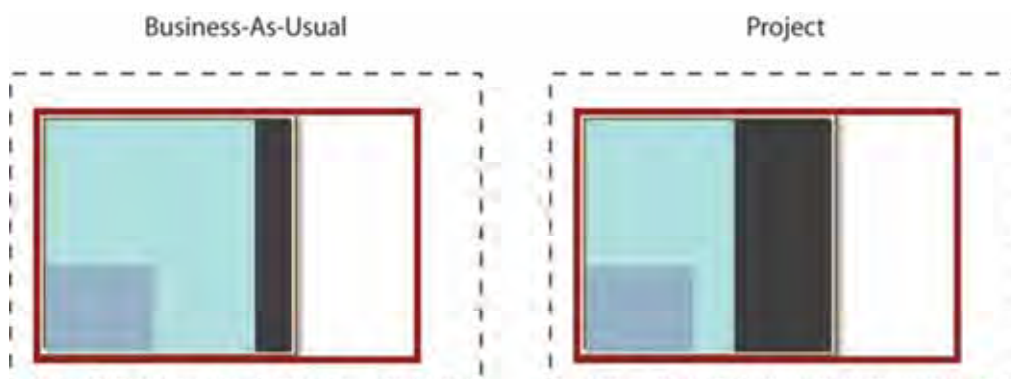
## 4.2 Emissions Abatement

It can be seen from the summary provided in Table 8 that for the worked examples the stock method estimates the largest abatement followed by the simplified method.

The simplified method inaccurately only shows a small difference between the two alternatives to landfill, combustion and slow-pyrolysis, even though the slow-pyrolysis option results in a significant retention of C in a stable pool that would result in a lower atmospheric GHG concentration. Although the biogenic method results in a lower estimation of abatement achieved compared with the stock (net emissions) method, it does recognise the greater abatement for the alternative to landfill that sequesters carbon (slow-pyrolysis) over the alternative that releases it (combustion), so it provides an incentive for projects that deposit and maintain C in reservoirs.

It is therefore clear that both the stock and biogenic methods more accurately reflect the abatement achieved than the simplified approach, but which of the two methods provides the most accurate calculation of the GHG abatement achieved?

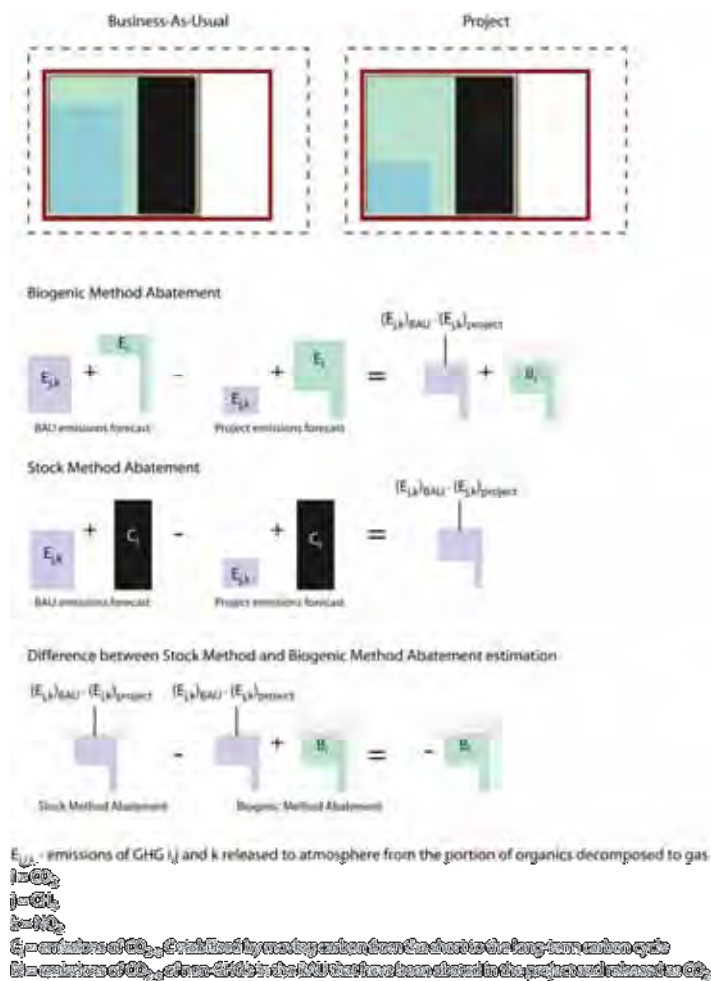
In an abatement scenario, such as that represented by Figure 5, where the non-CO<sub>2</sub> emission per unit of biomass is the same for the BAU as the project, but the proportion of CO<sub>2</sub> emitted compared to the amount retained in reservoir changes, both the biogenic and stock methods will result in the same estimation of abatement achieved. This is because the amount of CO<sub>2</sub> emitted is inversely proportional to the amount of C stabilised, therefore the difference between the project and reference cases in the quantity of CO<sub>2</sub> emitted is equal to the difference in the quantity of C stabilised.



**Figure 5: Abatement scenario where the level of non-CO<sub>2</sub> GHG remains constant, but the proportion of biomass C dissimilated compared to the amount retained changes**

In abatement Cases 1 and 3 however, the landfill BAU results in a greater portion of the dissimilated C going to non-CO<sub>2</sub> GHG's than in the project (i.e.  $a_{j,k-BAU} > a_{j,k-project}$ ). This is visually represented in Figure 6. The abatement estimated by the biogenic method in both of these cases is significantly lower than by the stock method. Case 1 and Case 3 are lower by 0.452 and 0.451 kg CO<sub>2</sub>-e/kg(dry) organics respectively. This difference has been demonstrated by Eq 6.c to be equal to the difference in biomass C released as CO<sub>2</sub> plus the difference in biomass C stabilised between the BAU and project cases. This is perhaps more usefully examined via Eq 6.e that demonstrates the difference in the two methods is the CO<sub>2</sub> equivalent of the difference in the fraction of biomass C released as non-CO<sub>2</sub> GHG between the BAU and project. This difference is visually represented in Figure 6.

554 The stock method does not recognise the additional CO<sub>2</sub> emissions resulting from  
 555 changes in levels of non-CO<sub>2</sub> GHGs evolved between the BAU and project scenarios. In  
 556 contrast, if some of the C is released as methane in the BAU and not in the project the  
 557 biogenic method will show an increase in the amount of CO<sub>2</sub> calculated in the project and  
 558 decrease in the non-CO<sub>2</sub> GHG's. The stock method will only show an abatement of  
 559 methane, and the additional CO<sub>2</sub> released (i.e. the C released as CO<sub>2</sub> that would have  
 560 been released as methane in the BAU) will not be accounted for. Hence the stock method  
 561 overestimates the abatement. This concept, proven by the derivation of Eq 6.e, is shown  
 562 below in Figure 6.



563

564 **Figure 6. The biogenic method accurately accounts for the abatement achieved by**  
 565 **converting non-CO<sub>2</sub> GHGs to CO<sub>2</sub>, while the stock method does not.**

566 The stock method is, therefore, not as accurate as the biogenic method in accounting for  
 567 the abatement achieved by projects that result in both CO<sub>2</sub> and non-CO<sub>2</sub> emissions  
 568 variations compared to the BAU practice (which is likely to be the case in all real-life  
 569 abatement projects). This shortcoming of the stock method, which also occurs in the  
 570 simplified method, could be overcome by including an additional term to the emissions  
 571 forecast that accounts for this flux. Inclusion of this additional term to the stock or  
 572 simplified method however, would mean that the emissions calculated using these  
 573 revised methods would be over-estimated in both the BAU and project forecasts.

574 A modified version of Eq 4 for the stock method for use in abatement calculations could  
 575 be expressed as follows:

576 **Eq. 4. a: GHG emissions abatement calculation using the stock method modified to account**  
 577 **for changes in proportions of non-CO<sub>2</sub> GHGs between the BAU and project emissions**  
 578 **forecasts.**

$$A_{stock} (modified) = (E_{BAU} - E_{project}) - B_{i(BAU/project)}$$

579

580 Where,

581 **Eq 7. Correction factor for stock method abatement calculation.**

$$B_{i(BAU/project)} = \left[ \frac{(d_{BAU} \times \sum_{j,k} a_{j,k,BAU} - d_{Project} \times \sum_{j,k} a_{j,k,Project})}{\text{difference\_in\_proportion\_of\_non-CO}_2\_GHG\_emissions\_between\_BAU\_and\_Project}} \right] \times m \times occ \times \frac{M_i}{M_c} \times WP_i$$

583 as derived by Eq 6.e.

584

585 A worked example for Case 3 using the modified stock method abatement calculation  
 586 has been provided in the supplementary information.

587 The results show that the biogenic method is the most accurate GHG accounting method  
 588 to use when calculating emissions abatement. The short-coming of the biogenic method  
 589 in forecasting, in not accounting for the initial draw-down of carbon during plant  
 590 growth, is over-come in the abatement calculation because this draw-down term occurs  
 591 with the exact same quantity in both the BAU and project case and hence cancels out.

## 592 5 Recommendations

- 593 • Emissions forecasting is most accurately calculated by the stock approach.  
 594 Therefore it is recommended that emissions inventories use this approach.
- 595 • Emissions abatement is most accurately calculated by the biogenic approach.  
 596 Therefore it is recommend that GHG abatement methodologies adopt this  
 597 approach.
- 598 • The stock approach can be adopted for abatement calculations if an additional  
 599 term is added to correct for the portion of non-CO<sub>2</sub> GHG that is released as  
 600 biogenic C emissions in the project.
- 601 • If no C is moved from the short-term C cycle to the long-term C cycle then the  
 602 simplified approach can be used to accurately estimate a net emission  
 603 inventory.
- 604 • If no C is moved from the short-term C cycle to the long-term C cycle and the  
 605 amount of non-CO<sub>2</sub> GHG is consistent between the project and the BAU then the  
 606 simplified approach can be used for abatement calculations.

## 607 6 Acknowledgements

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 609 work.

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# Supplementary Information

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## *Approaches to GHG Accounting Methods for Biomass*

Adriana Downie, David Lau, Annette Cowie and Paul Munroe

### **1 Worked Examples – Emissions forecasts**

Provided below are the worked examples for the biogenic, stock and simplified methods applied to the project scenarios to calculate the emissions forecasts for each.

#### **1.1 Landfill - biogenic method**

Applying the assumptions outlined in Table 2 to the equations (Eq 1.1.a and b), the GHG emissions forecast, calculated using the biogenic method, from the landfill treatment of the organic waste is:

$$\begin{aligned} E_{biogenic}(landfill) &= CO_2 \text{ from landfill} + \text{non-}CO_2 \text{ GHGs from landfill} \\ &= 0.463 + 3.465 \\ &= \underline{\underline{3.928 [kg CO_2\text{-e/kg (dry organics)]}}} \end{aligned}$$

#### **1.2 Slow-pyrolysis - biogenic method**

Applying the assumptions outlined in Table 2 to the equations (Eq 1.2.a,b and c), the GHG emissions forecast, calculated using the biogenic method, from the slow-pyrolysis of the organic waste is:

$$\begin{aligned} E_{biogenic}(pyrolysis) &= CO_2 \text{ from syngas} \\ &+ \text{non-}CO_2 \text{ GHGs from syngas} \\ &+ CO_2 \text{ from biochar decomposition} \\ &+ \text{non-}CO_2 \text{ GHGs from biochar decomposition} \\ &= 0.718 + 0.005 + 0.100 + 0.002 \\ &= \underline{\underline{0.826 [kg CO_2\text{-e/kg(dry organics)]}}} \end{aligned}$$

#### **1.3 Combustion - biogenic method**

Applying the assumptions outlined in Table 2, to the equation (Eq 1.3.a), the GHG emissions forecast calculated, using the biogenic method, from combustion of the organic waste is:

$$\begin{aligned}
E_{biogenic}(combustion) &= CO_2 \text{ from combustion} + \text{non-}CO_2 \text{ GHGs from combustion} \\
&= 1.795 + 0.014 \\
&= \underline{\underline{1.809 [kg CO_2\text{-}e/kg(dry organics)]}}
\end{aligned}$$

#### 1.4 Landfill - stock method

Applying the assumptions outlined in Table 2 to the equations (Eq 2.1.a and Eq 1.1.b), the GHG emissions forecast calculated using the stock method, from the landfill treatment of the organics waste is:

$$\begin{aligned}
E_{stock}(landfill) &= \text{non-}CO_2 \text{ GHGs from landfill} + CO_2\text{-}e \text{ C stabilised in landfill} \\
&= 3.465 - 0.917 \\
&= \underline{\underline{2.548 [kg CO_2\text{-}e/kg(dry organics)]}}
\end{aligned}$$

#### 1.5 Slow-pyrolysis - stock method

Applying the assumptions outlined in Table 2 to the equations (Eq 2.2.a, Eq 1.2.b and Eq 1.2.c), the GHG emissions forecast calculated using the direct sink method, from the slow-pyrolysis of the organics waste is:

$$\begin{aligned}
E_{stock}(pyrolysis) &= \text{non-}CO_2 \text{ GHGs from syngas} \\
&\quad + \text{non-}CO_2 \text{ GHGs from biochar decomposition} \\
&\quad + CO_2\text{-}e \text{ of C stabilised in biochar} \\
&= 0.005 + 0.002 - 1.014 \\
&= \underline{\underline{-1.007 [kg CO_2\text{-}e/kg (dry organics)]}}
\end{aligned}$$

#### 1.6 Combustion - stock method

Applying the assumptions outlined in Table 2 to the equation (Eq 2.3.a), the GHG emissions forecast calculated using the stock method, from combustion of the organics waste is:

$$\begin{aligned}
E_{stock}(combustion) &= \text{non-}CO_2 \text{ GHGs from combustion} \\
&\quad + CO_2\text{-}e \text{ of C stabilised by combustion residue} \\
&= 0.014 - 0.009 \\
&= \underline{\underline{0.005 [kg CO_2\text{-}e/kg(dry organics)]}}
\end{aligned}$$

## 65 1.7 Landfill - simplified method

66 Applying the assumptions outlined in Table 2 to the equations (Eq 3.1.a and Eq  
67 1.1.b), the GHG emissions forecast calculated using simplified method, from the  
68 landfill treatment of the organics waste is:

69

$$\begin{aligned} 70 \quad E_{\text{simplified}}(\text{landfill}) &= \text{non-CO}_2 \text{ GHGs from landfill} \\ 71 &= \underline{\underline{3.465 \text{ [kg CO}_2\text{-e/kg(dry organics)]}}} \end{aligned}$$

72

## 73 1.8 Slow-pyrolysis - simplified method

74 Applying the assumptions outlined in Table 2 to the equations (Eq3.2.a, Eq 1.2.b  
75 and Eq 1.2.c), the GHG emissions forecast calculated using simplified methods,  
76 from the slow-pyrolysis of the organics waste is:

77

$$\begin{aligned} 78 \quad E_{\text{simplified}}(\text{pyrolysis}) &= \text{non-CO}_2 \text{ GHGs from syngas} \\ 79 &+ \text{non-CO}_2 \text{ GHGs from biochar decomposition} \\ 80 &= 0.0055 + 0.0023 \\ 81 &= \underline{\underline{0.0078 \text{ [kg CO}_2\text{-e/kg(dry organics)]}}} \end{aligned}$$

82

## 83 1.9 Combustion - simplified method

84 Applying the assumptions outlined in Table 2 to the equation (Eq 3.3.a), the GHG  
85 emissions forecast calculated using simplified method, from combustion of the  
86 organics waste is:

87

$$\begin{aligned} 88 \quad E_{\text{simplified}}(\text{combustion}) &= \text{non-CO}_2 \text{ GHGs from combustion} \\ 89 &= \underline{\underline{0.014 \text{ [kg CO}_2\text{-e/kg(dry organics)]}}} \end{aligned}$$

## 90 2 Equation derivation for differences in emissions forecast 91 between methods

### 92 2.1 Biogenic vs Simplified Method – Emissions forecast

93 Eq 5.a: Comparison of emissions forecast by biogenic and simplified methods

$$94 \quad \delta_{\text{biogenic/simplified}} = (E_{\text{biogenic}} - E_{\text{simplified}})$$

95

96 Substituting Eq. 1 and Eq. 3 into Eq. 5.a gives:



97

98 
$$(\delta_{biogenic/simplified}) = (E_i + E_{j,k})_{Biogenic} - (E_{j,k})_{simplified}$$

99

100 Given that,

101

102 
$$(E_{j,k})_{biogenic} = (E_{j,k})_{simplified}$$

103

104 Eq 5.a. can be simplified to:

105

106 
$$\delta_{biogenic/simplified} = (E_i)_{biogenic}$$

## 107 2.2 Stock vs Simplified Method – Emissions forecast

108 **Eq 5.b: Comparison of emissions forecast by stock and simplified methods**

109 
$$\delta_{simplified / stock} = (E_{simplified} - E_{stock})$$

110

111

112 Substituting Eq. 2 and Eq. 3 into Eq. 5.b gives:

113 
$$\delta_{simplified / stock} = (E_{j,k})_{simplified} - (E_{j,k} - C_i)_{stock}$$

114

115 Given that,

116

117 
$$(E_{j,k})_{simplified} = (E_{j,k})_{stock}$$

118

119 Eq 5.b. can be simplified to:

120

121 
$$\delta_{simplified / stock} = (C_i)_{stock}$$

## 122 2.3 Biogenic vs Stock Method – Emissions forecast

123 **Eq 5.c: Comparison of emissions forecast by biogenic and stock methods**

124 
$$\delta_{biogenic / stock} = (E_{biogenic} - E_{stock})$$

125

Substituting Eq. 1 and Eq. 2 into Eq. 5.c gives:

$$\delta_{biogenic / stock} = (E_i + E_{j,k})_{biogenic} - (E_{j,k} - C_i)_{stock}$$

Given that,

$$(E_{j,k})_{stock} = (E_{j,k})_{biogenic}$$

Eq 5.c. can be simplified to:

$$\delta_{biogenic / stock} = (E_i)_{biogenic} + (C_i)_{stock}$$

### 3 Worked Examples – Difference in emissions forecast between methods

#### 3.1 Landfill - biogenic vs simplified emissions forecast

The result can be confirmed through a worked example by using the data shown in Table 4, where:

$$E_{biogenic}(landfill) = 3.928 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

$$E_{simplified}(landfill) = 3.465 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

Applying Eq 5.a, the difference between these two methods is 0.463 kg CO<sub>2</sub>-e/kg(dry) organics.

It can be confirmed from Table 4 that;

$$(E_i)_{biogenic}(landfill) = 0.463 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

#### 3.2 Slow-pyrolysis - simplified vs stock emissions forecast

This result can be confirmed through a worked example by using the data shown in Table 5, where:

$$E_{simplified}(pyrolysis) = 0.007 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

$$E_{stock}(pyrolysis) = -1.007 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

Applying Eq 5.b., the difference between these two methods is 1.014 kg CO<sub>2</sub>-e/kg(dry) organics.

It can be confirmed from Table 5 that;

$$(C_i)_{stock}(pyrolysis) = 1.014 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

### 3.3 Slow-pyrolysis – biogenic vs stock emissions forecast

This result can be confirmed through a worked example by using the data shown in Table 5, where:

$$E_{biogenic}(pyrolysis) = 0.825 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

$$E_{stock}(pyrolysis) = -1.007 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

Applying Eq 5.c., the difference between these two methods is 1.832 kg CO<sub>2</sub>-e/kg(dry) organics.

It can be confirmed from Table 5 that;

$$\begin{aligned} (E_i)_{biogenic}(pyrolysis) - (C_i)_{stock}(pyrolysis) &= (0.718 + 0.100) + (1.014) \\ &= 1.832 \text{ kg CO}_2\text{-e/kg(dry) organics} \end{aligned}$$

## 4 Equation derivation for differences in emissions abatement between methods

### 4.1 Biogenic vs Simplified Method

A comparison of emissions abatement calculated by the biogenic and simplified methods can be made by applying Eq. 1 and Eq. 2 to Eq. 6, as follows;

**Eq 6.a: Comparison of emissions abatement by biogenic and simplified methods**

$$\Delta_{biogenic/simplified} = \left[ \underbrace{(E_{j,k} + E_i)_{BAU} - (E_{j,k} + E_i)_{Project}}_{\text{abatement\_by\_biogenic\_method}} \right] - \left[ \underbrace{(E_{j,k})_{BAU} - (E_{j,k})_{Project}}_{\text{abatement\_by\_simplified\_method}} \right]$$

Given that,

$$\underbrace{(E_{j,k})_{BAU}}_{\text{biogenic\_method}} = \underbrace{(E_{j,k})_{BAU}}_{\text{simplified\_method}}$$

and,

$$\underbrace{(E_{j,k})_{Project}}_{\text{biogenic\_method}} = \underbrace{(E_{j,k})_{Project}}_{\text{simplified\_method}}$$

Eq 6.a can be simplified to:

$$\Delta_{biogenic/simplified} = \underbrace{\left[ (E_i)_{BAU} - (E_i)_{Project} \right]}_{\text{difference\_in\_biogenic\_emission\_between\_BAU\_and\_project}}$$

## 4.2 Simplified vs Stock Method

A comparison of emissions abatement calculated by the stock and simplified methods can be made by applying Eq. 2 and Eq. 3 to Eq. 6, as follows;

**Eq 6.b: Comparison of emissions abatement by stock and simplified methods**

$$\Delta_{\text{simplified / stock}} = \left[ \underbrace{(E_{j,k})_{BAU} - (E_{j,k})_{\text{Project}}}_{\text{abatement\_by\_simplified\_method}} \right] - \left[ \underbrace{(E_{j,k} - C_i)_{BAU} - (E_{j,k} - C_i)_{\text{Project}}}_{\text{abatement\_by\_stock\_method}} \right]$$

Given that,

$$\underbrace{(E_{j,k})_{BAU}}_{\text{simplified\_method}} = \underbrace{(E_{j,k})_{BAU}}_{\text{stock\_method}}$$

and,

$$\underbrace{(E_{j,k})_{\text{Project}}}_{\text{simplified\_method}} = \underbrace{(E_{j,k})_{\text{Project}}}_{\text{stock\_method}}$$

Eq 6.b can be simplified to:

$$\Delta_{\text{simplified / stock}} = \underbrace{[(C_i)_{BAU} - (C_i)_{\text{Project}}]}_{\text{difference\_in\_C\_stabilised\_between\_BAU\_and\_project}}$$

## 4.3 Biogenic vs Stock Method

A comparison of emissions abatement calculated by the biogenic and stock methods can be made by applying Eq. 1 and Eq. 2 to Eq. 6, as follows;

**Eq 6.c: Comparison of emissions abatement by stock and simplified methods**

$$\Delta_{\text{biogenic / stock}} = \left[ \underbrace{(E_{j,k} + E_i)_{BAU} - (E_{j,k} + E_i)_{\text{Project}}}_{\text{abatement\_by\_biogenic\_method}} \right] - \left[ \underbrace{(E_{j,k} - C_i)_{BAU} - (E_{j,k} - C_i)_{\text{Project}}}_{\text{abatement\_by\_stock\_method}} \right]$$

Given that,

$$\underbrace{(E_{j,k})_{BAU}}_{\text{biogenic\_method}} = \underbrace{(E_{j,k})_{BAU}}_{\text{stock\_method}}$$

and,

$$\underbrace{(E_{j,k})_{\text{Project}}}_{\text{biogenic\_method}} = \underbrace{(E_{j,k})_{\text{Project}}}_{\text{stock\_method}}$$

Eq 6.c can be simplified to:

$$\Delta_{\text{biogenic / stock}} = \underbrace{[(E_i)_{BAU} - (E_i)_{\text{Project}}]}_{\text{biogenic\_method}} + \underbrace{[(C_i)_{BAU} - (C_i)_{\text{Project}}]}_{\text{stock\_method}}$$

## 205 5 Worked examples for differences in emissions abatement 206 between methods

### 207 5.1 Case 1 - biogenic vs simplified abatement

208 For Case 1, Eq. 6.a becomes;

209

$$\Delta_{biogenic/simplified} = \frac{\left[ (E_i)_{landfill} - (E_i)_{pyrolysis} \right]}{\text{difference\_in\_biogenic\_emission\_between\_landfill\_and\_pyrolysis}}$$

210

211

212 This result can be confirmed through a worked example by using the data shown  
213 in Table 8.

$$214 \quad A_{biogenic} (Case 1) = 3.103 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

$$215 \quad A_{simplified} (Case 1) = 3.458 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

216 Applying Eq. 6, the difference between these two methods is -0.355 kg CO<sub>2</sub>-  
217 e/kg(dry) organics.

218 It can be confirmed from Table 4 and Table 5 that, for Case 1 where the BAU is  
219 landfill and the project is slow-pyrolysis, the application of Eq. 6.a gives;

$$220 \quad (E_i)_{biogenic}(landfill) - (E_i)_{biogenic}(pyrolysis) = 0.463 - (0.718 + 0.100)$$

$$221 \quad = -0.355 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

### 222 5.2 Case 1 - simplified vs stock abatement

223 For Case 1, Eq 6.b becomes;

224

$$\Delta_{simplified / stock} = \frac{\left[ (C_i)_{landfill} - (C_i)_{pyrolysis} \right]}{\text{difference\_in\_C\_stabilised\_between\_landfill\_and\_pyrolysis}}$$

225

226 This result can be confirmed through a worked example by using the data shown  
227 in Table 8.

$$228 \quad A_{simplified} (Case 1) = 3.458 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

$$229 \quad A_{stock} (Case 1) = 3.555 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

230 Applying Eq 6, the difference between these two methods is -0.097 kg CO<sub>2</sub>-  
231 e/kg(dry) organics.

232 It can be confirmed from Table 4 and Table 5 that, for Case 1 where the BAU is  
233 landfill and the project is slow-pyrolysis, the application of Eq 6.a gives;

$$234 \quad (C_i)_{stock}(landfill) - (C_i)_{stock}(pyrolysis) = 0.917 - 1.014$$

$$235 \quad = -0.097 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

### 236 5.3 Case 1 – biogenic vs stock abatement

237 For Case 1, Eq 6.c becomes;

$$238 \Delta_{biogenic / stock} = \underbrace{\left[ (E_i)_{landfill} - (E_i)_{pyrolysis} \right]}_{\text{difference\_in\_biogenic\_C\_emitted\_between\_BAU\_and\_project}} + \underbrace{\left[ (C_i)_{landfill} - (C_i)_{pyrolysis} \right]}_{\text{difference\_in\_C\_stabilised\_between\_BAU\_and\_Project}}$$

239 This result can be confirmed through a worked example by using the data shown  
240 in Table 8.

$$241 A_{biogenic} (\text{Case 1}) = 3.103 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

$$242 A_{stock} (\text{Case 1}) = 3.555 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

243 Applying Eq 6, the difference between these two methods is -0.452 kg CO<sub>2</sub>-  
244 e/kg(dry) organics.

245 It can be confirmed from Table 4 and Table 5 that, for Case 1 where the BAU is  
246 landfill and the project is slow-pyrolysis, the application of Eq 6.c gives;

$$\begin{aligned} 247 & [(E_i)_{biogenic(landfill)} - (E_i)_{biogenic(pyrolysis)}] + [(C_i)_{stock(landfill)} - (C_i)_{stock(pyrolysis)}] \\ 248 & = (0.463 - (0.718 + 0.100)) + (0.917 - 1.014) \\ 249 & = -0.355 - 0.097 \\ 250 & = -0.452 \text{ kg CO}_2\text{-e/kg(dry) organics} \end{aligned}$$

### 251 5.4 Case 3 - biogenic vs stock abatement

252 The expression Eq 6.e shows that the difference in emissions abatement between  
253 the stock and biogenic methods is also equal to the CO<sub>2</sub> equivalent of the  
254 difference in the portion of biogenic C released as non-CO<sub>2</sub> GHG between the BAU  
255 and project.

256 This result can be confirmed through a worked example by using the data shown  
257 in Table 8.

$$258 A_{biogenic} (\text{Case 3}) = 2.092 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

$$259 A_{stock} (\text{Case 3}) = 2.543 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

260 Applying Eq 6, the difference between these two methods is -0.451 kg CO<sub>2</sub>-  
261 e/kg(dry) organics.

262 For Case 3, Eq 6.e becomes;

$$263 \Delta_{biogenic / stock} = - \left[ \underbrace{\left( d_W \times \sum_{j,k} z_{j,k,landfill} - d_C \times \sum_{j,k} v_{j,k,combustion} \right)}_{\text{difference\_in\_proportion\_of\_non-CO}_2\text{\_GHG\_emissions}} \right] \times m \times occ \times \frac{M_i}{M_c} \times WP_i$$

264 Substitution of Eq 1.1.b for  $z_{j,k}$  and application of the assumptions from Table 3  
265 gives:

$$\begin{aligned} 266 \Delta_{biogenic / stock} & = -[(0.5 \times 0.55 \times (1-0.1)) - (0.995 \times 0.001)] \times 1 \times 0.5 \times (44/12) \times 1 \\ 267 & = -[0.247500 - 0.000995] \times 1.833333 \\ 268 & = -0.452 \text{ kg CO}_2\text{-e/kg(dry) organics} \end{aligned}$$

269 The difference of 0.001 kg CO<sub>2</sub>-e/kg(dry) organics found between the two  
 270 calculated results is due to the rounding to 3 decimal points of values in Tables 4  
 271 -6.

## 272 **6 Worked Example – Case 3, stock method abatement** 273 **modified**

274 Table 8 shows the abatement calculated using the stock method developed in  
 275 section 3.2 for the various project scenarios. The abatement achieved by the  
 276 modified stock method, introduced in Section 4.2, with the addition of term B<sub>i</sub>  
 277 has been examined through a worked example.

278 For Case 3, where the where the BAU is landfill and the project alternative is  
 279 combustion, Eq 4 a. becomes:

$$280 \quad A_{stock(modified)} (Case\ 3) \quad = E_{stock(landfill)} - E_{stock(combustion)} \\
 281 \quad \quad \quad \quad \quad \quad \quad - B_i(landfill/combustion)$$

282 and Eq 7. becomes,

$$283 \quad B_{i(landfill/combustion)} = \underbrace{\left[ \frac{\left( d_W \times \sum_{j,k} z_{j,k,landfill} - d_C \times \sum_{j,k} v_{j,k,combustion} \right)}{\text{difference\_in\_proportion\_of\_non-CO}_2\_GHG\_emissions} \right]}_{\text{non\_CO}_2\_GHGs\_abated\_and\_released\_as\_CO_2} \times m \times occ \times \frac{M_i}{M_c} \times WP_i$$

284 Substitution of values from Table 4 and 6, and application of the assumptions  
 285 from Table 3 gives:

$$286 \quad A_{stock(modified)} (Case\ 3) \quad = (2.548) - (0.005) - (0.247500 - 0.000995) \times \\
 287 \quad \quad \quad \quad \quad \quad \quad 1.833333 \\
 288 \quad \quad \quad \quad \quad \quad \quad = 2.091 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

289 This is the same abatement as calculated using the biogenic method as expected.

$$290 \quad A_{biogenic} (Case\ 3) \quad = 2.092 \text{ kg CO}_2\text{-e/kg(dry) organics}$$

291 The difference of 0.001 kg CO<sub>2</sub>-e/kg(dry) organics found between the two  
 292 calculated results is due to the rounding to 3 decimal points of values in Tables 4  
 293 -6.

294



## Chapter 7

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### *Co-Authored Publications*

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#### *Agronomic values of greenwaste biochar as a soil amendment*

Chan, K. Y., Van Zwieten, L., Meszaros, I., **Downie, A.** & Joseph, S. (2007).  
Agronomic values of greenwaste biochar as a soil amendment. Australian  
Journal of Soil Research, 45, 629-634.

Journal Impact Factor: 1.007

The co-author contribution to this publication was by way of forming the research collaboration between institutes, producing the biochar samples, assisting with experimental design, characterisation of biochars, along with contributing to, reviewing and editing the manuscript.

Full paper provided as Appendix A.

#### Abstract:

A pot trial was carried out to investigate the effect of biochar produced from greenwaste by pyrolysis on the yield of radish (*Raphanus sativus* var. Long Scarlet) and the soil quality of an Alfisol. Three rates of biochar (10, 50 and 100 t/ha) with and without additional nitrogen application (100 kg N/ha) were investigated. The soil used in the pot trial was a hardsetting Alfisol (Chromosol) (0–0.1 m) with a long history of cropping. In the absence of N fertiliser, application of biochar to the soil did not increase radish yield even at the highest rate of 100 t/ha. However, a significant biochar × nitrogen fertilizer interaction was observed, in that higher yield increases were observed with increasing rates of biochar application in the presence of N fertiliser, highlighting the role of biochar in improving N fertiliser use efficiency of the plant. For example, additional increase in DM of radish in the presence of N fertiliser varied from 95% in the nil biochar control to 266% in the 100 t/ha biochar-amended soils. A slight but significant reduction in dry matter production of radish was

observed when biochar was applied at 10 t/ha but the cause is unclear and requires further investigation. Significant changes in soil quality including increases in pH, organic carbon, and exchangeable cations as well as reduction in tensile strength were observed at higher rates of biochar application (>50 t/ha). Particularly interesting are the improvements in soil physical properties of this hardsetting soil in terms of reduction in tensile strength and increases in field capacity.

### *Using poultry litter biochars as soil amendments*

Chan, K.Y., Van Zwieten, L., Meszaros, I., **Downie, A.** & Joseph, S. (2008).  
Using poultry litter biochars as soil amendments. Australian Journal of Soil  
Research, 46, 437-444

Journal Impact Factor: 1.007

The co-author contribution to this publication was by way of forming the research collaboration between institutes, producing the biochar samples, assisting with experimental design, characterisation of biochars, along with contributing to, reviewing and editing the manuscript.

Full paper provided as Appendix B.

#### Abstract:

Despite the recent interest in biochars as soil amendments for improving soil quality and increasing soil carbon sequestration, there is inadequate knowledge on the soil amendment properties of these materials produced from different feedstocks and under different pyrolysis conditions. This is particularly true for biochars produced from animal origins. Two biochars produced from poultry litter under different conditions were tested in a pot trial by assessing the yield of radish (*Raphanus sativus* var. Long Scarlet) as well as the soil quality of a hardsetting Chromosol (Alfisol). Four rates of biochar (0, 10, 25, and 50 t/ha), with and without nitrogen application (100 kg N/ha) were investigated. Both biochars, without N fertiliser, produced similar increases in dry matter yield of radish, which were detectable at the lowest application rate, 10 t/ha. The yield increase (%), compared with the unamended control rose from 42% at 10 t/ha to 96% at 50 t/ha of biochar application. The yield increases can be attributed largely to the ability of these biochars to increase N availability. Significant additional yield increases, in excess of that due to N fertiliser alone, were observed when N fertiliser was applied together with the biochars, highlighting the other beneficial effects of these biochars. In this regard, the non-activated poultry litter biochar produced at lower temperature (450°C) was more effective than the activated biochar produced at higher temperature (550°C), probably due to higher available P content. Biochar

addition to the hardsetting soil resulted in significant but different changes in soil chemical and physical properties, including increases in C, N, pH, and available P, but reduction in soil strength. These different effects of the 2 different biochars can be related to their different characteristics. Significantly different changes in soil biology in terms of microbial biomass and earthworm preference properties were also observed between the 2 biochars, but the underlying mechanisms require further research. Our research highlights the importance of feedstock and process conditions during pyrolysis on the properties and, hence, soil amendment values of biochars.

*Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility*

van Zwieten, L., Kimber, S., Morris, S., Chan, K.Y., **Downie, A.**, Rust, J., Joseph, S. and Cowie, A. (2009) Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant and Soil*, 327, 235-246.

Journal Impact Factor: 2.517

The co-author contribution to this publication was by way of forming the research collaboration between institutes, producing the biochar samples, assisting with experimental design, characterisation of biochars, along with contributing to, reviewing and editing the manuscript.

Full paper provided as Appendix C.

**Abstract:**

The amendment of two agricultural soils with two biochars derived from the slow pyrolysis of paper- mill waste was assessed in a glasshouse study. Characterisation of both biochars revealed high surface area ( $115 \text{ m}^2 \text{ g}^{-1}$ ) and zones of calcium mineral agglomeration. The biochars differed slightly in their liming values (33% and 29%), and carbon content (50% and 52%). Molar H/C ratios of 0.3 in the biochars suggested aromatic stability. At application rates of  $10 \text{ t ha}^{-1}$  in a ferrosol both biochars significantly increased pH, CEC, exchangeable Ca and total C, while in a calcarosol both biochars increased C while biochar 2 also increased exchangeable K. Biochars reduced Al availability (ca.  $2 \text{ cmol (+) kg}^{-1}$  to  $<0.1 \text{ cmol (+) kg}^{-1}$ ) in the ferrosol. The analysis of biomass production revealed a range of responses, due to both biochar characteristics and soil type. Both biochars significantly increased N uptake in wheat grown in fertiliser amended ferrosol. Concomitant increase in biomass production (250% times that of control) therefore suggested improved fertiliser use efficiency. Likewise, biochar amendment significantly increased biomass in soybean and radish in the ferrosol with fertiliser. The calcarosol amended with fertiliser and biochar however gave varied crop responses: Increased soybean biomass, but reduced wheat and radish biomass. No

significant effects of biochar were shown in the absence of fertiliser for wheat and soybean, while radish biomass increased significantly. Earthworms showed preference for biochar-amended ferrosol over control soils with no significant difference recorded for the calcarosol. The results from this work demonstrate that the agronomic benefits of papermill biochars have to be verified for different soil types and crops.

*A glasshouse study on the interaction of low mineral ash biochar with nitrogen in a sandy soil*

van Zwieten, L., Kimber, S., **Downie, A.**, Morris, S., Petty, S., Rust, J. and Chan, K.Y. (2010). A glasshouse study on the interaction of low mineral ash biochar with nitrogen in a sandy soil. Australian Journal of Soil Research, 48, 569-576.

Journal Impact Factor: 1.007

The co-author contribution to this publication was by way of forming the research collaboration between institutes, producing the biochar samples, assisting with experimental design, characterisation of biochars, along with contributing to, reviewing and editing the manuscript.

Full paper provided as Appendix D.

Abstract:

The effect of a low mineral ash biochar on biomass production and nitrogen (N) uptake into plants was tested with wheat and radish in a Yellow Earth used for commercial vegetable production. The biochar had an acid neutralising capacity  $<0.5\%$   $\text{CaCO}_3$ , a total C content of 75%, and a molar H/C ratio of 0.45, indicating stability due to its aromaticity. A pot trial was established under climate-controlled conditions. Five rates of N fertiliser (0, 17, 44, 88, 177 kg N/ha) were applied as urea in combination with 5 biochar rates (0, 1.1, 2.2, 4.4, 11% w/w). Analysis of biomass production revealed a significant biochar  $\times$  N fertiliser interaction. In particular, increasing biochar concentrations improved biomass production in both crop species at lower N application rates. The highest biochar application rate resulted in significantly greater accumulation of  $\text{NO}_3^-$ -N in the soil and lower  $\text{NH}_4^+$ -N averaged across the 5 N application rates. The biochar also decreased available P, and significantly increased microbial activity measured using the fluorescein diacetate method. Increasing N fertiliser application resulted in greater accumulation of  $\text{NO}_3^-$ -N with no changes to  $\text{NH}_4^+$ -N averaged across the 5 biochar application rates. Nitrogen fertiliser application did not influence microbial activity or biomass C. The trial suggests that in some cropping systems, biochar application will enable reduced N fertiliser input while maintaining productivity.



*Influence of biochars on flux of N<sub>2</sub>O and CO<sub>2</sub> from Ferrosol*

van Zwieten, L., Kimber, S., Morris, S., **Downie, A.**, Berger, E., Rust, J. and Scheer, C. (2010). Influence of biochars on flux of N<sub>2</sub>O and CO<sub>2</sub> from Ferrosol. Australian Journal of Soil Research, 48, 555-568.

Journal Impact Factor: 1.007

The co-author contribution to this publication was by way of forming the research collaboration between institutes, producing the biochar samples, assisting with experimental design, characterisation of biochars, along with contributing to, reviewing and editing the manuscript.

Full paper provided as Appendix E.

Abstract:

Biochars produced by slow pyrolysis of greenwaste (GW), poultry litter (PL), papermill waste (PS), and biosolids (BS) were shown to reduce N<sub>2</sub>O emissions from an acidic Ferrosol. Similar reductions were observed for the untreated GW feedstock. Soil was amended with biochar or feedstock giving application rates of 1 and 5%. Following an initial incubation, nitrogen (N) was added at 165 kg/ha as urea. Microcosms were again incubated before being brought to 100% water-filled porosity and held at this water content for a further 47 days. The flooding phase accounted for the majority (<80%) of total N<sub>2</sub>O emissions. The control soil released 3165 mg N<sub>2</sub>O-N/m<sup>2</sup>, or 15.1% of the available N as N<sub>2</sub>O. Amendment with 1 and 5% GW feedstock significantly reduced emissions to 1470 and 636 mg N<sub>2</sub>O-N/m<sup>2</sup>, respectively. This was equivalent to 8.6 and 3.8% of applied N. The GW biochar produced at 350°C was least effective in reducing emissions, resulting in 1625 and 1705 mg N<sub>2</sub>O-N/m<sup>2</sup> for 1 and 5% amendments. Amendment with BS biochar at 5% had the greatest impact, reducing emissions to 518 mg N<sub>2</sub>O-N/m<sup>2</sup>, or 2.2% of the applied N over the incubation period. Metabolic activity as measured by CO<sub>2</sub> production could not explain the differences in N<sub>2</sub>O emissions between controls and amendments, nor could NH<sub>4</sub><sup>+</sup> or NO<sub>3</sub><sup>-</sup> concentrations in biochar-amended soils. A decrease in NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> following GW feedstock application is

likely to have been responsible for reducing N<sub>2</sub>O emissions from this amendment. Reduction in N<sub>2</sub>O emissions from the biochar-amended soils was attributed to increased adsorption of NO<sub>3</sub><sup>-</sup>. Small reductions are possible due to improved aeration and porosity leading to lower levels of denitrification and N<sub>2</sub>O emissions. Alternatively, increased pH was observed, which can drive denitrification through to dinitrogen during soil flooding.

*Effect of biochar on soil carbon storage, fertility and productivity in  
subtropical pasture*

Sinclair, K., Slavich, P., Morris, S.G., Kimber, S., **Downie, A.** and Van Zwieten, L. (submitted). Effect of biochar on soil carbon storage, fertility and productivity on subtropical pasture. Plant and Soil.

Journal Impact Factor: 2.519

The co-author contribution to this publication was by way of forming the research collaboration between institutes, producing the biochar samples, assisting with experimental design, characterisation of biochars, along with contributing to, reviewing and editing the manuscript.

Full paper provided as Appendix F.

Abstract:

This study provides timely evidence of the impacts of biochar in a subtropical pasture, where very high inputs of fertiliser and lime are required to maintain productivity. Biochars from beef feedlot manure [FM] and municipal greenwaste [GW] were soil incorporated at 10t ha<sup>-1</sup> and tested for their capacity to influence storage of C in soil, pasture productivity and soil fertility. The biochars differed in their chemical properties with FM and GW biochars having a carbon content of 44 and 76% with molar H/C ratios of 0.51 and 0.71, and liming values of 13 and 5.6% respectively.

Significant accumulation of soil C occurred over the 3-year trial period in the biochar amended plots. Soil initially contained 4.7% C which increased to between 5.1- 5.4% following amendment with biochar. With GW biochar and farmer-practice fertiliser rates, soil C increased to 6.5% after 3 years. No significant increases were detected for non - biochar amended controls. The FM biochar gave significant increases (almost double) in plant available P in both the fertilised and unfertilised plots 3 years following trial establishment. FM biochar provided significant increases in yield of annual ryegrass, but this

was not evident for the GW biochar. There was no significant difference in soil microbial biomass between treatments.

*Biochars in soil for climate mitigation and adaptation*

Waters, D., Van Zwieten, L., Singh, B., **Downie, A.**, Cowie, A. and Lehmann, J. (under review) Chapter 18: Biochars in soil for climate mitigation and adaptation. In B.P. Singh, A.L. Cowie and K.Y. Chan (Eds.), *Soil Health and Climate Change, Soil Biology Series*. Springer

This book chapter did not include an abstract. Full paper provided as Appendix G.

*Biochar effects on nutrient leaching*

Major, J., Steiner, C., **Downie, A.** and Lehmann, J. (2009). Chapter 15: Biochar effects on nutrient leaching. In J. Lehmann & S. Joseph (Eds.), *Biochar for Environmental Management: Science and Technology*. Earthscan. pg.271-282. ISBN: 978-1-84407-658-1

This book chapter did not include an abstract. Full paper provided as Appendix H.

## Chapter 8

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### *Discussion and Conclusions*

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The compilation of publications that form the basis of this thesis represent a significant contribution to the field of biochar research and development. Research in this field has attracted a dramatic increase in attention over recent years. As the approach for utilising biochar as a tool for environmental management is relatively new, the work presented in this thesis is broad in scope, covering a range of fundamental considerations for biochar production and use. All the papers presented, however, have a common theme and assist in building the understanding for future research and the emerging industrial application of the technology.

Chapter 2 comprises of the first ever published, extensive literature review on the physical properties of biochars. Some creativity was applied in compiling this review. As the number of peer-reviewed research papers directly presenting data on the physical characterization of biochar were very limited, an extended search and review of chars made for a variety of purposes, such as for producing gun powder and filtration media, were included. This broad approach was able to identify common trends and fundamental characteristics typical of these materials.

Some key relationships identified (Downie *et al.*, 2009) include:

- Biochars stable molecular structure develops with highest treatment temperature (HTT) and residence time. The first stages of thermal processing result in an increased proportion of aromatic C, highly disordered in amorphous mass. Higher temperatures (>350°C) and longer residence times result in growing sheets of conjugated aromatic carbon, turbostratically arranged. At higher temperatures still (> 1000°C) the structures become graphitic, with order in the third dimension;
- Operating parameters during the pyrolysis process that influence the resultant physical properties of biochar of any given biomass feedstock include heating rate, highest treatment temperature (HTT), pressure, reaction residence time, reaction vessel (orientation, dimensions, stirring regime, catalysts, etc.), pre-treatment (drying, comminution, chemical activation, etc.), the flow rate of ancillary inputs

(e.g. nitrogen, carbon dioxide, air, steam, etc.), and post-treatment (crushing, sieving, activation, etc.);

- Under slow-pyrolysis conditions the residual cellular structures of botanical origin that are present and identifiable in biochars contribute the majority of the macroporosity present;
- The chemical composition (i.e. proportion of ash, water, hemicellulose, cellulose and lignin) of the biomass feedstock has a direct impact upon the physical nature of the biochar produced as it influences the degree of reactivity and, hence, the degree to which the physical structure is modified during processing;
- The surface area of biochars generally increase with increasing HTT until a temperature is reached at which deformation occurs, resulting in subsequent, dramatic decreases in surface area;
- High heating rates, increased pressure, high HTT, high ash contents (or low ash melting points) and long retention times (in combination with high temperatures) have all been held accountable for the loss of surface area and porosity in biochar type products;
- Pore sizes distributed in the micropore range make the greatest contribution to the total surface area of biochar materials;
- Heating rates determine the extent of micropore formation;
- Although micropore surface areas are significantly larger than macropore surface areas in biochars, macropore volumes can be larger than micropore volumes. It is possible that these broader volumes could result in greater functionality in soils than narrow surface areas;
- Linear shrinkage of the particles being pyrolysed can be seen to take place in conjunction with the loss of volatile matter;
- Due to both shrinkage and attrition during pyrolysis, particle sizes of the organic matter feedstock are likely to be greater than the resultant biochar;
- The faster the heating rate required, the smaller the feedstock particles need to be to facilitate the heat and mass transfer of the pyrolysis reactions. Fast pyrolysis feedstocks, for example, often are pre- processed to a fine dust or powder; therefore, the resultant biochar is very fine;



- The solid density of biochar increases with increasing HTT and longer heating residence times, in accordance with the conversion of low-density disordered C to higher-density turbostratic and graphitic C;
- Increase in solid density is accompanied by a decrease in apparent densities as porosity develops during pyrolysis; and
- Biochars can be physically or chemically activated to enhance physical and adsorptive properties. Surface areas increase with activation time, temperature and quantity of steam used.

The review of the physical structures of biochar-like materials also highlighted areas deserving more focused research efforts. Some of these gaps in the literature were filled in the chapter by synthesis of original experimental data. This includes scanning electron microscope (SEM) imaging of poultry litter biochars, bulk density and particle size distribution assessments for a range of biochar feedstocks and process conditions.

A clear understanding of the physical attributes of biochar materials, and how they can be influenced with feedstock selection and processing conditions, is essential if biochar products are to be optimized for maximum functionality in soils and for C storage. The Chapter identifies some desired characteristics for biochars, including; both macro and micro surface area, molecularly stable C structures, particle size distributions that are not very fine, and with high solids yields. This finding points to the selection of slow-pyrolysis technology from the range of thermal conversion technologies on offer.

When slow-pyrolysis technology is utilised for bioenergy and biochar production the following benefits can be achieved (Downie *et al.*, in press):

- Generating renewable, distributed energy and improving energy security;
- Mitigating greenhouse gases and sequestering carbon;
- Recycling nutrients back to agricultural land while increasing soil carbon levels;
- Increasing the sustainability of agricultural production through enhancing soil properties, hence improving food security;
- Improving land use outcomes through minimising waste going to landfill; and
- Ensuring air quality and human health through strict environmental and operational standards.

The benefits achievable, however, need to be considered in regard to the risks posed by biomass feedstock sourcing, biochar production and use. The risk assessment work presented in Chapter 3 addresses hazards that pose a potential threat to environmental, social, economic and human health if not adequately managed. However, the work goes beyond this typical scope to also include threats to the GHG benefits of the technology. If the technology is to be employed as a geo-engineering solution to combat climate change then ensuring the GHG mitigation potential of the technology is achieved is a key factor. For example, areas identified as a possible risk to the GHG balance across the system were the recalcitrance of the biochar in a given soil system, and hence its ability to withhold the C it contains from the atmosphere, and also the impact of the biochar once it was added to the soil. If the biochar had adverse effects on soil properties any environmental gains made in other areas would have to be discounted. For example, if it accelerated the turnover of native soil C, hence causing a net release of GHG emissions.

The net GHG abatement achieved via biochar production and use are offset, or discounted, by various steps along the biochar production lifecycle. Some aspects identified in the chapter include:

- Use of fossil fuels for harvesting, transporting and processing;
- Fugitive emissions from feedstock degradation whilst being stored or pre-processed;
- Emissions from the processing plant, such as uncombusted syngas; and
- Land use change, for example biomass requirements provide a market for more purpose grown organics that may result in deforestation.

The synthesis of the potential risks to the GHG mitigation potential of biochar production highlights several technology considerations that should be optimised to ensure carbon negative balances are achieved, these include:

- Energy efficiency of processes;
- Emissions control, including utilisation of syngas;
- Limited distances for feedstock collection and product distribution; and
- Alternate, higher, uses of organics are fully considered to ensure sustainable utilisation of feedstocks e.g. waste organics are sourced over purpose grown feedstocks.

One tool to be used for assessing the long-term risks of applying charred organic matter to soil is through the investigation of ancient sites where such a practice has been undertaken. The discovery and investigation of *Terra Preta Australis* presented in Chapter 4 is highly significant to the research field. The paper quantifies, through an extensive experimental program, the impact that the anthropological activity that occurred many hundreds of years ago has had on soil fertility and C levels. These Cumulic Anthrosols are recognised as not simply oven mounds, but as examples of an Australian dark earth, for which we suggest and justify the title of *Terra Preta Australis*. This nomenclature has been derived from the Portuguese, Terra Preta or dark earth, to demonstrate the analogy between these soils and those created by pre-columbian Indians in the Amazon basin that are widely studied by biochar researchers. These soils however, may justify a unique name that reflects their Australian aboriginal origin.

To date, the relevance of these Australian anthropogenic oven mounds, or kitchen middens, to long-term C sequestration and soil fertility has not been investigated. This discovery provides a case study for anthropogenic addition of charred organic materials and their long-term impact on the soil system, under Australian environmental conditions, over a long-term. The findings of this investigation were considered in light of today's pressing issues of climate change, food security and agricultural sustainability.

The work demonstrates that Australian agricultural soils are suitable precursors of *Terra Preta* formation and that C and fertility levels are not necessarily limited to the upper limits of levels found in the native soil. It therefore redefines the potential of Australian soils to store carbon. If an increase of 4% points in soil C (i.e. an increase from 1% C to 5% C), a level observed possible in *Terra Preta Australis* sites discovered, was achieved through the application of biochar to all of Australia's 42 million ha of cropped soils to a 30 cm depth, 7.5 Gt of solid C or 27 Gt of CO<sub>2-e</sub> would be sequestered. Considering that Australia's net greenhouse gas emissions across all sectors totalled 576 Mt CO<sub>2-e</sub> in 2006, 27 Gt represents 48 years of Australia emissions at this level (Downie *et al.*, 2011). A 10 cm incorporation depth may be more practical from an applications perspective. Incorporation to this depth only would reduce the potential sequestration of 2.5 Gt of solid C or 16 years of Australia's emissions at 2006 levels.

These C sequestration calculations based on the soil C levels, achieved by the *Terra Preta Australis* examples, indicate that biochar could represent a very significant global sink for atmospheric C, which could be anthropogenically managed on the immense scale required to reduce atmospheric C levels.

The extensive characterisation of *Terra Preta Australis* will accelerate our understanding of biochar's potential in the Australian environment and in other soils in temperate regions. The characterisation also provides a reference to compare the new biochars produced with those that have been in the soil ecosystem for hundreds of years. Knowledge of how to improve soil traits provides the opportunity to enhance the sustainability of agriculture and, hence, enhance ongoing food security.

The *Terra Preta Australis* investigation demonstrates that it could be the sustainable sourcing of biomass and the logistics of biochar production, rather than the capacity of soils to beneficially hold biochar, limits the sequestration potential of this technology. Via extrapolating the data of sequestration achieved by this limited number of soil samples to all cultivated soils in Australia, the potential to sequester C is demonstrated to be very large. It should however be noted that the potential of cultivated soils is likely to vary greatly and hence the actual achievable quantity of sequestration is likely to be different to that presented.

The commercial framework surrounding biochar production, such as sustainable feedstock sourcing from existing industries, capital installation required, operating costs, production methods and markets has been developed in Chapter 5. The development of industry case studies for pulp and paper, municipal greenwaste and intensive livestock have identified the organics feedstocks that might be available for biochar manufacture, the benefits and disadvantages of their use and the possible options for integrating with existing operations in that industry. It was found that all of these industries are presented with significant opportunities to achieve higher rates of resource recovery and energy efficiency by incorporating biochar production technology into their existing operations. The biochars from each industry will have distinct properties due to the unique composition of feedstocks available from each. Biochar produced will therefore be able to access different markets due

to the different soil constraints they may address and locations at which they will be produced.

To complement the case studies the agronomic benefits of biochars produced from these industries needs to be understood. The agronomic values of biochars derived from these three industries have therefore been assessed in three individual papers; *Greenwaste biochar as a soil amendment* (Chan et al., 2007) (Appendix A), *Using poultry litter biochars as soil amendments* (Chan et al., 2008) (Appendix B), and *Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility* (Van Zwieten et al., 2010b) (Appendix C). Each of these papers uses an extensive and scientifically rigorous experimental program to understand the unique chemical and physical characteristics of biochars derived from the different industrial sources. The investigations then examine the response of plant growth in fully replicated, biometrically designed pot trials.

The key findings of the agronomic assessments of these industry derived biochar products include:

#### Biomass Yields -

- Both poultry litter derived biochars examined significantly increased total dry matter (TDM) of radish in a hardsetting Chromosol (Alfisol). The yield increased from 142% of the control at 10t/ha application rate, to 196% with biochar application at 50t/ha;
- The poultry litter biochars were found to have plant available N, with increases in TDM with biochar plus N fertilizer compared to fertilizer alone; they also contained significant amounts of plant available P;
- The non-activated 450°C poultry litter derived biochar had a greater TDM response than the 550°C biochar, probably due to higher available P content;
- The papermill waste derived biochars revealed both positive and negative responses in biomass production;
- Wheat, radish and soybean grown with the alkaline biochar amendments performed well when used in conjunction with fertiliser in the acidic Ferrosol with the greatest increase of a 2.5-fold increase in wheat yield compared to the control. Radish was also significantly increased in the Ferrosol with biochar without fertilizer;
- In the alkaline Calcarosol the alkaline papermill derived biochar in the presence of fertilizer significantly reduced biomass production of wheat and radish treatments;

- Soybean biomass production in both the Calcarosol was not affected by papermill waste derived biochar in the absence of fertilizer, however a significantly positive interaction with biochar and fertilizer was observed;
- Radish grown in Calcarosol yielded more biomass when amended with the papermill biochar, with the lower pH biochar giving the most significant result;
- Greenwaste derived biochar applied to an Alfisol for radish production did not show significant increase in TDM compared with the control when no N-fertiliser was applied;
- Greenwaste derived biochar was shown to have a significant interaction with N-fertiliser resulting in increases in TDM yields of up to 266% at the highest biochar rate; and
- A small but significant reduction in radish growth in Alfisol was observed for when biochar was applied at the lowest application rate of 10 tonnes per hour.

#### Soil Chemical and Physical Changes -

- Application of poultry litter biochars significantly changed all the measured chemical parameters of Alfisol - increased EC, pH, total N, total C, Colwell P, exchangeable cations (Ca, Mg, Na, and K), and effective cation exchange capacity, but decreased exchangeable Al;
- In Alfisol the greenwaste derived biochars increased pH, organic C, and exchangeable cations;
- In Ferrosol both papermill waste derived biochars significantly increased pH, CEC, exchangeable Ca and total C, while in Calcarosol both biochars increased C, while biochar 2 also increased exchangeable K;
- Application of the all greenwaste and poultry litter derived biochars significantly reduced soil strength of the hardsetting Chromosol (Alfisol); and
- The liming effect of the papermill and poultry litter derived biochars increased soil pH and reduced exchangeable Al to below detection limits.

#### Earthworm, germination and Microbiological response -

- Earthworms demonstrated a preference for non-activated 450°C poultry litter derived biochar over activated 550°C biochar and non-amended Alfisol;
- Distinct preference by the worms were observed for papermill waste derived biochar amended Ferrosol compared to the controls, but no preference when the same biochar was used to amend Calcarosol;
- A measure of the microbiological activity of the greenwaste derived biochar amended Alfisol by FDA showed significant reductions compared to the controls, however the dramatic reductions caused by N-fertilizer application were significantly remediated by biochar application at the higher rates;
- Germination of wheat in Ferrosol was significantly improved in the presence of papermill derived biochar however this biochar did not affect the germination of soybean or radish, and did not affect the germination of wheat in Calcarosol;
- Poultry litter derived biochar was found to significantly increase microbial biomass C of the Alfisol, however the different processing conditions of the biochars resulted in significantly different responses;

Observed changes in biological properties, namely microbial biomass and earthworm preference, are interesting as they highlight the potential of biochars to change the soil biology and therefore ecosystem functioning of the soil. This is an area of research that is likely to attract further attention in future due to the highly significant but complex and largely unexplained influences being observed and published.

The inclusion of ecotoxicity type testing, such as germination and OECD earthworm avoidance testing is an important aspect of this research. The utilization of these tests was a risk management strategy proposed in the paper *Biochar as a Geo-engineering Climate Solution: Hazard Identification and Risk Management* (Downie et al., in press) (Chapter 3 of this thesis). This is especially important for industrial organic waste derived biochars, such as those derived from poultry litter and papermill waste, as the risk of contamination exists in these intensive processes.

The different effects of the two poultry litter biochars made from the same feed material, but under differing process conditions, highlight the importance of understanding and reporting processing conditions with experimental work and the opportunity presented for



optimizing processing conditions for maximized agronomic performance. The papermill waste derived biochar, where two biochars were made from differing proportions of waste organics giving significantly different crop response outcomes, show that feedstock composition and source is also a critical factor in describing biochar products. The papermill waste derived biochar experiment highlights that the same biochar will have different impacts according to the type of soil that it is applied to and the plant species cropped. Therefore, the successful application of biochar for enhanced soil properties and crop productivity needs to include careful selection of a biochar product that has properties that will address the particular soil constraints according to the needs of the specific plant species. For example, a lower temperature poultry litter biochar may be the choice for a soil and crop system that is limited by available P, alternatively a papermill waste biochar might be selected for beneficial use in a soil that is limited by Al toxicity.

All three of the pot trial experiment publications provided some evidence of significant fertilizer with biochar interactions. It is evident that biochar can improve the efficiency of use of N-fertilizer by the crop. This raised the question, as to how much fertilizer application could be reduced by when biochar was in the soil to achieve the same biomass yield or crop response? Using the results from this initial work as the basis for the experimental design, a further experiment was conducted to provide some insight. The peer-reviewed publication of this second stage experiment, *A glasshouse study on the interaction of low mineral ash biochar with nitrogen in a sandy soil* (Van Zwieten *et al.*, 2010a), is presented here as Appendix E. This demonstrated that significantly less N-fertiliser could be applied to achieve the same crop response when biochar was incorporated into the soil.

The ability to reduce N-fertiliser application does not only have a significant impact on the costs associated with growing the crop, but it also has a significant impact on the GHG balance. N-fertiliser is made via a GHG intensive process (Wood and Cowie, 2004). In addition to this, when it is added to soils a portion of the N is volatilised as the potent GHG nitrous oxide (N<sub>2</sub>O). Some literature indicates that biochar in soils decreases N<sub>2</sub>O emissions from the soil (Van Zwieten *et al.*, 2009). The relationship between these two findings has the potential to make a significant contribution to agricultural GHG emissions. Therefore, an experimental program was conducted to further investigate the relationship between biochar in soils and GHG emissions from those soils. Appendix F of this thesis presents the

paper publishing the findings of this work, titled *Influence of biochars on flux of N<sub>2</sub>O and CO<sub>2</sub> from Ferrosol (Van Zwieten et al., 2010c)*. The key finding of this investigation was that biochars produce by the slow-pyrolysis of greenwaste, poultry litter and papermill, and biosolids could significantly reduce N<sub>2</sub>O emissions from and acidic Ferrosol.

An additional pathway by which N can leave the soil system and not be available to the crop is via leaching. The book chapter, titled *Biochar effects on nutrient leaching* is included as Appendix H of this thesis. The adsorptive properties, especially of high surface area biochars, have been shown to retain nutrients, preventing them from readily leaching from the soil profile.

The impact of biochar on crop productivity, soil properties, N-fertiliser use efficiency and soil GHG emissions can only be tested to a limited degree via pot trials. The relevance however to application in a commercial agricultural business requires more extensive in-field trials to be demonstrated. Appendix G of this thesis presents the results of one such in-field trial, titled *Productivity and nutrient availability: the role of biochar in a high input annual ryegrass (Lolium multiflorum) pasture on a red Ferrosol*. One of the most significant findings of this work was that in addition to the increases in soil C attributed directly to the C added as biochar, more sequestration was achieved via retention of labile C by the biochar in the soil system.

The stabilisation of labile C, both in the soil system as discussed above or in waste organics such as animal manure and crop residues, into terrestrial sinks can provide a significant contribution to reducing concentrations of GHG. To incentivize these activities greenhouse gas methodologies for the accounting of this C balance need to gain accreditation. The paper on GHG balance methodologies presented as Chapter 6, is intended to make a positive contribution to justifying both the choice and accuracy of the methodologies to be used. It was found that the stock method, which aims to account for only the biomass C that is removed from the short-term carbon cycle, is the preferred method the accounting required to compile inventories. However, when this method is applied to abatement projects it is possible that the release of biomass C as CO<sub>2</sub> in the project case, which would have been released as non-CO<sub>2</sub> GHG in the business-as-usual scenario, can result in inaccuracies. Therefore, an additional term has been derived for inclusion in the methodology when it is

applied to projects that abate non-CO<sub>2</sub> GHG emissions. For example, when a biochar production project is used as an alternative treatment for waste organics that are currently going to landfill and producing significant quantities of methane, the biochar production method will offset methane production, however this will result in some of this methane being released as CO<sub>2</sub>. A calculation that only takes into account the stored C will result in an inaccurate prediction of the GHG abatement achieved. A method has therefore been developed and proposed that accurately achieves this abatement calculation without requiring the onerous accounting task of having to consider all biogenic C emissions.

Biochar has been demonstrated throughout this thesis to provide multiple pathways for greenhouse gas sequestration and mitigation. An overview of the contribution that biochar can make along with extensive discussion of the mechanisms for action has been compiled in the book chapter, titled *Biochars in soil for climate mitigation and adaptation*, presented as Appendix G of this thesis. This chapter acknowledges the need for thorough life cycle analysis of biochar production and use systems to develop a holistic understanding of the true greenhouse gas implications. Although some aspects of biochar use may result in leakage of the abatement, such as the increased need for biocides or native soil carbon loss, there are many factors that positively contribute to the greenhouse gas mitigation benefits of the technology.

## Recommendations

Well-engineered, slow-pyrolysis technology, optimized for the production of bioenergy and biochar from sustainable feedstocks, could deliver significant environmental and economic advantages to existing industries. Industries that manage non-contaminated organic wastes and have on-site power requirements could especially benefit. It is recommended that these industries be targeted for industrial scale commercialisation of biochar production technology.

Utilisation of biochar products as a soil amendment could contribute to ongoing food security and agricultural productivity, however it is possible for some biochars to pose adverse risks to the natural environment and hence need to be adequately managed. Biochar production and sequestration can result in the net removal of greenhouse gases from the atmosphere, making the technology a potentially valuable tool for climate change mitigation. Careful consideration of the entire lifecycle of the production process needs to be made, however, if the true net benefit of the technology is to be understood. It is recommended that the emerging biochar production industry is well regulated and that quality assurance and sustainability mechanisms are adopted. This will optimize the net benefit of the technology.

A research focus on the sustainable harvesting of biomass and environmentally responsible production of biochar will assist in understanding the potential of biochar to mitigation atmospheric concentrations of GHG. As the *Terra Preta Australis* investigation indicates, these will be the limiting factors, rather than the capacity of biochar to be stored beneficially in the landscape.

Further demonstration of biochar in larger scale field trials is required to further understand the commercial relevance of the technology to agricultural industries. It is recommended that biochar trials attempt to cover a range of biochar feedstocks, process conditions, soils, crops and climate regions, as all of these have been demonstrated in this thesis to have significant influence on the ability of biochar to enhance productivity. Likewise, biochar application should be targeted to address specific constraints in the soil system for maximised success. This work has demonstrated that biochars can have diverse chemical

and physical properties and hence are able to be tailored to the needs of a soil system for greatest benefit. It is recommended that future research programs seek to understand the fundamental characteristics of a biochar product and directly target this to remediate one or more limitations or constraints of the soil in commercial production systems.

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## Appendices

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*Appendix A - Agronomic values of greenwaste biochar as a soil amendment*



## Agronomic values of greenwaste biochar as a soil amendment

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**Abstract.** A pot trial was carried out to investigate the effect of biochar produced from greenwaste by pyrolysis on the yield of radish (*Raphanus sativus* var. Long Scarlet) and the soil quality of an Alfisol. Three rates of biochar (10, 50 and 100 t/ha) with and without additional nitrogen application (100 kg N/ha) were investigated. The soil used in the pot trial was a hardsetting Alfisol (Chromosol) (0–0.1 m) with a long history of cropping. In the absence of N fertiliser, application of biochar to the soil did not increase radish yield even at the highest rate of 100 t/ha. However, a significant biochar × nitrogen fertiliser interaction was observed, in that higher yield increases were observed with increasing rates of biochar application in the presence of N fertiliser, highlighting the role of biochar in improving N fertiliser use efficiency of the plant. For example, additional increase in DM of radish in the presence of N fertiliser varied from 95% in the nil biochar control to 266% in the 100 t/ha biochar-amended soils. A slight but significant reduction in dry matter production of radish was observed when biochar was applied at 10 t/ha but the cause is unclear and requires further investigation.

Significant changes in soil quality including increases in pH, organic carbon, and exchangeable cations as well as reduction in tensile strength were observed at higher rates of biochar application (>50 t/ha). Particularly interesting are the improvements in soil physical properties of this hardsetting soil in terms of reduction in tensile strength and increases in field capacity.

**Additional keywords:** charcoal, char, agrichar, soil strength, soil carbon sequestration, hardsetting soil, slow pyrolysis.

### Introduction

Biochars refer to the high carbon materials produced from the slow pyrolysis (heating in the absence of oxygen) of biomass. Chars and charcoal-like materials occur naturally in soils and are considered part of the soil organic carbon pools (Skjemstad *et al.* 1996). High fertility associated with the anthropogenic soils, *terra preta*, in the Amazon has been related to the high content of organic carbon in the form of char and the practice of ‘slash and char’ by the pre-Columbian indigenous people of the Amazon (Glaser *et al.* 2001). Recently, there has been much interest in biochars, which is driven by 2 major global issues: climate change and the realisation of the need for more sustainable soil management. First, artificially produced biochar is a product of the renewable-energy-focused pyrolysis technology which produces biofuel to displace fossil fuel use. Apart from the carbon offset due to the production of biofuel, the relatively stable nature of biochar material also could have carbon sequestration value (Lehmann *et al.* 2006). Second, biochars can potentially be used as soil amendments for improving the quality of agricultural soils (Glaser *et al.* 2002a, 2002b; Lehmann *et al.* 2003). The long turnover time and therefore the inert nature of biochar has often been emphasised for this purpose.

As pointed out by Day *et al.* (2004), using biochar to sequester carbon in agricultural land as a way to combat climate change can only be accomplished economically if the sequestered C has

beneficial soil amendment and/or fertiliser values. Currently, very little biochar material is being used in agriculture in Australia and elsewhere. Therefore, in the future development of agricultural markets for biochars, agronomic values of these products in terms of crop response and soil health benefits need to be quantified. Beneficial effects of biochar in terms of increased crop yield and improved soil quality have been reported (e.g. Iswaran *et al.* 1980; Glaser *et al.* 2002a, 2002b). However, review of previous research showed a huge range of biochar application rates (0.5–135 t/ha of biochar) as well as a huge range of plant responses (–29–324%) (Glaser *et al.* 2002a). More importantly, in much of this research, properties of the biochar used in the investigation were not reported. Biochars can be produced from a range of organic materials and under different conditions resulting in products of varying properties (Baldock and Smernik 2002; Nguyen *et al.* 2004; Guerrero *et al.* 2005). Little research has been published elucidating the mechanisms responsible for the reported benefits of the biochars on crop growth, production, and soil quality. Such understanding is essential for development of agricultural markets for biochars and for the future development of technology for the production of biochar products with improved quality and value.

Greenwaste refers to the plant pruning and grass clippings collected from parks, gardens, and agricultural fields which have traditionally been disposed of by burning and landfilling.

While conversion of these materials to compost has been a much-promoted option, currently only a very small amount of the products is being used in agriculture in Australia, e.g. only 4% of compost products is being used in agriculture in New South Wales due to various market barriers including high transport costs (Dorahy *et al.* 2005; Chan *et al.* 2007). Little is known of the agronomic value of biochar produced from greenwaste. In this paper, we report results of a research project designed to assess the agronomic value of biochar produced from greenwaste on plant yield and soil quality in a glasshouse pot experiment.

## Materials and methods

### Soil

The soil was collected from the Flat Paddock at the Centre for Recycled Organic in Agriculture (CROA) site, Menangle, near Camden (70 m AHD; 02883278E, 6224546N), NSW. The soil was an Alfisol (a Chromosol according to Australian Soil Classification; Isbell 1996). It is a typical agricultural soil of NSW and the site had a long history of cropping. The hardsetting A horizon had low soil organic carbon concentration and was acidic, with pH<sub>Ca</sub> of 4.5 (Table 1). A composite sample was collected from the 0 to 0.1 m layer, brought back to the laboratory, and sieved through a 6-mm aperture sieve.

### Biochar

The feedstock of biochar was greenwaste which was a mixture of grass clippings, cotton trash, and plant prunings. It was manufactured at a temperature of around 450°C in a low temperature pyrolysis plant by BEST Energies Australia. The temperature was chosen based on the recommendation of Day *et al.* (2004) on the manufacturing of biochar for soil amendment purposes. The biochar was alkaline in nature, high in total carbon but low in total nitrogen (1.3 g/kg), with C/N of 200 and extremely low in mineral nitrogen (<0.5 mg/kg) (Table 1).

### Pot trial

The experiment was carried out in a temperature-controlled glasshouse (20–26°C). The experimental design used was factorial randomised block design with 5 replications. Four biochar rates (0, 10, 50, 100 t/ha) combined with 2 nitrogen fertiliser rates (0, 100 kg/ha) were used.

Air-dried soil and biochar-amended soils (1.25 kg oven-dried equivalent) were packed into black plastic cylindrical pots (14 cm i.d. by 14.5 cm tall) to achieve a bulk density of 1.2 Mg/m<sup>3</sup>. Nitrogen fertiliser (NH<sub>4</sub>NO<sub>3</sub>), in solution was

added in equivalent amounts to half of the pots. All the pots were then wetted up to field capacity using de-ionised water. Ten seeds of radish (*Raphanus sativus* var. Long Scarlet) were planted in each pot and thinned to 5 seedlings after emergence. The pots were placed in a shallow tray and regularly watered to maintain water content at approximately field capacity throughout the duration of the experiment. Radish was chosen for the pot trial because it is the indicator plant used for assessing composts, soil conditioners, and mulches (Standards Australia 2003).

### Soil, biochar, and plant analyses

At the completion of the pot trial (6 weeks), the whole radish plants were harvested by removing them from the individual pots. The plants were washed with de-ionised water, and oven-dried at 70°C to constant weight before weighing to determine the dry matter production.

After harvesting, the soil from each pot was air-dried at 36°C, mixed thoroughly, and crushed gently to pass through a 4-mm sieve. A subsample was ground further to pass through a 2-mm sieve. The samples <2 mm were then analysed for pH, total carbon, total nitrogen, extractable phosphorus (Colwell), and exchangeable cations following Rayment and Higginson (1992); pH was measured in 1:5 soil/0.01 M CaCl<sub>2</sub> extract; total carbon and total nitrogen were measured by combustion method; extractable phosphorus was determined by Colwell method and exchangeable cations were determined using the Gillman and Sumpster method. Soil water content at field capacity (–10 kPa) and permanent wilting point (–1.5 MPa) were determined on <2 mm soil samples using tension plate and pressure plate techniques respectively. The fluorescein diacetate hydrolysis test (FDA test) for microbial activity (based on Schnurer and Rosswall 1982) was carried out on samples <2 mm after re-wetting and equilibrating the samples at field capacity soil water content. Hydrolysis of fluorescein diacetate was assayed using a modified method described by Zelles *et al.* (1991).

### Soil tensile strength determination

Air-dried soil samples (<4 mm) collected after the pot trial from all the different biochar rates treatments (only nil N treatments) were quickly wetted by pouring into perspex soil cylinders (2.5 cm i.d. by 1.4 cm height), which were immersed in water in a shallow tray. After 4 h of equilibration, the soil cylinders were drained to remove free water and dried at 40°C to constant weight. The soil cylinders were then crushed between parallel plates to determine the crushing force. The tensile strength (T, in

**Table 1.** Basic chemical properties of the soil and biochar used in the pot trial experiment

EC (dS/m)	pH CaCl <sub>2</sub>	Colwell P	KCl-extract. ammonium-N (mg/kg)	KCl-extract. nitrate-N	N (g/kg)	C (g/kg)	Al	Exchangeable cations (cmol/kg)					CEC
								Ca	K	Mg	Na		
0.05	4.5	34	6.1	12	<i>Soil</i>								7.7
3.2	9.4	400	<0.30	<0.20	<i>Char</i>								24

kPa) of soil cylinder was calculated using the equation (Dexter and Kroesbergen 1985):

$$T = 2F \times 98.1/(\pi DL)$$

where  $F$  is crushing force (kg),  $D$  is diameter of soil cylinder (cm), and  $L$  is height of soil cylinder (cm). Each treatment was replicated 8 times.

The tensile strength determination is a soil strength measurement and was used here to compare the biochar treatments in term of their effect on soil hardsettingness (Mullins *et al.* 1990).

### Statistical analyses

All data were analysed by 2-way analyses of variance using GENSTAT 9.1 (Lawes Agricultural Trust 2006). The treatment means were compared using least significant differences for the main effects of biochar and nitrogen fertiliser as well as their interactions. Unless otherwise stated, differences were significant at  $P = 0.05$ .

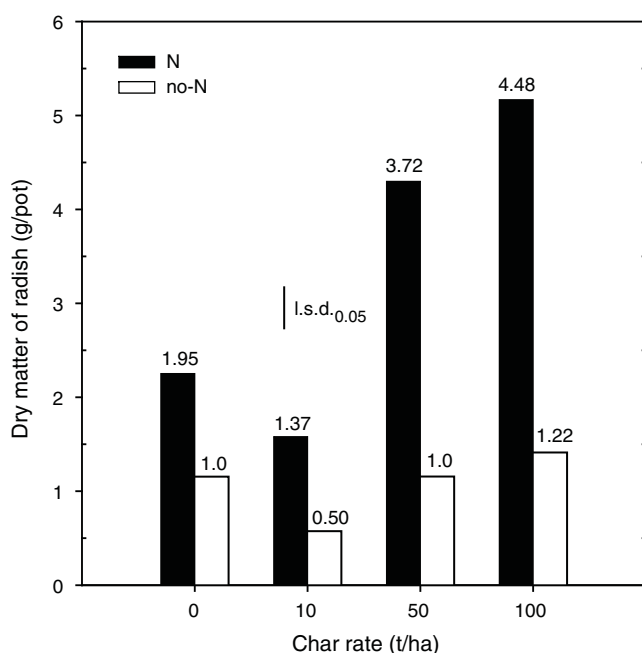
## Results

### Plant responses — dry matter production

In the absence of nitrogen fertiliser, application of biochar made from greenwaste did not increase the dry matter (DM) production of radish even at the highest rate (100 t/ha) (Fig. 1). Instead, at 10 t/ha of biochar, yield was slightly depressed compared with the nil biochar control. With the addition of nitrogen fertiliser (100 kg N/ha), significant increases in radish yield were observed in all the biochar treatments

(including the nil biochar control), and there was a significant interaction between biochar application rates and nitrogen fertiliser addition. The latter refers to the observation that the increases in DM of radish with nitrogen addition were much greater in the biochar-amended soils than the nil biochar control and that the magnitude of yield response increased with the application rate of biochar. For example, additional increase in DM of radish due to N fertiliser varied from 95% in the nil biochar control to 266% in the 100 t/ha biochar-amended soils (Fig. 1). Interestingly, the depression in yield at 10 t/ha of biochar was not eliminated by the addition of N fertiliser. When the DM results are expressed as relative yield (RY), namely DM of a treatment as a proportion of DM of the control (nil biochar and nil N), RY was 0.5 at 10 t/ha and did not increase significantly above 1.0 at higher rates of biochar application in the absence of N fertiliser (Fig. 1). With N fertiliser addition, RY of radish increased to 1.95 at nil rate of biochar and this increase could therefore be attributed to the N fertiliser alone. It has been estimated that for biochar rates >20 t/ha, RY exceeded 2.0 and finally increased to 4.5 at 100 t/ha of biochar (Fig. 1). Therefore, there was an additional yield increase as a result of increased biochar application for rates >20 t/ha which could not be solely attributed to the addition of N fertiliser.

Plant tissue analyses of radish revealed significantly higher nitrogen concentration as a result of N fertiliser application (mean of 6.27 v. 2.17%) (Table 2). Without N fertiliser, N content of radish remained <3% but this increased to >6% in the presence of N fertiliser. This and the marked DM responses of radish plants to N fertiliser (95% increase in DM at nil biochar treatment) (Fig. 1) indicated that the soil was limiting in N. Given the low N content (1.3 g/kg), negligible mineral N, and high C/N ratio (200) of the biochar used in this investigation (Table 1), its addition to soil did not provide any additional available nitrogen to the radish plants, and therefore did not result in yield increase even at the rate of 100 t/ha. This is further confirmed by the results for N uptake by radish, in that N uptake remained low and unchanged at different biochar rates in the absence of N fertiliser but increased markedly as a result of N fertiliser application (Table 3). Biochar application increased P, K, and Ca but not Mg concentration of the radish plants and significant increases were found only at the higher application rates of 50 and 100 t/ha (when no N was applied) (Table 2). The increase in P and K contents of the radish plants growing in biochar-amended soil was related to the high concentrations of available P and exchangeable K present in the greenwaste biochar (Table 1). As N is principally taken up as  $\text{NO}_3^-$  and is a dominant nutrient, its uptake has to be balanced by cations to maintain electrical neutrality. From nutrient uptake data (Table 3), increasing N uptake at higher biochar rates was accompanied by increased K and to a lesser extent Ca uptake, it is therefore clear that K was the dominant counter cation. The lower P concentration of the radish plants found in the presence of N fertiliser (compared with nil N fertiliser) (Table 2) was a dilution effect due to the larger DM production. This is confirmed by the P uptake results which indicated higher uptake at higher biochar rates in the presence of N fertiliser. Mg concentration of the radish plants was fairly similar at all different rates of biochar application but a slight reduction was detected at 10 t/ha in the absence of N and at 50 t/ha in the presence of N fertiliser (Table 2).



**Fig. 1.** Dry matter production of radish with and without nitrogen fertiliser as a function of rate of biochar. Numbers on top of bar refer to relative yield, i.e. DM of a treatment as a proportion of DM of the control (nil biochar and nil N).

**Table 2. Nutrient concentration (%) of radish plants grown in biochar-amended soils at different rates and with and without N fertiliser**  
Within rows, means followed by the same letter are not significantly different ( $P > 0.05$ ); n.s., not significant ( $P > 0.05$ ); \* $P < 0.05$ , \*\* $P < 0.01$ , \*\*\* $P < 0.001$

Biochar rate:	Nil N				N				Significance level		
	0	10	50	100	0	10	50	100	Biochar rate	N	Biochar $\times$ N
				(t/ha)							
N	2.11c	2.78b	1.85c	1.94c	6.66a	6.23a	6.08a	6.08a	**	***	***
P	0.25d	0.24d	0.53b	0.62a	0.16e	0.16e	0.21d	0.31c	***	***	***
K	2.67d	2.44de	3.40c	3.75bc	2.17e	2.62d	3.86b	5.88a	***	***	***
Ca	1.32c	1.26c	1.59b	1.61ab	1.50b	1.63ab	1.38c	1.72a	*	**	**
Mg	0.32b	0.28c	0.35ab	0.36ab	0.37a	0.39a	0.32b	0.37a	n.s.	*	***

**Table 3. Uptake of nutrients (g) by radish plants grown in biochar-amended soils at different rates and with and without N fertiliser**  
Within rows, means followed by the same letter are not significantly different ( $P > 0.05$ ); \*\*\* $P < 0.001$

Biochar rate:	Nil N				N				Significance level		
	0	10	50	100	0	10	50	100	Biochar rate	N	Biochar $\times$ N
				(t/ha)							
N	0.024e	0.015e	0.021e	0.027e	0.151c	0.098d	0.263b	0.323a	***	***	***
P	0.003de	0.002e	0.006c	0.009b	0.004d	0.002e	0.009b	0.016a	***	***	***
K	0.031cd	0.013d	0.039cd	0.052c	0.050c	0.041cd	0.168b	0.301a	***	***	***
Ca	0.015de	0.007e	0.019d	0.023d	0.033c	0.025d	0.059b	0.088a	***	***	***
Mg	0.004e	0.002f	0.004e	0.005cd	0.008c	0.006d	0.014b	0.019a	***	***	***

#### Soil quality changes

Changes in a range of soil chemical properties as a result of different rates of biochar application, as measured at the end of the pot experiment, are presented in Table 4. The changes included increases in pH, organic carbon, and exchangeable Na, K, and Ca as well as extractable P but decreases in exchangeable Al. The magnitude of changes was roughly proportional to the rate of biochar application (e.g. increases with increasing rate of biochar application). In many cases, statistical difference was detectable only in the higher rates, namely 50 and 100 t/ha of biochar application but not at 10 t/ha (Table 4). The pH increased by 1.22 (4.77 v. 5.99) between the nil char and 100 t/ha char treatment in the absence of N fertiliser and the

corresponding increase was 0.61 unit in the presence of N fertiliser. The pH increases were accompanied by significant reduction in exchangeable Al by >50% at the higher rates of biochar application, i.e. 50 and 100 t/ha (Table 4).

Tensile strength of the hardsetting soil under investigation decreased with increasing rate of biochar application (Table 5). However, no significant change was detectable at the low rate of 10 t/ha and significant reduction was only observed at 50 and 100 t/ha of biochar application. Field capacity of the biochar-amended soil increased with increasing rate of biochar application but significant increases were detected only at the higher rates of 50 and 100 t/ha of biochar (Table 5). Biochar application also had significant effect on soil biological activities

**Table 4. Changes in soil chemical properties as a result of different rates of biochar application with and without nitrogen fertiliser application**  
Within rows, means followed by the same letter are not significantly different ( $P > 0.05$ ); n.s., not significant ( $P > 0.05$ ); \* $P < 0.05$ , \*\* $P < 0.01$ , \*\*\* $P < 0.001$

Biochar rate:	Nil N				N				Significance level		
	0	10	50	100	0	10	50	100	Biochar rate	N	Biochar $\times$ N
				(t/ha)							
pH <sub>ca</sub>	4.77c	4.75c	5.38b	5.99a	4.58c	4.61c	4.75c	5.19b	***	***	***
C (g/kg)	21.6c	27.0c	43.4b	64.6a	21.2c	23.0c	42.4b	64.6a	***	n.s.	n.s.
Total N (g/kg)	1.7a	1.4a	1.5a	1.6a	—	—	—	—	n.s.	—	—
Ex. Na (cmol/kg)	0.60b	0.58b	0.74a	0.84a	0.48c	0.46c	0.60a	0.69b	***	***	n.s.
Ex. K (cmol/kg)	0.24f	0.40e	0.92c	1.60a	0.21f	0.39e	0.56d	1.30b	***	***	***
Ex. Ca (cmol/kg)	5.50b	5.18b	5.58b	6.30a	5.40b	5.28b	5.68b	6.20a	***	n.s.	n.s.
Ex Mg (cmol/kg)	1.84a	1.70b	1.86a	1.88a	1.80a	1.56b	1.76a	1.86a	**	***	n.s.
Ex Al (cmol/kg)	0.25a	0.23a	0.10b	0.10b	0.27a	0.29a	0.12b	0.10b	***	**	n.s.
eCEC (cmol/kg)	8.42c	8.08c	9.10b	10.60a	8.18c	7.96c	8.68b	9.94a	***	***	n.s.
Colwell P (mg/kg)	23.8c	26.6c	32.6b	40.8a	28.6c	24.6c	29.6b	40.8a	***	n.s.	*



**Table 5. Changes in soil physical and biological properties as a result of different rates of biochar application with and without nitrogen fertiliser application**Within rows, means followed by the same letter are not significantly different ( $P > 0.05$ ); n.s., not significant ( $P > 0.05$ ); \*\*\* $P < 0.001$ . NA, not available

Biochar rate:	Nil N				N				Significance		
	0	10	50	100	0	10	50	100	Biochar rate	N	Biochar × N
				(t/ha)							
FC (kg/100 kg)	0.255c	0.244c	0.270b	0.320a	0.252c	0.246c	0.270b	0.320a	***	n.s.	n.s.
Tensile strength (kPa)	64.4a	69.2a	31.7b	18.8c	NA	NA	NA	NA	***	—	—
FDA(μg fluorescein/g soil.min)	13.2a	11.3b	11.9b	11.5b	10.1c	8.6d	11.2b	11.2b	***	***	***

as indicated by FDA enzymatic test. The FDA test is a measure of microbiological activity based on enzymatic activities (Schnurer and Rosswall 1982). The highest microbial activity (highest FDA hydrolysed) was found in the nil biochar nil N soil. In the absence of N fertiliser, FDA hydrolysed was higher in the nil biochar soil. However, the reverse was true when N was applied, in that FDA was higher in the biochar-amended soils than the nil biochar control soil, with the exception of the 10 t/ha treatment, which had the lowest FDA of all treatments (Table 5).

## Discussion

### *Agronomic value of greenwaste biochar*

Biochar application did not increase radish dry matter yield even at the highest rate of application (100 t/ha). Given the low N content and high C/N (200) of the biochar, growth of radish in the biochar-amended soil alone was likely to be limited by N supply. This was confirmed by the large yield increase (95%) observed when N fertiliser was applied in the nil char treatment. The additional increases in radish yield observed at higher rates of biochar applications (50 and 100 t/ha) in the presence of N fertiliser (up to 266% in the case of 100 t/ha biochar application) indicated the potential of greenwaste biochar in increasing nitrogen fertiliser use efficiency of plants. This might be a consequence of the various improvements in soil quality detected in the biochar-amended soils. Particularly significant are the improvements in soil physical conditions of the soil, namely reduction in tensile strength and higher field capacity water content. Both improved the physical soil environment of this hardsetting soil (Mullins *et al.* 1990), rendering it a more favourable root growth environment and therefore increasing the ability of the plants to utilise the applied N, with the resulting increases in DM. The increases in pH and the corresponding reduction in exchangeable Al (Table 4) could also have improved the chemical environment of the biochar-amended soils for the radish plants. Furthermore, the increased DM of radish at higher biochar rates could partly be attributed to the increased supply of P and K in the biochar-amended soils when N was no longer limiting (i.e. in the presence of N fertiliser). The biochar used in the investigation was high in both of these nutrients (Table 1). From the pot trial results, we cannot identify the reason(s) for the negative yield observed at 10 t/ha of biochar application. However, it is interesting to point out that most of the positive changes in soil quality reported for the higher rates of biochar application, e.g. reduction in tensile strength, were not detectable at this low rate. Negative plant responses due to biochar application have been previously reported (Mikan and

Abrams 1995) and further research is needed to identify the cause(s).

### *Improvement in soil quality*

Results highlight the potential effectiveness of the greenwaste biochar as a soil conditioner for the hardsetting soil. The changes in soil properties, such as increases in organic carbon and pH and reduction in soil strength were consistent with the properties of the greenwaste biochar used in this investigation, which was alkaline and high in carbon content. The apparent contradictory effect of biochar on soil microbiological activities as indicated by the FDA test in the absence compared to the presence of N fertiliser could be related to short-term nature of the pot trial conditions and requires further research.

Hardsetting soils are very widespread in Australia, and it has been estimated there are around 100 Mha (Mullins *et al.* 1990), covering many of the agriculturally important soils, e.g. Chromosols, Sodosols. They are characterised by their fragile soil structural conditions and associated physical limitations to agriculture. Under cropping, SOC is often low, ~1%, and nitrogen fertiliser is a major input for crop production in these soils. Our results therefore highlight the potential benefits of biochar application in improving the quality of these soils, particularly in increasing the N fertiliser use efficiency of these soils. However, given the short-term nature of the pot trial, further research in field trials is needed to fully quantify the long-term benefits of using this biochar as soil amendment. Of particular interest is the stability of the carbon in the biochar in soil environment and hence the long-term soil carbon sequestration value. Field experiments are also needed to allow hypotheses to be tested that cannot be addressed under pot trial conditions. These include effects of biochar on soil biology, nutrient leaching/retention, and long-term soil structural changes. Some of the changes to biochar when applied to soils could have long-term significance to biogeochemical processes in soils, e.g. increases in cation exchange capacity in relation to nutrient cycling (Liang *et al.* 2006).

## Conclusions

Application of greenwaste biochar alone to a hardsetting soil did not result in significant increases in radish dry matter yield, even at the highest rate of application (100 t/ha). However, significantly yield increases additional to that due to N fertiliser were observed when biochar was applied together with the fertiliser, therefore highlighting the role of biochar in improving N fertiliser use efficiency. Our pot experiment results also

indicated significant changes in soil quality including increases in pH, organic carbon, and exchangeable cations as well as reduction in tensile strength at higher rates of biochar application (>50 t/ha) but field experiments are needed to confirm and quantify the long-term benefits.

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*Appendix B - Using poultry litter biochars as soil amendments*



## Using poultry litter biochars as soil amendments

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**Abstract.** Despite the recent interest in biochars as soil amendments for improving soil quality and increasing soil carbon sequestration, there is inadequate knowledge on the soil amendment properties of these materials produced from different feed stocks and under different pyrolysis conditions. This is particularly true for biochars produced from animal origins. Two biochars produced from poultry litter under different conditions were tested in a pot trial by assessing the yield of radish (*Raphanus sativus* var. Long Scarlet) as well as the soil quality of a hardsetting Chromosol (Alfisol). Four rates of biochar (0, 10, 25, and 50 t/ha), with and without nitrogen application (100 kg N/ha) were investigated. Both biochars, without N fertiliser, produced similar increases in dry matter yield of radish, which were detectable at the lowest application rate, 10 t/ha. The yield increase (%), compared with the unamended control rose from 42% at 10 t/ha to 96% at 50 t/ha of biochar application. The yield increases can be attributed largely to the ability of these biochars to increase N availability. Significant additional yield increases, in excess of that due to N fertiliser alone, were observed when N fertiliser was applied together with the biochars, highlighting the other beneficial effects of these biochars. In this regard, the non activated poultry litter biochar produced at lower temperature (450°C) was more effective than the activated biochar produced at higher temperature (550°C), probably due to higher available P content. Biochar addition to the hardsetting soil resulted in significant but different changes in soil chemical and physical properties, including increases in C, N, pH, and available P, but reduction in soil strength. These different effects of the 2 different biochars can be related to their different characteristics. Significantly different changes in soil biology in terms of microbial biomass and earthworm preference properties were also observed between the 2 biochars, but the underlying mechanisms require further research. Our research highlights the importance of feedstock and process conditions during pyrolysis on the properties and, hence, soil amendment values of biochars.

**Additional keywords:** hardsetting soil, char, soil carbon sequestration, earthworms, microbial biomass, poultry manure, pyrolysis.

### Introduction

Biochars refer to the carbon-rich materials produced from the slow pyrolysis (heating in the absence of oxygen) of biomass. Recently, there has been much interest in biochars as soil amendments to improve and maintain soil fertility and to increase soil carbon sequestration (Glaser *et al.* 2002a, 2002b; Lehmann *et al.* 2003). The latter can be attributed to the relative stable nature and, hence, long turnover time of biochar in soil is of particular relevance to the solution of climate change (Lehmann *et al.* 2006).

Currently, biochars are little used in agriculture in Australia and elsewhere in the world. Beneficial effects of biochar as a soil amendment in terms of increased crop yield and improved soil quality have been reported but the responses have been very variable (e.g. Iswaran *et al.* 1980; Glaser *et al.* 2002a; Chan *et al.* 2007b). Biochars can be produced from a range of organic materials and under different conditions resulting in products of varying properties (Baldock and Smernik 2002; Nguyen *et al.*

2004; Guerrero *et al.* 2005) and, therefore, of different soil amendment values. Biochars from plant materials are often low in nutrient content, particularly N, compared with other organic fertilisers (Lehmann *et al.* 2003; Chan *et al.* 2007b). Recently, Chan *et al.* (2007b) reported a lack of positive plant response when greenwaste biochar was applied at up to 100 t/ha and attributed this to the low N availability of the plant-derived biochar. Due to the generally higher nutrient content of animal wastes than plant wastes (Shinogi 2004), biochars produced from animal origins may have higher nutrient content, but their agronomic value as soil amendments has not been investigated.

Poultry litter refers to the mixture of poultry manure and bedding material from poultry farms. In Australia and elsewhere, it has been widely used by farmers, e.g. vegetable growers, as a source of plant nutrients. However, there are food safety and environmental concerns about its application on agricultural land in unmodified forms (Wilkinson 2003; Chan *et al.* 2007a). Wilkinson (2003) recommended only composted

poultry litter should be used for side-dressing of vegetable crops because of possible pathogen contamination. Several recent studies (e.g. Vories *et al.* 2001; Chan *et al.* 2007a) have associated land applications of poultry litter with a higher potential risk of phosphorus contamination to surface waters. Conversion of poultry litter to biochar using pyrolysis could be a safer and more effective alternative to utilise this resource in agriculture but hitherto no research has been carried out to demonstrate this. Utilising poultry litter as a pyrolysis feedstock also has advantages over typically used plant-derived material because it is a by-product of another industry and in some regions is considered a waste material with little or no value. It can therefore provide a lower cost base and alleviate sustainability concerns related to using purpose-grown biomass for the process.

In this paper, we report results of a research project designed to assess the agronomic values of 2 biochars produced from poultry litter on plant yield and soil quality in a glasshouse pot experiment.

## Materials and methods

### Soil

The soil was collected from the Flat Paddock at the Centre for Recycled Organics in Agriculture (CROA) site, Menangle, near Camden (70 m AHD, 02883278E and 6224546N), New South Wales. The soil was an Alfisol (a Chromosol according to Australian Soil Classification; Isbell 1996). It is a typical agricultural soil of New South Wales and the site had a long history of cropping. The hardsetting A horizon has low soil organic carbon concentration and is acidic, with pH<sub>Ca</sub> of 4.5 (Table 1). A composite sample was collected from the 0–0.1 m layer, brought back to the laboratory, and sieved through a 6-mm aperture sieve.

### Biochars

Poultry litter was used as the feedstock of 2 biochars which were produced in the BEST Energies continuous slow pyrolysis pilot unit (Downie *et al.* 2007). The first biochar (L1) was manufactured at a temperature of around 450°C, and the second (L2) was produced at a higher temperature of 550°C and was activated using high temperature steam. The biochars were both alkaline in nature. The non-activated biochar (L1) was higher in C, total N, and available P, whereas L2 had higher pH, liming value, and EC. Both biochars were very low in mineral N (<3.0 mg/kg) (Table 1).

### Pot trial

The experiment was carried out in a temperature-controlled glasshouse (20–26°C). The experimental design used was factorial randomised block design with 4 replications. Four biochar rates (0, 10, 25, and 50 t/ha) combined with 2 N-fertiliser rates (0, 100 kg/ha) were used. The biochar application at different rates was calculated based on 0.10 m depth of incorporation in the field.

Air-dried soil and biochar-amended soils (1.25 kg oven-dried equivalent) were packed into black plastic cylindrical pots (14 cm i.d. by 14.5 cm tall) to achieve a bulk density of 1.2 Mg/m<sup>3</sup>. Nitrogen fertiliser (NH<sub>4</sub>NO<sub>3</sub>) in solution was added in equivalent amounts (equivalent to 100 kg/ha) to half of the pots. All the pots were then wetted up to field capacity using de-ionised water. Ten seeds of radish (*Raphanus sativus* var. Long Scarlet) were planted in each pot and thinned to 5 seedlings after emergence. The pots were placed individually in a shallow tray and regularly watered to maintain water content at approximately field capacity throughout the duration of the experiment. Radish was chosen for the pot trial because it is the indicator plant used for assessing composts, soil conditioners, and mulches (Standards Australia 2003).

A supplementary experiment was also carried out using the same soil without biochar but with 5 rates of N-fertiliser (0, 25, 50, 100, and 150 kg/ha) and 4 replicates.

### Soil and plant analyses

At the completion of the pot trial (6 weeks), the whole radish plants were harvested by removing them from the individual pots. The plants were washed with de-ionised water, oven-dried at 70°C to constant weight before weighing to determine the dry matter production. The plant materials were fine-ground and then after acid digestion analysed for N, P, K, Ca, Mg, and Na. Nitrogen was determined by Dumas combustion, and the cations determined by ICP-AES after acid digestion (Kalra 1998; USEPA 1996). Nutrient uptake (g/pot) was calculated from the plant elemental analyses and the dry matter weights.

After harvesting, the soil from each pot was air-dried at 36°C, mixed thoroughly, and crushed gently to pass through a 4-mm sieve. A subsample was ground further to pass through a 2-mm sieve. The <2-mm samples were then analysed for pH, total C, total N, extractable P (Colwell), and exchangeable cations following Rayment and Higginson (1992). The pH was measured in 1:5 soil/0.01 M CaCl<sub>2</sub> extract; total C and total N were measured by combustion method; extractable P was determined by Colwell method; and exchangeable cations were determined using the Gillman and Sumpter method (Gillman

**Table 1.** Some properties of the soil and biochars used in the pot trial experiment  
NA, Not applicable

	EC <sup>A</sup> (dS/m)	pH <sup>A</sup>	Colwell P	KCl-extractable NH <sub>4</sub> -N    NO <sub>3</sub> -N (mg/kg)		N (%)	C	C : N	%CO <sub>3</sub>	Exchang. cations (cmol(+)/kg) Al    Ca    K    Mg    Na				
Soil	0.05	4.5	23	8.3	21	0.23	1.97		<0.5	0.9	6.8	0.3	2.2	0.7
Char L1	5.6	9.9	11 600	1.8	0.6	2.00	38	19	15	NA	NA	NA	NA	NA
Char L2	14	13	1800	1.1	1.5	0.85	33	39	35	NA	NA	NA	NA	NA

<sup>A</sup>Soil measured in 1:5 soil/0.01 M CaCl<sub>2</sub>, biochar measured in water extract following AS:4454 (Standards Australia 2003).

and Sumpter 1986). Microbial biomass C (MBC) of the soil samples after harvesting was measured using the microwave irradiation and extraction method of Islam and Weil (1998). Suitability of the soil samples from the different biochar treatments as earthworm substrate was assessed after harvesting using the earthworm avoidance test by comparing L1 and L2 amended soils against control soil in pair-wise manner (OECD 1984). Soil tensile strength was determined by measuring the force required to crush soil cylinders prepared from air-dried soil samples (<4 mm) collected at the end of the pot trial from all the different biochar rates treatments (only nil N treatments) (Chan *et al.* 2007b).

### Statistical analyses

All data were analysed by analyses of variance using GENSTAT 9.1. The treatment means were compared using least significant differences for the main effects of biochar and N-fertiliser as well as their interactions.

Earthworm avoidance data were treated as Tally data ( $X$ ) and analysed by assuming to follow a Bernoulli distribution with  $P=0.5$  where  $P$  is the probability of individual earthworms in avoiding the biochar-amended soils (OECD 1984). The test statistic used is a normal deviate ( $z$ ) given as follows:  $z = (X - P) / \sqrt{\{P(1 - P)/n\}}$  where  $z$  has a standardised normal distribution with mean 0 and variance unity, and  $n$  is the total number of earthworms. Unless otherwise stated, differences were significant at  $P \leq 0.05$ .

## Results

### Plant yield

In the absence of N fertiliser, both biochars significantly increased total dry matter (TDM) of radish even at the lowest rate of application (10 t/ha), and the yield increased with increasing rate of biochar application to 50 t/ha (Fig. 1). Effect on TDM of radish was similar between the 2 biochars, i.e. an average increase of 42% at 10 t/ha which rose to 96% at 50 t/ha when compared with the nil biochar control.

Results of the supplementary experiment using increasing rates of N fertiliser (N-rates 0–150 kg/ha) in the absence of biochar indicated a significant linear increase in TDM of radish with increasing rates of N fertiliser:

$$\text{TDM} = 0.0196 * \text{N-rate} + 3.376; \quad r^2 = 0.99^{***}, n = 5 \quad (1)$$

Based on the equation, the increase in TDM production due to the application of 100 kg N/ha in the absence of biochar was only 2.12 g/pot, which was a 67% increase when compared with the nil biochar, nil N control soil (Fig. 1).

Additional increases in TDM, in excess of those due to N fertiliser alone, were observed when biochars were applied. The increase was similar at 10 t/ha for the 2 biochars but differed at higher rates of application (Fig. 1). For rates >10 t/ha, radish TDM production from L2 remained the same but further increases were observed in the case of L1 such that at 50 t/ha of biochar application, DM production for L1 was significantly higher than that of L2 (10.0 v. 8.4 g/pot) (Fig. 1). The highest TDM observed in this experiment was that for L1 at 50 t/ha in the presence N fertiliser, which was 320% that of the nil biochar, nil N control (Fig. 1).

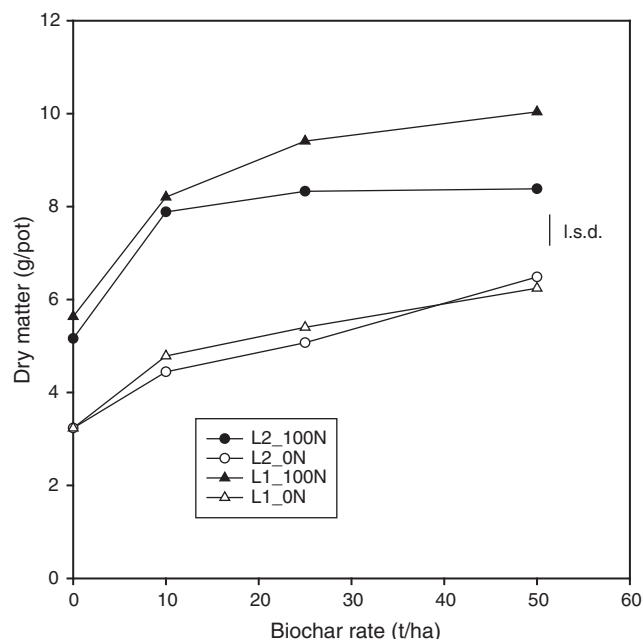


Fig. 1. Dry matter production of radish with and without nitrogen fertiliser as function of application rate of two poultry litter biochars.

### Plant elemental concentration

In the absence of N fertiliser, the addition of both biochars significantly changed the plant elemental composition of radish (Table 2). Biochar application increased N, P, S, Na, Ca, and Mg concentrations of the radish plants. For K, biochar application significantly reduced its concentration but only at the lowest application rate, i.e. 10 t/ha. Significant biochar-type effect was found for S and Ca, in that their concentrations were significantly higher when grown in L2 than L1 amendment. In the case of P, significant biochar  $\times$  biochar rate interaction was detected, in that while addition of both biochars resulted in a similar increase in concentration (>double) at 10 t/ha application rate, it was different at increasing biochar application rates. For L1, it increased and then remained constant, while for L2, it decreased with increasing application rates particularly 50 t/ha (Table 2). As a consequence, the difference in P concentration of radish plants grown in the 2 biochars increased with increasing rates of biochar application (Table 2).

Plant tissue analyses of radish also revealed a much higher N concentration as a result of N fertiliser application (mean of 2.39 v. 1.69%); however, plant N concentration decreased significantly with the rate of biochar application (Table 2). Nitrogen uptake results were similar for both biochars and indicated significantly higher N uptake with N fertiliser application and increasing uptake with increasing rate of biochar application (Table 3). These results indicated N-deficiency of the radish plants without N fertiliser application. From nutrient uptake data, increasing N uptake at higher biochar rates was accompanied by increased K, and to less extent Ca and Mg uptake. It is therefore clear that K was the dominant counter cation accompanying the uptake of N as nitrate ions. Phosphorus uptake data indicated a significant 3-way biochar type  $\times$  biochar rate  $\times$  N interaction (Fig. 2). In the absence of N, P uptake

**Table 2.** Plant elemental composition (%) of radish grown under 2 poultry litter biochars (L1, L2) added at different rates (0, 10, 25, 50 t/ha) without and with nitrogen fertilisern.s., Not significant at  $P=0.05$ ; \* $P<0.05$ ; \*\* $P<0.01$ ; \*\*\* $P<0.001$ 

	0		10		25		50		Significance		
	L1	L2	L1	L2	L1	L2	L1	L2	Char type	Rate	Char × rate
<i>Nil N fertiliser</i>											
N	1.63	1.58	1.63	1.63	1.65	1.83	1.63	1.90	n.s.	**	n.s.
P	0.20	0.24	0.57	0.53	0.67	0.51	0.62	0.44	***	***	***
S	0.63	0.72	0.73	0.78	0.71	0.83	0.71	0.79	***	***	n.s.
Na	0.40	0.41	0.46	0.50	0.54	0.54	0.67	0.65	n.s.	***	n.s.
K	3.65	3.85	3.10	3.53	3.58	3.80	3.80	3.70	n.s.	**	n.s.
Ca	1.43	1.50	1.73	2.00	1.65	1.93	1.48	1.70	***	***	n.s.
Mg	0.32	0.34	0.37	0.37	0.38	0.40	0.42	0.40	*	***	n.s.
<i>With N fertiliser</i>											
N	2.88	2.78	2.15	2.30	2.10	2.25	2.13	2.50	n.s.	**	n.s.
P	0.14	0.16	0.54	0.40	0.59	0.35	0.61	0.37	***	***	***
S	0.45	0.53	0.49	0.52	0.63	0.57	0.68	0.79	***	***	n.s.
Na	0.74	0.72	0.66	0.77	0.75	0.67	0.83	0.93	n.s.	***	n.s.
K	4.15	3.98	4.10	4.33	4.50	4.43	4.45	4.58	n.s.	*	n.s.
Ca	1.55	1.75	1.58	1.68	1.53	1.58	1.28	1.65	***	***	n.s.
Mg	0.33	0.39	0.33	0.35	0.36	0.34	0.35	0.40	*	***	n.s.

**Table 3.** Nutrient uptake (g/pot) by radish grown in 2 types of poultry litter (L1, L2) biochars added at different rates (0, 10, 25, 50 t/ha) in the absence and presence of nitrogen fertilisern.s., Not significant at  $P=0.05$ ; \* $P<0.05$ ; \*\* $P<0.01$ ; \*\*\* $P<0.001$ 

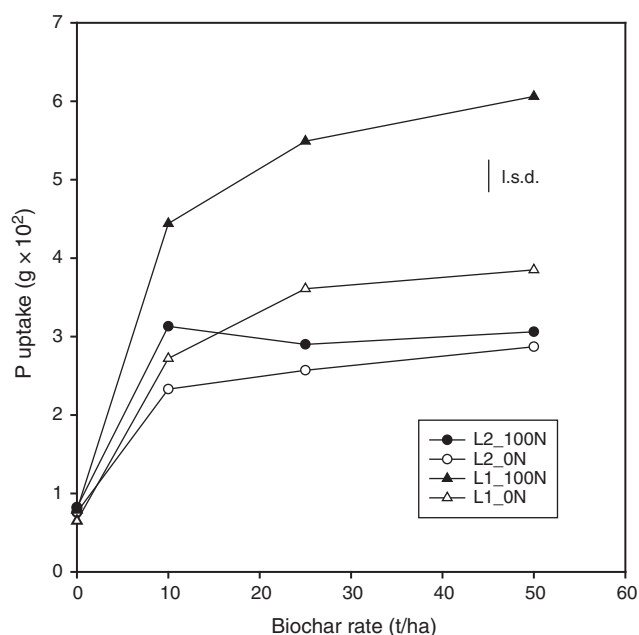
	0		10		25		50		Significance		
	L1	L2	L1	L2	L1	L2	L1	L2	Char type	Rate	Char × rate
Nil N fertiliser											
N	0.053	0.051	0.077	0.072	0.088	0.092	0.101	0.123	n.s.	***	**
P	0.007	0.008	0.027	0.023	0.036	0.026	0.039	0.029	***	***	**
S	0.020	0.023	0.034	0.034	0.038	0.042	0.044	0.051	**	***	n.s.
Na	0.013	0.013	0.022	0.022	0.029	0.027	0.042	0.042	n.s.	***	n.s.
K	0.118	0.124	0.150	0.156	0.193	0.193	0.240	0.240	n.s.	***	n.s.
Ca	0.046	0.049	0.082	0.089	0.089	0.098	0.092	0.110	**	***	n.s.
Mg (%)	0.01	0.011	0.018	0.017	0.020	0.02	0.026	0.026	n.s.	***	n.s.
With N fertiliser											
N	0.161	0.147	0.176	0.178	0.197	0.187	0.213	0.209	n.s.	**	n.s.
P	0.008	0.008	0.044	0.031	0.055	0.029	0.061	0.031	***	***	***
S	0.025	0.027	0.040	0.040	0.059	0.048	0.068	0.066	***	***	n.s.
Na	0.041	0.038	0.054	0.061	0.070	0.056	0.083	0.078	n.s.	***	n.s.
K	0.232	0.206	0.334	0.338	0.423	0.369	0.446	0.383	n.s.	*	n.s.
Ca	0.090	0.090	0.129	0.131	0.143	0.131	0.128	0.138	***	***	n.s.
Mg (%)	0.018	0.020	0.027	0.027	0.034	0.029	0.033	0.033	*	***	n.s.

increased with increasing biochar application but was higher for L1 than L2, particularly for rate >10 t/ha. However, with N fertiliser, while P uptake for L1 was significantly higher than nil N treatment and increased with increasing rates of biochar application to 50 t/ha, for L2 it was only significantly higher than nil N treatment at 10 t/ha and did not change with increasing rates of biochar application.

#### Soil quality changes

Application of poultry litter biochars significantly changed all the chemical parameters of the soil—increased EC, pH, total N, total C, Colwell P, exchangeable cations (Ca, Mg, Na, and K), and effective cation exchange capacity but decreased exchangeable Al (Table 4). However, the effects were different for the different

parameters as indicated by significant biochar × rate interactions in all cases, with the exception of C and exchangeable Al. In the case of C, there were significant biochar and rate effects in that C concentration increased with increasing rate of biochar application but its concentration was consistently higher in L1 than L2. For exchangeable Al, for both biochars, concentration was reduced to zero even at the lowest application rate and remained so with higher rates of application (Table 4). While L1 was more effective in increasing C, total N, and Colwell P, L2 was more effective in increasing pH, Na, Ca, and eCEC of the soil (Table 4). With increasing rate of biochar application, Colwell P of both amended soils increased but the increases were much higher in the case of L1, such that it was 5.05 times of that L2 at 50 t/ha (258 v. 51 mg/kg).



**Fig. 2.** Phosphorus uptake by radish with and without nitrogen fertiliser as function of application rate of two poultry litter biochars.

Application of both biochars significantly reduced soil strength of the hardsetting soil as indicated by the tensile strength measurements, and the effect of the 2 biochars was similar. Average tensile strength of control soil was 192 kPa, and this was significantly reduced to 135, 107, and 71 kPa at, respectively, 10, 25, and 50 t/ha of biochar application.

Biochar application to the soil significantly increased MBC but the 2 biochars behaved differently depending on whether N fertiliser was added (Fig. 3). In the absence of N fertiliser, MBC did not change significantly when L1 was applied. For L2, MBC at the higher rates of application, 25 and 50 t/ha, was significantly higher (122 and 94%, respectively) than the unamended control. In the presence of N fertiliser, MBC increased with increasing rates of biochar application only in the L1 biochar amended soil and was up to 270% compared with

control soil at 50 t/ha application. However, for L2, MBC was not affected by biochar application (Fig. 3). Earthworm avoidance results provided no evidence that the introduced earthworms avoided the L1 or L2 amended soil when compared with the control soil. In fact, the proportion of earthworms found in L1 was significantly higher than that in the L2-amended soil ( $P < 0.001$ ). Therefore, the introduced earthworm demonstrated a preference for L1-amended soil over that of the L2-amended and control soils (Table 5).

## Discussion

### Agronomic value of poultry litter biochar

Results of the pot trial indicate that both poultry litter biochars can significantly improve yield of radish when applied even at the lowest rate of 10 t/ha and further increase yield with increasing rate of application. The increasing N uptake with increasing biochar rate application suggests the ability of these biochars to supply N. This is in contrast to previous research using biochar from plant origin (Chan *et al.* 2007b). In that study a biochar from greenwaste provided no positive yield effect on radish even when applied at a rate of 100 t/ha and this was attributed to the very low N availability of the biochar used. The 2 poultry litter biochars were fairly high in total N (2 and 0.8%) but were also very low in mineral N (Table 1). This suggests the ability of the poultry litter biochars to release available N once applied in the soil via mineralisation. Another possibility was increased mineralisation of native soil N due to the application of biochar, as result of the priming effect (Hamer *et al.* 2004). Hamer *et al.* (2004) demonstrated that biochar (from maize and rye residues) in soils can promote mineralisation of both labile C compound as well as the biochar as a result of enhanced growth of microorganisms. Further research is needed to resolve this.

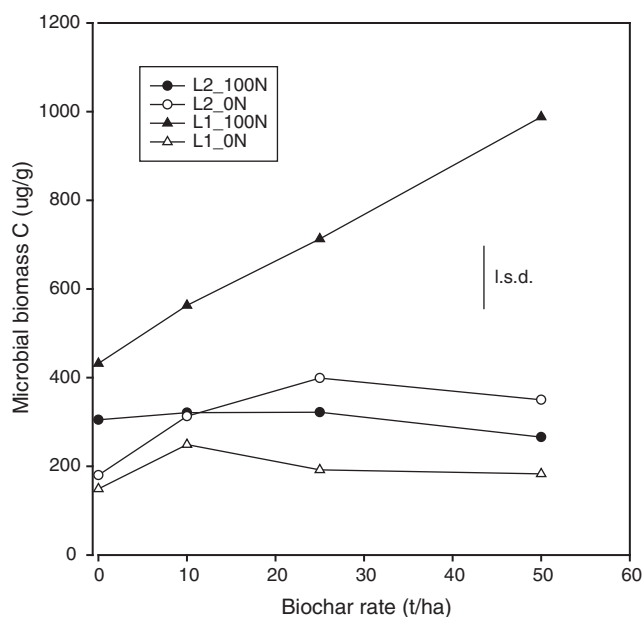
The additional yield increases in TDM of radish, in excess of that due to N fertiliser application observed in the presence of biochars, had to be due other factors, such as higher available P, liming value (Van Zwieten *et al.* 2007), and decreased tensile strength. The liming effect of the biochars which increased soil pH and completely removed exchangeable Al was observed in both biochar-amended soils even at the lowest rate of biochar

**Table 4.** Changes in soil chemical properties as a result of different rates of char application (0, 10, 25, 50 t/ha) for the 2 poultry manure chars (L1, L2)

n.s., Not significant at  $P = 0.05$ ; \* $P < 0.05$ ; \*\* $P < 0.01$ ; \*\*\* $P < 0.001$

	0		10		25		50		Significance		
	L1	L2	L1	L2	L1	L2	L1	L2	Char type	Rate	Char × rate
EC (1:5)	0.11	0.13	0.15	0.17	0.20	0.25	0.29	0.28	***	***	***
pH <sub>ca</sub>	5.01	4.83	6.07	6.66	6.60	7.29	7.06	7.78	***	***	***
C (%)	2.00	1.95	2.38	2.27	2.80	2.48	3.60	3.20	*	***	n.s.
Total N (%)	0.23	0.22	0.26	0.23	0.28	0.23	0.33	0.25	***	***	***
Colwell P (mg/kg)	21	24	93	39	168	41	258	51	***	***	***
Exchang. cations (cmol(+)/kg):											
Na	0.61	0.78	0.74	0.77	0.89	1.03	1.13	1.38	***	***	**
K	0.28	0.40	0.55	0.59	0.90	0.85	1.68	1.45	**	***	***
Ca	6.23	7.28	7.30	9.43	8.25	12.50	8.78	13.25	***	***	***
Mg	2.00	2.35	2.28	2.40	2.75	2.90	3.48	3.38	n.s.	***	***
eCEC	9.12	11.07	10.87	13.19	12.79	17.28	15.07	19.46	***	***	**
Al	0.18	0.26	0.00	0.00	0.00	0.00	0.00	0.00	n.s.	***	n.s.





**Fig. 3.** Microbial biomass carbon of soils amended with different application rate of two poultry litter biochars with and without nitrogen fertiliser.

**Table 5.** Earthworm avoidance of biochar amended and control soils

Soil	Proportion of avoidance	95% Confidence interval	<i>P</i> ( <i>z</i> )
Char L2 v. control	0.43	0.331–0.529	<i>P</i> >0.05
Char L1 v. control	0.19	0.113–0.267	<i>P</i> <0.001
Control v. control	0.47	0.365–0.575	<i>P</i> >0.05

application (Table 4). Our results also indicated differences in the ability of the 2 biochars in further increasing radish yield in the presence of N fertiliser. At a rate of >10 t/ha, the observed different yield responses between the 2 biochars (Fig. 1) were probably related to P availability. For L1, which had significantly higher available P (available P concentration of L1 was 6.4 times that of L2, Table 1), further yield increases were observed with increasing rates of biochar application. However, further yield increase did not occur in the case of L2 probably because of its inability to supply more P to the crop as indicated by P uptake data (Fig. 2). As a consequence, the non-activated poultry litter biochar has a greater ability to increase the N fertiliser use efficiency of plants when N is not the limiting factor.

#### Improvement in soil quality

The changes in soil properties, such as increases in organic C and pH and reduction in soil strength of the biochar-amended soils were consistent with the properties of the biochars used in this investigation which were alkaline and high in C content. The differences in chemical changes between the 2 biochar-amended soils reflected the different properties of the biochars. L2 had higher carbonate equivalent content, hence higher liming value and EC, whereas available P, C, and N were higher in L1 (Table 1).

Our results highlight the potential benefits of biochar application in improving the physical properties of the hardsetting soils which are very widespread in Australia (Mullins *et al.* 1990). This has been previously reported in the case of greenwaste biochar (Chan *et al.* 2007b) and could be partly responsible for the higher radish yield observed in the biochar-amended soils. The observed changes in biological properties, namely microbial biomass and earthworm preference, are interesting as they highlight the potential of biochars to change the soil biology and therefore ecosystem functioning of the soil. Previous research has reported enhanced biological N fixation (Rondon *et al.* 2007) and improved colonisation of mycorrhizal fungi (Saito and Marumoto 2002) by addition of wood biochar to soils. Topoliantz and Ponge (2005) also reported greater casting activity by earthworm species, *P. corethrurus*, in a charcoal/soil mixture compared with soil alone and attributed this to the ability of the charcoal to improve the soil as a living substrate. However, our data did not help to explain the observed differences in microbial biomass and earthworm preference between the 2 biochars. Our data also did not explain the very large difference in MBC between L1 and L2 observed in the presence of N fertiliser (Fig. 3). Furthermore, it is not clear why the introduced earthworms demonstrated a preference for L1 over L2. These differences in responses may be related to the different characteristics of the 2 biochars, which were produced from the same feedstock, but further research is needed to elucidate the underlying mechanisms.

#### Research needs to improve soil amendment values of biochar

Soil amendment value is important for agricultural market development of biochars, and its improvement will facilitate the use of biochar for soil carbon sequestration (Day *et al.* 2004). Our results clearly show that biochar from poultry litter had higher nutrient value (both N and P) than those produced from plant materials. These biochars might have value as slow-release organic fertilisers (N and P). Our results further highlight the importance of processing conditions during pyrolysis such as temperature and activation in determining the potential agronomic value of the final product. The biochar produced at lower temperature (450°C) and without activation had higher C, total N, and available P and, as demonstrated by plant production data, is a superior soil amendment at higher application rates used in conjunction with N fertiliser. However, from the current data we cannot ascertain whether it is the temperature or activation process that has created the observed differences in properties of the 2 biochars.

It is expected that the composition and properties of biochar vary with different pyrolysis conditions (temperature, rate of heating, and pressure) and feedstock (Brown *et al.* 2006; Hammes *et al.* 2006; Chan and Xu 2009). During pyrolysis with increasing temperature, loss of elements such as N, P, and cations occurs via volatilisation, which is accompanied by complex changes in the structural forms of carbon and microporosity of the biochar materials (Chun *et al.* 2004; Shinogi 2004). Shinogi (2004) reported a reduction of total N in biochar from sewage sludge from 5.0% at 400°C to 2.26% at 800°C. Baldock and Smernik (2002) studied the relationship

between changes in chemical composition and biological inertness of char C obtained by heating *Pinus resinosa* sapwood to temperature between 70 and 350°C. With increasing temperature, data indicated a conversion of O-alkyl C to aryl and O-aryl furan-like structure. This was accompanied by a reduction in C mineralisation rate constant by an order of magnitude for wood heated to >200°C. Such reduction in substrate bioavailability for microbes of soil organic matter has also been reported in field soil after burning (Almendros *et al.* 2003). Bagreev *et al.* (2001) also detected significant increases in porosity of the biochar between 400 and 600°C and attributed the increases to water molecules released by dehydroxylation acting as a pore former and activation agent, thus creating very small (Angstrom-size) pores in the char. The increases in porosity resulted in a 3-fold increase in surface area (from 35 to 108 m<sup>2</sup>/g). These changes can potentially have large impact on the content and availability of nutrients as well as other soil amendment properties of the biochars. Furthermore, the responses of different feedstocks to the biochar production process can be different, but little is known about these. Therefore, the effect of process conditions such as temperature and rate of heating on biochar properties and hence soil amendment values for different feedstock materials requires further investigation.

## Conclusions

This is the first report on the use of poultry litter biochars as soil amendments. Application of both of the poultry litter biochars to a hardsetting soil resulted in significant increases in dry matter yield of radish, detectable at the lowest rate of application (10 t/ha). The yield increases were largely due to the ability of these biochar to increase nutrient availability, particularly N. Significant additional yield increases in excess of that due to N fertiliser alone that were observed when N fertiliser was applied highlighted the other beneficial effects of biochar on soil quality. In this regard, the non activated (450°C) poultry litter biochar (L1) was more effective than the activated (550°C) biochar (L2). The different effects of the 2 different biochars on soil chemical and physical quality can be related to their different characteristics. Our research highlights the importance of feedstock and process conditions during pyrolysis in determining the soil amendment values of biochars.

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*Appendix C - Effects of biochar from slow pyrolysis of papermill waste on  
agronomic performance and soil fertility*

## Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility

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**Abstract** The amendment of two agricultural soils with two biochars derived from the slow pyrolysis of papermill waste was assessed in a glasshouse study. Characterisation of both biochars revealed high surface area ( $115 \text{ m}^2 \text{ g}^{-1}$ ) and zones of calcium mineral agglomeration. The biochars differed slightly in their liming values (33% and 29%), and carbon content (50% and 52%). Molar H/C ratios of 0.3 in the biochars

suggested aromatic stability. At application rates of  $10 \text{ t ha}^{-1}$  in a ferrosol both biochars significantly increased pH, CEC, exchangeable Ca and total C, while in a calcarosol both biochars increased C while biochar 2 also increased exchangeable K. Biochars reduced Al availability (ca.  $2 \text{ cmol (+) kg}^{-1}$  to  $<0.1 \text{ cmol (+) kg}^{-1}$ ) in the ferrosol. The analysis of biomass production revealed a range of responses, due to both biochar characteristics and soil type. Both biochars significantly increased N uptake in wheat grown in fertiliser amended ferrosol. Concomitant increase in biomass production (250% times that of control) therefore suggested improved fertiliser use efficiency. Likewise, biochar amendment significantly increased biomass in soybean and radish in the ferrosol with fertiliser. The calcarosol amended with fertiliser and biochar however gave varied crop responses: Increased soybean biomass, but reduced wheat and radish biomass. No significant effects of biochar were shown in the absence of fertiliser for wheat and soybean, while radish biomass increased significantly. Earthworms showed preference for biochar-amended ferrosol over control soils with no significant difference recorded for the calcarosol. The results from this work demonstrate that the agronomic benefits of papermill biochars have to be verified for different soil types and crops.

**Keywords** Biochar · Papermill · Carbon characterisation · Earthworm · Agronomic performance · Waste management · Soil health

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## Introduction

Anthropogenic enhancement of soil by the application of charcoal has been implemented for several thousand years. The Terra Preta—dark earth—soils of the Amazon, an example of such enhanced soils, have recently been the focus of international attention (Glaser et al. 2001), and are the subject of a growing pool of literature (Lehmann et al. 2003). These soils have sparked a resurgence of interest in application of charcoal as the potential value for modern society, both economically and environmentally, is being realised.

Black carbon manufactured through pyrolysis of biomass has become known as ‘biochar’ (Lehmann et al. 2006). Biochar can be produced from a wide range of biomass sources including woody materials, agricultural wastes such as olive husk, corncob and tea waste (Demirbas 2004; Ioannidou and Zabaniotou 2007), greenwaste (Chan et al. 2007) animal manures and other waste products (Downie et al. 2007; Lima et al. 2008; Chan et al. 2008). Application of biochar has been shown to have many advantages including improvements in soil quality and plant growth (Chan et al. 2007, Chan et al. 2008) and reduction in greenhouse gas emissions from soil (Yanai et al. 2007; Van Zwieten et al. 2009). Furthermore, pyrolysed products are protected from rapid microbial degradation, so are able to securely sequester carbon, offering substantial potential for mitigation of greenhouse gas emissions (Lehmann et al. 2006).

Conversion of papermill wastes into biochar through slow pyrolysis has further environmental advantages. LaFleur (1996) outlines environmental risks of chemicals used in the conversion of wood to bleached pulp. Papermill wastes can include considerable quantities of contaminants including sulphates, fine pulp solids, bleaching chemicals, mercaptans, sulphides, carbonates and hydroxides, casein, clay, ink, dyes, grease, oils and small fibres (Nemerow and Agardy 1998). When applied in the environment, these chemicals have been shown to exert toxic effects in a range of ecotoxicological tests including *Pseudomonas putida* growth inhibition, *Vibrio fischeri* luminescence, algal growth, *Daphnia magna* mobility and Zebra fish hatching and survival (Servos 1996). The thermal processing of wastes into biochar has been identified as an opportunity to destroy contaminants (Glover 2009), making beneficial land application possible.

The average papermill produces around 50 dry kg of paper sludges per tonne of paper produced (National Council for Air and Stream Improvement 2005). These waste sludges are generally disposed of in landfills where they decompose yielding the potent greenhouse gas methane. The importance of eliminating wastes from the paper industry going into landfill has been highlighted in Europe where legislation and increasing taxes are promoting re-use of the wastes through energy recovery projects or land application (Monte et al. 2009). Slow pyrolysis of papermill wastes to produce biochar can potentially achieve the advantages of enhanced plant growth and soil quality seen with biochars from other feedstocks (Chan et al. 2007; Chan et al. 2008).

The objectives of this study were quantify the agronomic responses of papermill biochar additions to two agricultural soils.

## Materials and methods

### Biochar production

Two biochars were produced by BEST Energies Australia using a semi-continuous 40 kg h<sup>-1</sup> pilot slow-pyrolysis unit located at Somersby, NSW, from waste materials from an Australian paper mill producing around 500,000 tonnes of paper per year. The papermill produces paper products from unbleached softwood pulp, neutral sulphite semi-chemical hardwood pulp and bleached eucalypt kraft pulp (wood pulped with sodium hydroxide and sodium sulphate).

Biochar 1 was produced from 32.6% (by mass) enhanced solids reduction (ESR) sludge, 18.8% clarifier sludge and 48.6% waste wood chips. Biochar 2 was produced from 19.5% ESR sludge, 11.2% clarifier sludge and 69.3% waste wood chips. Both biochars were produced at a highest treatment temperature (HTT) of 550°C and a heating rate of 5–10°C min<sup>-1</sup>. These chars were sieved to below 2 mm prior to analysis and application to soils.

### Soils

Two contrasting agricultural soils were collected from the 0–100 mm horizon. A ferrosol was sourced from a dairy pasture at Wollongbar Agricultural Institute

(28°50'S, 153°25'E) in north eastern NSW, Australia. A loamy calcarosol was sourced from a vineyard near Red Cliffs (34°18' S, 142°11'E) in north-western Victoria, Australia. Both soils were sieved to 2 mm and thoroughly homogenised.

Each biochar was mixed with 25 kg soil to give an equivalent rate of 10 t ha<sup>-1</sup>, assuming incorporation of biochar to 50 mm soil depth. Correcting for soil bulk density, incorporation rates were equivalent to 2% by dry weight biochar in the ferrosol, and 1.5% by dry weight biochar in the calcarosol. Mixing was achieved in a 50 L electric concrete mixer for 2 h.

#### Plant growth trials

Pot trials were used to compare plant growth in six soil treatments per soil type. The treatments were: unamended soil, soil with biochar 1, and soil with biochar 2, each with and without fertiliser. Fertilised pots were amended with 1.25 g Nutricote® controlled release fertiliser, and homogenised thoroughly. The fertiliser contained 15.2% N, 4.7% P, 8.9% K, 3.3% Ca, 1.1% S, and micronutrients. Plant test species were radish (*Raphanus sativus*), wheat (*Triticum aestivum*) and soybean (*Glycine max*).

Nursery pots 100 mm diameter by 100 mm deep (tapered) were filled with 250 g (dry weight equivalent) of each soil mix. Irrigation was applied with an automated drip system set to minimise leaching from the pots. The trial was located in a climate controlled glasshouse with day/night temperatures of 25/15°C. The pots were arranged on benches in six separate arrays. Each array comprised eight replicates of the six soil treatments on a grid containing four rows by twelve columns of pots. The soil treatments were allocated to positions in each array under a randomised complete block design so that groups of six pots within each row comprised one replicate. This was repeated for each of the three plant species.

Seed was sown at a depth of approximately 10 mm for all test species. A total of five seeds were sown per pot for radish, and thinned to the best 3 following germination, three soybean seeds were thinned to one and ten wheat seeds were thinned to 8.

The dry weight of biomass was measured at harvest (42 d post germination for radish, and 56 d for soybean and wheat). The above ground plant material was harvested, weighed and placed into a plant dehydrator (70°C) for 48 h, before being

reweighed. Results for biomass production per pot are given on a dry weight basis. Nitrogen uptake was recorded for the wheat only and results are presented as mg N uptake into biomass per pot.

Associations between the plant responses and experimental factors were examined by fitting linear models. Predictors in each model included the treatment factors biochar addition, fertiliser addition and their interaction as well as experimental design factors such as replicate, row and column. The models were used to construct analysis of variance tables and to estimate the average response at each biochar and fertiliser combination. The modelling was accomplished by use of the *asreml* package in the R environment (R Development Core Team 2008).

#### Earthworm avoidance studies

Toxicity testing of biochar-amended soils was conducted using the Organisation for Economic Co-operation and Development (OECD) earthworm avoidance method (OECD 1984), using the prescribed test species *Eisenia fetida*.

Transparent plastic containers (170×120×70 mm) were divided in half with a plastic divider. Amended soil (200 g at field capacity) was placed on one side and unamended soil, of the same soil type, was placed on the other side. The divider was then removed and the container tapped lightly to settle the soil.

Four biochar by fertiliser combinations were studied for each soil type: “Biochar 1 vs. control”, “biochar 2 vs. control”, “biochar 1 + fertiliser vs. control + fertiliser” and “biochar 2 + fertiliser vs. control + fertiliser”. Ten replicates were prepared for each combination. The soils were sourced from the pot trial post-harvest, and following sub sampling for physico-chemical analyses. The soils were not adjusted for pH as this was a test parameter which was influenced by the application of biochar to the soil.

Ten clitellate (mature) worms were placed on the soil surface in the centre of each container. Once the worms were observed to enter the soil, the container was covered with a perforated lid. The containers were placed in a controlled-environment chamber at 22°C (±2°C) under constant illumination.

After 48 h, the containers were gently removed from the chamber, and the control and test soils separated along the mid-line with a spatula and the plastic divider replaced. Worms found in contact with

the centre-line were removed; these individuals were recorded as mid-line. The soils from each side of the container were decanted into separate containers and the worms present in each soil were counted.

A logistic regression model was used to predict earthworm response to nutrient, biochar type and the interaction between nutrient and biochar type. The model enabled estimation of the proportion of worms preferring biochar under each choice along with the associated standard error. The model also enabled a statistical assessment of the contribution of each term to variability in the proportion of worms found in the biochar side. Half the worms detected on the midline (two in the ferrosol, 54 in the calcarosol) were assigned to either side after a similar analysis showed that there was no significant impact of soil type on midline frequency.

#### Germination inhibition study

Germination trays with individual wells were used to test rates of germination of the three plant species for each soil type, with and without biochar. The effect of nutrient addition was not tested in this study. The wells had a small non-absorbent cottonwool plug placed in the bottom, and 15 g soil mix added (dry weight equivalent). Soils in the wells were incubated in the glasshouse for 22 d prior to addition of the seed.

All trays were housed in a single chamber in the controlled environment glass house set at 25/15°C day/night temperatures. Watering was via a mist irrigation system set to operate for 5 s every 45 min. Each well was sown with one seed. In total, there were 110 seeds per plant species/ soil and biochar combination. Observations of germination were conducted daily between days 2 and 9 following sowing of seed.

The proportion of seeds germinated under each soil amendment was calculated and then compared by constructing a logistic regression model for the probability of germination as a function of amendment. The model enabled a statistical test of the hypothesis that germination was not affected by amendment, and calculation of the standard error about each proportion.

#### Analysis of microbial activity

Soil was sampled from four of the eight replicate pots of each treatment for analysis of microbial activity.

Tests were done in triplicate on each of these soil samples and the average of the three measurements analysed statistically using the same methods as for the plant response data.

Hydrolysis of fluorescein diacetate (FDA) was assayed according to methods described by Zelles et al. (1991) and Fontvieille et al. (1991). In brief, soil (500 mg oven-dry equivalent, sieved <2 mm) was weighed into 115 mL glass screw top jars, 20 mL of 0.1 M sodium phosphate buffer (pH 7.6) was added and the samples incubated in an orbital mixer/incubator at 150 revolutions per minute for 15 min at 23°C. After 15 min, 100 µL FDA stock solution (2 mg mL<sup>-1</sup> in HPLC grade acetone) was added to the samples before shaking for a further 45 min. After 45 min, 20 mL acetone (HPLC grade) was added, the samples were transferred into 40 mL screw-cap centrifuge tubes and centrifuged for 15 min at 2,900 G. Fluorescence of supernatant was measured using a BMG Fluostar Galaxy fluorescent plate reader, with excitation filter of 485 nm and emission filter of 520 nm, against a sodium fluorescein standard curve (six point calibration). Results were analysed using 3-way Analysis of Variance.

These analyses were undertaken in an ISO9001:2000 quality certified laboratory at NSW Department of Primary Industries, Australia.

#### Chemical analyses and quality assurance

All soil and biochar chemical analyses were undertaken in a NATA (National Association of Testing Authorities, Australia) facility accredited to ISO17025. Soils were collected after completion of the pot trial by bulking the eight replicates for each soil type, species and treatment: Samples (200 g) were then air dried at 40°C and passed through a 2 mm sieve, homogenised and subsampled. Total C and N were measured by Dumas combustion using an Elementar vario MAX CN analyser with combustion chamber set at 900°C and oxygen flow rate of 125 mL min<sup>-1</sup>.

The pH was measured in 0.01 M CaCl<sub>2</sub> (1:5) according to method 4B2 of Rayment and Higginson (1992). Cations and CEC were assessed using compulsive exchange using 1 M NH<sub>4</sub>OAc described in method 15E1. Liming value measured as carbonate equivalent was determined using method 19A1 (Rayment and Higginson 1992).



### Electron microscopy and biochar characterisation

The biochar samples were sputter coated with chromium and examined using an FEI Quanta 200 environmental scanning electron microscope (ESEM) coupled with energy-dispersive X-ray (EDS) analysis. The beam energy used was set at 20 kV.

The surface area of both biochar 1 and its unpyrolysed feedstock were assessed by Micromeritics ASAP 2000 analyser. The samples were initially degassed for 2 h at 250°C before the nitrogen adsorption isotherms were measured at 77 K. The surface areas were calculated by applying the BET equation (Brunauer et al. 1938).

## Results

### Characterisation of biochar

Results of chemical analysis of homogenous biochar samples (Table 1) showed biochar 1 had a pH of 9.4, compared to 8.2 for biochar 2. Both biochars had a liming value around 30% that of  $\text{CaCO}_3$ . Biochar 1 had slightly higher total nitrogen content (0.48%) compared to Biochar 2 (0.31%). Biochar 2 had a slightly higher carbon percentage than biochar 1 (52% and 50% respectively), and had considerably higher levels of exchangeable cations (Ca in particular).

Using electron microscopy, the structure of the biochar was found to be highly heterogeneous with a large degree of macro-porosity in the 1 to 10 micron scale (Fig. 1). The EDS analysis at Point A (b) indicated that the paper sludge biochar particles consisted of high calcium mineral agglomerates on higher carbon content fibres (c) with structures typical of their biomass origins. Wood particles (d) were easily distinguishable from paper sludge particles with EDS analysis (e) again showing Ca deposits associated with carbon from wood.

The surface area was found to increase from  $2.9 \text{ m}^2 \text{ g}^{-1}$  to  $114.9 \text{ m}^2 \text{ g}^{-1}$  as a result of the pyrolysis processing.

The biochar yields from the slow pyrolysis process were 32% and 29% (on a dry mass basis) for biochar 1 and 2 respectively. The ultimate analysis (Australian Standards 1038.6.3.3 method) revealed that the molar H/C ratio of feedstock was 1.36 and this reduced to 0.30 for biochar 1 and 0.32 for biochar 2. This indicates the disproportional loss of hydrogen as the carbon forms more stable, conjugated aromatic structures.

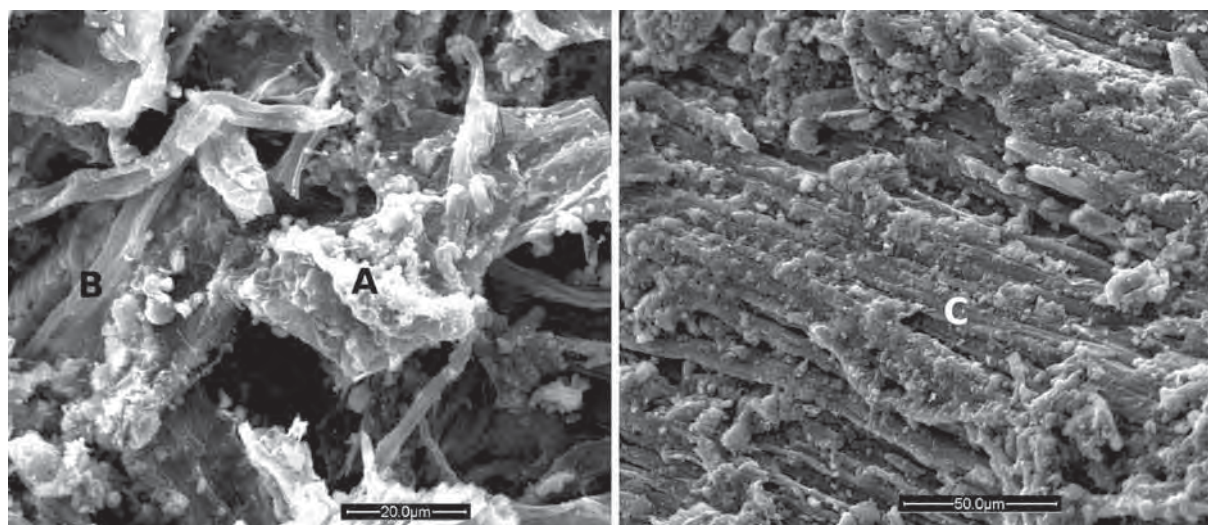
### Soil quality changes

Both biochars significantly increased pH of the ferrosol, but had no effect on the calcarosol. Biochar 1 amendment raised the pH from 4.20 to 5.93 in the absence of fertiliser, and from 4.13 to 5.73 with fertiliser. Biochar 2 amendment raised the pH to 5.40 and 5.13 respectively. Differences between biochar 1 and 2 can be expected as biochar 1 had a slightly higher liming value (33% and 29% for biochar 1 and 2 respectively). Both biochars significantly reduced exchangeable Al compared to unamended soils, from  $2 \text{ cmol (+) kg}^{-1}$  to below detection in the ferrosol. There was no available Al in the calcarosol. Both biochar amendments elevated exchangeable Ca levels in the ferrosol from  $1.23 \text{ cmol (+) kg}^{-1}$  to 8.87 and 6.57 (biochar 1 and 2, respectively) in the absence of fertiliser, with similar levels of elevation with fertiliser. No significant effects on available Ca were seen in the calcarosol. Both biochars influenced the cation exchange capacity (CEC) in the ferrosol. The CEC of unfertilized pots was ca.  $4 \text{ cmol (+) kg}^{-1}$  and increased to  $10.5 \text{ cmol (+) kg}^{-1}$  for biochar 1 and  $7.57 \text{ cmol (+) kg}^{-1}$  with biochar 2. Mean CEC remained at ca.  $31 \text{ cmol (+) kg}^{-1}$  across all treatments in the calcarosol, with no changes detected in the presence of biochar. Total soil carbon was significantly elevated by around 0.5% for biochar 1 in the ferrosol while for biochar 2 the increase was closer to

**Table 1** Chemical analysis of biochars

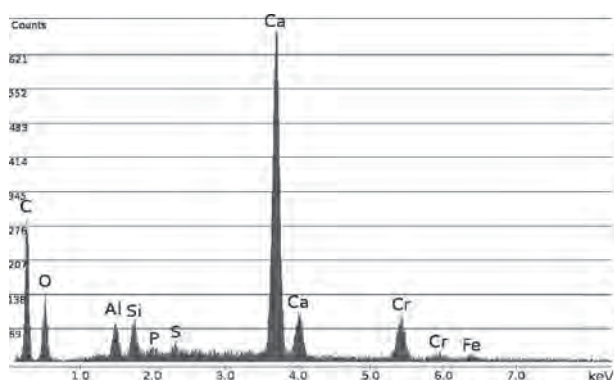
	pH ( $\text{CaCl}_2$ )	Al cmol (+) $\text{kg}^{-1}$	Ca cmol (+) $\text{kg}^{-1}$	K cmol (+) $\text{kg}^{-1}$	Mg cmol (+) $\text{kg}^{-1}$	Na cmol (+) $\text{kg}^{-1}$	CEC cmol (+) $\text{kg}^{-1}$	Total N %	Total C %	Acid neutralising ability (% $\text{CaCO}_3$ )
Biochar 1	9.4	<0.10	6.2	0.22	1.2	0.95	9.0	0.48	50	33
Biochar 2	8.2	<0.10	11	1.0	2.6	3.7	18	0.31	52	29



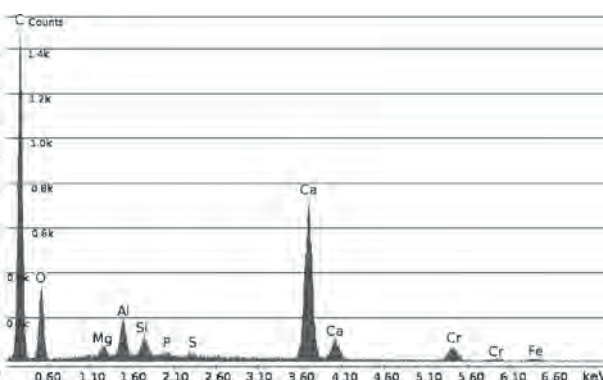


(a) Environmental scanning electron microgram of biochar

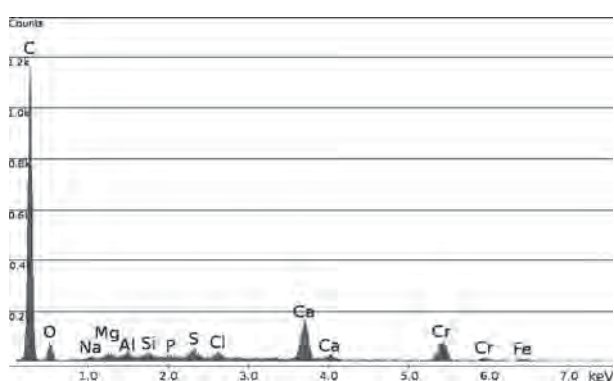
(d) Environmental scanning electron microgram of biochar using lower magnification



(b) EDS analysis of Point A depicting mineral agglomeration dominated by Ca



(e) EDS analysis of Point C depicting mineral agglomeration dominated by Ca



(c) EDS analysis of Point B depicting high C biochar with minor Ca mineral agglomeration

**Fig. 1** Environmental scanning electron micrograms and EDS analysis of biochar

**Table 2** Chemical analysis of soils following the pot trial. Results are averages of homogenised samples across the three plant trials

	pH (CaCl <sub>2</sub> )	Al cmol(+) kg <sup>-1</sup>	Ca cmol(+) kg <sup>-1</sup>	K cmol(+) kg <sup>-1</sup>	Mg cmol(+) kg <sup>-1</sup>	Na cmol(+) kg <sup>-1</sup>	CEC cmol(+) kg <sup>-1</sup>	Total N %	Total C %
<b>Ferrosol</b>									
Control	4.20	1.93	1.23	0.11	0.30	0.46	4.03	0.32	3.60
Control + fertiliser	4.13	2.10	1.12	0.72	0.49	0.44	4.90	0.35	3.57
Biochar 1	5.93	n.d.	8.87	0.66	0.67	0.48	10.5	0.29	4.00
Biochar 1+ fertiliser	5.73	n.d.	8.47	0.93	0.52	0.46	10.2	0.32	4.03
Biochar 2	5.40	n.d.	6.57	0.14	0.38	0.48	7.57	0.34	4.50
Biochar 2+ fertiliser	5.13	n.d.	6.20	0.52	0.47	0.46	7.77	0.36	4.40
lsd	0.11	0.19	0.83	0.84	0.43	0.12	1.39	0.03	0.16
se	0.04	0.06	0.27	0.27	0.14	0.04	0.45	0.01	0.05
<b>Calcarosol</b>									
Control	7.67	n.d.	21.7	2.07	6.23	0.74	31.0	0.18	2.03
Control+fertiliser	7.60	n.d.	22.7	2.27	6.53	0.81	32.3	0.21	2.03
Biochar 1	7.67	n.d.	20.3	2.23	6.10	0.76	29.3	0.20	2.73
Biochar 1+ fertiliser	7.67	n.d.	21.3	2.37	6.33	0.94	31.0	0.22	2.53
Biochar 2	7.77	n.d.	21.3	2.43	6.47	0.79	31.0	0.20	2.53
Biochar 2+ fertiliser	7.60	n.d.	22.3	2.43	6.57	0.89	32.3	0.21	2.47
lsd	0.27	0	1.8	0.37	0.56	0.28	2.8	0.03	0.50
se	0.09	0	0.58	0.12	0.18	0.09	0.91	0.01	0.16

Least significant difference and standard error of the means for each soil are shown. N.d. is not detected (<0.1 cmol (+) kg<sup>-1</sup>)

1%. Total carbon in the calcarosol was significantly elevated from 2.03% in the control soils to 2.73% and 2.53% for biochar 1 (unfertilised and fertilized respectively); and 2.53% for biochar 2 (unfertilised). The increase in soil carbon with biochar 2 in the presence of fertiliser was not significant (Table 2).

#### Soil microbial activity

The varied response of microbial activity to biochar and nutrient addition under each crop and soil type is

shown in Table 3. No differences were seen from fertiliser addition to any crop species or soil type, except for soybean in the calcarosol. Fertiliser resulted in higher microbial activity, increasing from an average of 2.2– 2.81  $\mu\text{g}$  fluorescein g<sup>-1</sup> min<sup>-1</sup>. Biochar 1 addition to ferrosol increased microbial activity in the soybean crop, but not in other plant species. The same biochar however resulted in significant decreases in microbial activity in the calcarosol with wheat only. Biochar 2 resulted in a decline in microbial activity for unfertilised soybean

**Table 3** Average microbial activity in soils following the pot trial ( $\mu\text{g}$  fluorescein g dry soil<sup>-1</sup> min<sup>-1</sup>)

	Ferrosol			Radish		
	Soybean	Radish	Wheat	Soybean	Radish	Wheat
Control	8.38	8.79	9.48	2.25	1.80	2.57
Control + fertiliser	8.51	7.85	9.14	2.81	1.87	2.62
Biochar 1	9.79	8.42	7.80	2.38	1.18	1.46
Biochar 1+ fertiliser	9.50	7.66	8.52	2.75	2.03	1.78
Biochar 2	7.46	7.42	6.58	2.62	1.23	1.75
Biochar 2+ fertiliser	7.90	7.13	5.95	3.06	1.62	2.04
lsd	0.90	1.29	1.74	0.28	0.83	0.42

and both fertilised and unfertilised radish and wheat in the ferrosol, but increased microbial activity in the calcarosol under soybean.

#### Earthworm behaviour study

Results from the earthworm avoidance test showed a very distinct preference by the worms for biochar-amended ferrosol compared to the controls. This was most marked for the fertilizer treated soils ( $p < 0.001$ ) (Table 4). Overall, the worms indicated a slightly higher preference for biochar 2 ( $p = 0.07$ ). In the calcarosol, there was no significant difference in soil preference.

#### Plant growth responses

Analysis of dry biomass production (Fig. 2) revealed both positive and negative responses to biochar addition. For wheat in the ferrosol there was no significant difference in the absence of fertiliser, however with fertiliser significant increases in biomass production were recorded, indicating a strong fertiliser by biochar interaction. The calcarosol provided more favourable conditions for wheat growth than the ferrosol as indicated by the greater biomass production. The unfertilised control yielded ca. 1.5 g biomass per pot, compared with 0.3 g in the ferrosol. Biochar 1 significantly reduced wheat biomass both with and without fertiliser, however biochar 2 showed no difference.

Soybean biomass production in both the ferrosol and calcarosol was not affected by biochar in the absence of fertiliser. Again, a biochar by fertiliser interaction was evident in the ferrosol such that biomass yield in the biochar + fertiliser treatments exceeded that of fertilised controls. A similar positive biochar by fertiliser interaction trend was seen for the biomass yield with biochar 1 in the calcarosol, however biochar 2 gave no significant differences in biomass.

**Table 4** Percentage of worms found in the char amended soil over ten replicates (100 worms) of each choice

Biochar	Ferrosol	Calcarosol
1	61 (5)	54 (5)
1+ fertiliser	92 (3)	62 (5)
2	75 (4)	60 (5)
2+ fertiliser	92 (3)	57 (5)

Standard error of the means in brackets

Radish dry biomass production (bulb + shoots) was significantly increased in the ferrosol, both in the presence and absence of fertiliser. Biochar 1 significantly outperformed biochar 2. In the calcarosol, significantly increased biomass production was found in the absence of fertiliser with biochar 2 amendment, while biochar 1 had no significant effect. In the presence of fertiliser however, both biochar 1 and biochar 2 significantly reduced biomass production.

#### Nitrogen uptake

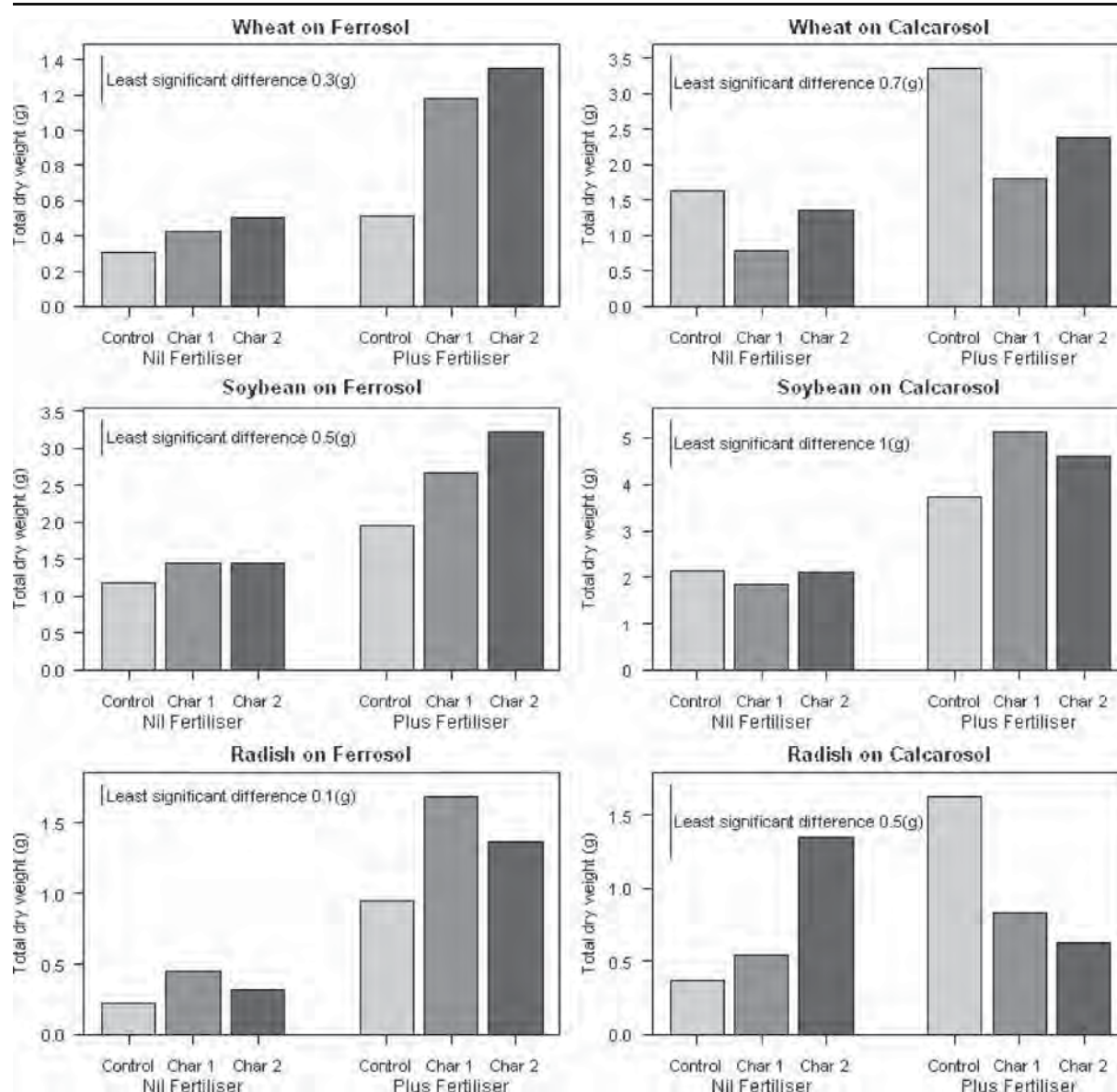
Analysis of nitrogen uptake in wheat is shown in Table 5. Addition of fertiliser in the ferrosol did not provide significant increases in N uptake, nor did the application of biochar 1. However, application of biochar 1 with fertiliser significantly increased uptake of plant N. Biochar 2 significantly increased uptake of plant N in both the unfertilised and fertilised treatments. Biochar 1 with fertiliser significantly outperformed biochar 2 with fertiliser. Fertiliser treatment in the calcarosol significantly increased N uptake compared to the control. Application of the biochars did not affect N uptake when compared to either the unfertilised or fertilised controls.

#### Germination study

Germination of wheat in the ferrosol was significantly improved in the presence of either biochar (from 97%  $\pm$  2% in the control to 100% for both biochar treatments) (Table 6). No other treatment significantly affected germination.

## Discussion

Plant response to biochars varied between biochar characteristic, soil type and plant species. There was an interaction between biochar and fertiliser addition: generally there was little response to biochar in the absence of fertiliser except for the radish which gave statistically increased dry biomass production in the ferrosol for both biochars, and increased biomass for biochar 2 in the calcarosol. The greatest increase was observed with the application of biochar to the acidic red ferrosol, sown to wheat, where an almost 2.5-fold increase in plant biomass production was observed in the biochar + fertiliser treatment. Similarly increased



**Fig. 2** Biomass production (g dry weight) in response to biochar and fertiliser amendment. Least significant differences shown for each plant species and soil type interaction

biomass production in the presence of fertiliser was observed for the other plant species in the ferrosol. Significant decreases in wheat and radish biomass production were observed in the calcarosol in the presence of fertiliser, but this trend was not observed in the absence of fertiliser. Similarly, Steiner et al. (2007) observed a large grain yield enhancement in rice (*Oryza sativa* L.) and sorghum (*Sorghum bicolor* L.) where charcoal with NPK fertiliser were applied to an acidic, highly weathered tropical soil. The availability of soil nutrients remained higher in the treatments with

charcoal in the Steiner et al. (2007) study, despite greater nutrient removal from the site due to higher grain yields.

The positive response observed in the ferrosol could be partly explained by its liming value. Ferrosol controls had available Al up to  $2.1 \text{ cmol (+) kg}^{-1}$  which was reduced to below detection with biochar amendment. No effects on pH were observed in the calcarosol. Similarly, unpyrolysed papermill wastes irrigated onto soil (30 mm per week over 16 months) (Wang et al. 2005) were shown to increase pH in two soil types of between 0.25 and almost 1 unit. These



**Table 5** Average nitrogen uptake (mg) per pot ( $n=8$ )

	Ferrosol	Calcarosol
Control	3.2	14.7
Control + fertiliser	7.1	42.6
Biochar 1	6.2	4.8
Biochar 1+ fertiliser	20.5	29.7
Biochar 2	10.2	26.7
Biochar 2+ fertiliser	14.8	48.1
lsd	5.6	17.4
se	2.1	5.9

Least significant difference and standard error of the means for each soil are shown

effects were most pronounced in an acidic volcanic soil. With the application of biochar produced from papermill waste in this current study, increases of soil pH in ferrosol were up to 1.5 units. The acid neutralising ability (33% and 29% equivalency) of the biochars presented in our study may be the result of the Ca complexes detected (Fig. 1) in the biochars, arising from components such as  $\text{CaCO}_3$  which can be present in the clarifier sludge.

In addition to the liming effect, biochars may have provided other benefits including adsorption of both anions and cations which may have reduced leaching of applied nutrients (Major et al. 2009). Although this study aimed to minimise leaching from the pots, there was still some loss which was not quantified. The CEC of newly-produced biochars (Table 1) was 9 cmol and 18 cmol (+)  $\text{kg}^{-1}$ , while the ferrosol soil was around 4 cmol (+)  $\text{kg}^{-1}$  (Table 2). By the end of the study, CEC of the ferrosol treated with biochar 1

increased CEC to 10.5 cmol (+)  $\text{kg}^{-1}$  in the absence of fertiliser, with similar gains seen in the presence of fertiliser. Biochar 2, despite having a CEC double that of biochar 1, increased the CEC of the ferrosol to 7.57 cmol (+)  $\text{kg}^{-1}$ . This difference could be partly explained by the lower liming value observed for biochar 2, and the subsequent lower pH of ferrosol with biochar 2 compared with biochar 1 amendment. CEC of biochar materials is found to increase with aging (Lehmann 2007), due mainly to increasing carboxylation of carbon via abiotic oxidation (Cheng et al. 2006; Liang et al. 2006). Glaser et al. (2001) discussed the importance of ageing to obtain the increases in CEC of black carbon found in the Terra Preta soils of the Amazon. The results of N uptake by the wheat (Table 6) clearly demonstrate increased N uptake efficiency with biochar amendment to the ferrosol, while no significant effects were observed with the calcarosol. Greater nutrient retention due to higher CEC, in conjunction with a more favourable root environment due to reduction in acidity and available Al are probably responsible for the increase in N use efficiency in the ferrosol. Chan et al. (2007) similarly observed an increase in N uptake efficiency of radish in a hard setting chromosol with application of biochar derived from greenwaste. Increased fertiliser use efficiency through use of biochar has several potential agronomic and environmental benefits. A reduced N application can reduce the cost of producing food, while simultaneously decreasing emissions of nitrous oxide ( $\text{N}_2\text{O}$ ), a significant greenhouse gas. The Intergovernmental Panel on Climate Change estimates that, on average, 1.3% of applied N fertiliser is converted to  $\text{N}_2\text{O}$  via nitrification and

**Table 6** Observed proportion of seeds germinating under each amendment for each species

	Ferrosol			Calcarosol		
	Soybean	Radish	Wheat	Soybean	Radish	Wheat
Control	0.92 (0.03)	0.79 (0.04)	0.97 (0.02)	0.83 (0.04)	0.82 (0.04)	0.95 (0.02)
Biochar 1	0.94 (0.02)	0.89 (0.03)	1.00 (0.00)	0.88 (0.03)	0.90 (0.03)	0.96 (0.02)
Biochar 2	0.97 (0.02)	0.86 (0.03)	1.00 (0.00)	0.86 (0.03)	0.81 (0.04)	0.95 (0.02)
Hypothesis test	Accept ( $p=.18$ )	Accept ( $p=.11$ )	Reject ( $p=.04$ )	Accept ( $p=.50$ )	Accept ( $p=.11$ )	Accept ( $p=.76$ )

Hypotheses tests of no impact due to amendment

denitrification, directly or indirectly via volatilisation or leaching.

One of the advantages of pyrolysing biomass is the conversion of labile C into a more stable “aromatised” carbon (Krull et al. 2009). Biochars from the papermill waste had molar H/C ratios of 0.3, compared to the feedstock of 1.36. This low H/C ratio suggests increased aromaticity and maturation, and infers greater stability of the material when applied to soil. It is well established that carbon from papermills, when applied to soils, is rapidly mineralised. For example, papermill wastes were irrigated at 19 t ha<sup>-1</sup> C onto soil with no build-up of soil C (Wang et al. 2005). Carbon from papermill wastes was shown to mineralise to CO<sub>2</sub> in soil via microbial action (Wang et al. 2005; Zibilske 1987). Similarly, repeated addition of 15 t ha<sup>-1</sup> to 25 t ha<sup>-1</sup> of papermill residues on sandy soil did not result in a long-term build-up of soil C (Curnoe et al. 2006). This contrasts with papermill wastes that have been pyrolysed in this current study, where significant increases in total soil C were observed.

Biochar 1 increased microbial activity in the ferrosol with soybean, however, no significant changes were recorded for the other crop species. A significant decline in microbial activity with this biochar was found in the calcarosol under wheat, but again, no significant changes were seen with the other crops. Biochar 2 tended to suppress microbial activity in the ferrosol, although it increased activity in the calcarosol under wheat. Extracts from biochar derived from poultry litter (Das et al. 2008) have been shown to increase microbial growth, however, extracts derived from biochars made from pine timber tended to inhibit microbial growth. The increases in microbial growth from the poultry litter biochar were associated with protein derived compounds. As the papermill biochar was unlikely to contain these protein based substrates, it could be hypothesised that negative effects on microbial activity could be similar to those found by Das et al. (2008). Long-term effects could not be extrapolated from these studies.

The benefits of the papermill biochar on earthworms were evident in the ferrosol, where significant preference for biochar amended soil was found. Earthworms have been suggested as useful indicators of soil health (de Bruyn 1997; Paoletti et al. 1998), as they are highly mobile in soil and have the ability to detect and avoid soils with ecological implications

such as contamination (Yeardley et al. 1996). It was evident that papermill biochar did not have any contaminants that are likely to cause short, or long term effects on the earthworms. No statistical significant differences in earthworm behaviour were determined in the calcarosol. Similarly, there were no negative effects on plant germination in the presence of biochar further suggesting the absence of detrimental components.

## Conclusion

The conversion of papermill wastes to biochar offers industry an attractive option for minimising waste product and reducing costly transport of essentially wet biomass. The biochars from papermill wastes were shown to provide benefits to ferrosol at 10 t ha<sup>-1</sup> giving improvement in both soil quality and crop performance. Some negative impacts were observed in the calcarosol, especially in the presence of fertiliser, suggesting careful evaluation of biochar type and soil properties before field scale biochar application. Because a major benefit of the papermill biochars derives from its liming value, they are most likely to be beneficial as amendments in acidic soils where Al toxicity limits plant growth. The CEC in the ferrosol was more than doubled in the presence of biochar, providing benefits to soil fertility. This was observed as improved biomass production when additional fertiliser was supplied, and significantly enhanced N use efficiency in wheat. These same phenomena were not observed in the calcarosol which was alkaline and had a much higher CEC than the ferrosol.

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*Appendix D - A glasshouse study on the interaction of low mineral ash  
biochar with nitrogen in a sandy soil*

## A glasshouse study on the interaction of low mineral ash biochar with nitrogen in a sandy soil

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**Abstract.** The effect of a low mineral ash biochar on biomass production and nitrogen (N) uptake into plants was tested with wheat and radish in a Yellow Earth used for commercial vegetable production. The biochar had an acid neutralising capacity <0.5% CaCO<sub>3</sub>, a total C content of 75%, and a molar H/C ratio of 0.45, indicating stability due to its aromaticity. A pot trial was established under climate-controlled conditions. Five rates of N fertiliser (0, 17, 44, 88, 177 kg N/ha) were applied as urea in combination with 5 biochar rates (0, 1.1, 2.2, 4.4, 11% w/w). Analysis of biomass production revealed a significant biochar × N fertiliser interaction. In particular, increasing biochar concentrations improved biomass production in both crop species at lower N application rates. The highest biochar application rate resulted in significantly greater accumulation of NO<sub>3</sub><sup>-</sup>-N in the soil and lower NH<sub>4</sub><sup>+</sup>-N averaged across the 5 N application rates. The biochar also decreased available P, and significantly increased microbial activity measured using the fluorescein diacetate method. Increasing N fertiliser application resulted in greater accumulation of NO<sub>3</sub><sup>-</sup>-N with no changes to NH<sub>4</sub><sup>+</sup>-N averaged across the 5 biochar application rates. Nitrogen fertiliser application did not influence microbial activity or biomass C. The trial suggests that in some cropping systems, biochar application will enable reduced N fertiliser input while maintaining productivity.

**Additional keywords:** biomass production, low mineral ash biochar, microbial activity, nitrogen, yellow earth.

### Introduction

The intensive use of nitrogen (N) fertilisers in modern agriculture is motivated by the economic value of high grain yields (Khan *et al.* 2007) and the need to provide food for an increasing population. It is estimated that 0.76 Mt of N, as synthetic fertilisers, was applied in Australia in 2007 (FIFA 2008). However, the efficiency of N fertiliser use has been reported to be <50% (Baligar and Bennett 1986). Routes of loss for N fertiliser in soil include leaching, run-off, and gaseous emissions as N<sub>2</sub>O, N<sub>2</sub>, and NH<sub>3</sub> (Bouwman 1996; Cassman *et al.* 2002; Khalil *et al.* 2009; Olarewaju *et al.* 2009). Nitrogen can also be removed from the available pool through incorporation into soil organic matter (Baligar *et al.* 2001) and microbial biomass (Doran 1986).

Matching the supply of N to crop demand will optimise N-use efficiency and outcomes for yield and environmental protection (Cassman *et al.* 2002). The incorporation of stubble (Newton 2001), conservation tillage practices which minimise leaching (Sharples and Smith 1994), and use of controlled release fertilisers (Shoji *et al.* 2001) are all important technologies for achieving this outcome.

There is interest in the use of charcoal or biochar as a soil amendment, and evidence is mounting that these amendments can influence N in soil. Glasshouse studies by Chan *et al.* (2007)

have shown a significant biochar × nitrogen fertiliser interaction where higher yield was observed with increasing rates of biochar application in the presence of N fertiliser. The application of a low nutrient biochar derived from timber into soil increased the retention of N in soil and uptake of N into crop biomass (Steiner *et al.* 2008). Similarly, the application of charcoal derived from bamboo into a sludge composting system provided significant increases in N retention in the compost (Hua *et al.* 2009). Those authors hypothesised that the charcoal was able to adsorb NH<sub>3</sub> and thus minimise its loss through volatilisation.

The capacity for biochar to retain water can also influence the N-use efficiency, by indirectly reducing the leaching of N through the soil profile. This was suggested as particularly relevant for sandy soils with low clay contents (Major *et al.* 2009).

Despite the interest in application of biochar into soil, we still have a rudimentary understanding of the mechanisms and specific responses that biochar generates within soil ecosystems. Results from previous pot trials have suggested that there is a biochar–nutrient interaction, particularly with N. The objective of the present study was to elucidate this interaction through a pot trial using a matrix of biochar and N application rates. Key soil properties were measured to identify soil processes controlling the interaction. The biochar used was specifically



produced for this study. It contained very low nutrient, avoiding confounding effects of nutrient variations across biochar application rates. It also featured a low molar H/C ratio, conferring stability, and minimising biodegradation and oxidation of biochar during the study.

## Methods

### Biochar

Biochar was produced by Pacific Pyrolysis (formerly BEST Energies Australia), using their continuous slow pyrolysis pilot plant at Somersby, NSW. Biochar was made from whole tree residue (green waste), sourced from local government contractors, at a highest treatment temperature (HTT) of 600°C. The biochar was ground and sieved to <2 mm before analysis and application to soils. Biochar physical analysis included: (i) imaging the material sputter-coated with gold using an FEI Quanta 200 environmental scanning electron microscope (ESEM), beam energy 20 kV; and (ii) surface area and pore size distribution using N adsorption isotherms at 77.3 K interpreted by the BET equation (Brunauer *et al.* 1938).

### Soil

Soil (60 kg) was collected from the 0–50 mm profile from a commercial vegetable farm in Somersby, NSW, Australia (33°20'S, 151°10'E). The soil was selected from this site to provide data on N and biochar application rates for a planned field demonstration. The soil was air-dried and manually sieved to 2 mm. The soil was a Yellow Orthic Tenosol (Isbell 1996).

Biochar was added to 10 kg oven-dried (40°C) soil at 5 rates: 0, 5, 10, 20, and 50 t/ha, calculated assuming effective mixing of biochar through the 0–50 mm soil profile and a measured soil bulk density of 0.86 Mg/m<sup>3</sup>. This equated to a concentration in soil of 0, 1.1, 2.2, 4.4, and 11% w/w (dry matter basis). Mixing was achieved using a 50-L electric concrete mixer for 2 h. Control soil (0% biochar) was also mixed according to the above description. The mixer was thoroughly cleaned between samples.

### Plant growth trials

Wheat (*Triticum aestivum* L.) and radish (*Raphanus sativus* L.) plants were grown in separate climate controlled glasshouses using a 25°C day and 15°C night regime. Combinations of the 5 biochar rates with 5 N fertiliser rates (0, 17, 44, 88, 177 kg N/ha) applied as solubilised urea (0, 24, 61, 122, 245 mg/pot) at planting used 6 replicates for both wheat and radish. Air-dried soil and biochar-amended soils (250 g oven-dried equivalent) were repacked into black plastic 500-mL nursery pots, 100 mm diameter by 100 mm deep. The base of each pot was lined with shade cloth to prevent soil loss. The pots were gravimetrically adjusted to maintain 70% water-filled porosity and were left to settle in the glasshouse for 1 week before seed sowing. Pots were arranged on benches within each glasshouse in arrays 15 rows wide by 10 deep. Treatments were allocated to pots under a randomised incomplete block design using rows and columns of pots as blocking factors.

Seeds were sown to a depth of 10 mm and were spaced equidistant from each other in a circular pattern. Radish (5 seeds sown) was thinned to the best 3 plants 1 week after germination,

and wheat (10 seeds sown) was thinned to the best 8 plants. At sowing, N was added, as urea, to each pot. Solutions of urea were prepared in Milli-Q water at concentrations sufficient to deliver the required N rates in a 5-mL aliquot. This was added to pots via pipette. Control pots received 5 mL Milli-Q water.

In order to maintain the pots at the required 70% water-filled porosity throughout the trial, a micro-irrigation system was installed, delivering moisture via 3-mm tube and an Arrow Dripper<sup>®</sup> positioned in each pot. All water lines from the manifold were kept at equal length. Water to the entire system in each chamber was controlled by a Galcon E.Z. Irrigation Controller<sup>®</sup>. Only very minimal leaching from the pots observed over the experimental period.

Above-ground biomass was harvested 65 days after germination for wheat and 64 days after germination for radish. Plants were cut off at soil level and placed in a dehydrator at 80°C. Dry weights were determined after 7 days. Samples were then ground to <1.0 mm with a SM100 Retsch grinder. Following final harvest, soil from all 6 replicates of each treatment within each plant species were bulked and subsampled for chemical analyses and soil biological activity.

### Chemical analyses and quality assurance

All soil, biochar, and plant tissue chemical analyses were undertaken in a NATA (National Association of Testing Authorities, Australia) facility accredited to ISO17025. Soil or biochar (200 g) was dried at 40°C and passed through a 2-mm sieve, homogenised, and subsampled. Total C and N in soil, biochar, and plant samples was measured by Dumas combustion using an Elementar vario MAX CN analyser with combustion chamber set at 900°C and oxygen flow rate of 125 mL/min. Details for the following methods are found in Rayment and Higginson (1992). In summary, oxidisable organic C was measured using the Walkely and Black wet oxidation by dichromate–sulfuric acid mixture (method 6A1). The pH was measured in 0.01 M CaCl<sub>2</sub> (1:5) (Method 4B2). Cations and cation exchange capacity (CEC) were assessed by using 1 M NH<sub>4</sub>OAc (Method 15E1). Available orthophosphate P was tested in soil using Bray #1 extraction (Method 9E2). Available orthophosphate P was also tested in biochar using Colwell bicarbonate extraction (method 9B1). Nitrate and ammonia were assessed using 2 M KCl extract and automated colourimetric procedures (method 7C2). Liming value was reported as carbonate equivalent (method 19A1).

Molar H/C ratio was determined by Bureau Veritas International Trade Australia using Australian Standard Method AS 1038.6.1 under a NATA quality control system.

### Analysis of microbial activity and biomass C

Bulked soil (before drying and grinding) from each plant, biochar rate, and N rate was analysed for microbial activity and biomass C. Tests were done in triplicate on each of these soil samples. Hydrolysis of fluorescein diacetate (FDA) was assayed using methods adapted from Zelles *et al.* (1991) and Fontvieille *et al.* (1992). Soil (500 mg oven-dry equivalent, sieved <2 mm) was weighed into 115-mL glass screw-top jars, 20 mL of 0.1 M sodium phosphate buffer (pH 7.6) was added, and the samples were incubated in an orbital mixer/incubator for 15 min at



23°C. Following this, 100 µL FDA stock solution (2 mg/mL in HPLC grade acetone) was added to the samples before shaking for a further 45 min. After 45 min, 20 mL acetone (HPLC grade) was added, and the samples were transferred into 40-mL screw-cap centrifuge tubes and centrifuged for 15 min at 2900G. Fluorescence of the supernatant was measured using a BMG Fluostar Galaxy fluorescent plate reader, with excitation filter of 485 nm and emission filter of 520 nm, against a sodium fluorescein standard curve.

Microbial biomass C was measured using the chloroform fumigation method described by Vance *et al.* (1987). In brief, 2 subsamples (10 g dry weight equivalent) of the same soil sample were incubated at 80% water-holding capacity for 3 days at 23°C. Following incubation, one subset of samples was exposed to chloroform under vacuum for 24 h. Chloroform was then evacuated from the samples and carbon extracted from both sample sets using 25 mL 0.5 M K<sub>2</sub>SO<sub>4</sub>. After extraction, the samples were centrifuged for 10 min at 3000G and the supernatant filtered (Whatman No. 40) and diluted for analysis using an Aurora 1030w Total Organic Carbon analyser using non-purgeable organic C (NPOC) mode. Prior to the NPOC analysis, inorganic C was purged by acidifying the sample to pH <2. The difference in organic carbon measured from the fumigated and non-fumigated samples represents the component derived from the microbial biomass. The instrument was calibrated with each sample run and quality assurance samples included blanks, a standard solution every 10 samples, and a duplicate analysis every 10 samples.

### Biometrical analysis

Estimates of the average plant response due to each amendment were obtained after a spatial analysis of the experimental design array as described by Gilmour *et al.* (1997). Hypothesis tests regarding the effects of biochar, fertiliser, and their interaction were conducted using the appropriate *F*-ratio tests. Pair-wise comparisons of the averages were made with reference to a calculated least significant difference at 5% critical value. The estimated plant responses to fertiliser and biochar are presented as bar charts (see Figs 2 and 3), including the scale of the least significant difference estimates. Hypothesis test results and statistical inference for specific biochar and fertiliser effects are cited throughout the results and discussion sections as required.

As replicate pots were bulked for measurement of soil chemical characteristics, an analysis of those data as a response to biochar rate, N level, and their interaction over the 2 crops was constructed. This approach uses the radish and wheat crops as replicates of the biochar and nitrogen combinations. In this case, interactions between crop and treatment are assumed to be of a magnitude comparable to the interaction between treatments and replicates. If there is a true impact on the soil chemistry due to interaction between treatment and crop then this approach will be conservative. Main effects of biochar rate (averaged over fertiliser and crops) and fertiliser levels (averaged over biochar and crops) are presented. Data analysis was accomplished using ASReml-R package (Butler *et al.* 2007) in the R environment (R Development Core Team 2008).

## Results

### Characterisation of green waste biochar and soils

The biochar had 78% total C (Table 1) and molar H/C ratio 0.45 (H% 2.92, C% 77.8). Compared with the soil used in the study, the biochar had low available P and mineral N contents and similar total K (Table 1). The biochar had a CEC of 3.2 cmol<sub>c</sub>/kg and liming equivalency <0.5% CaCO<sub>3</sub> (data not shown); however, a trend towards increasing soil pH was observed with increasing biochar application rate. Elemental analysis of the biochar indicated that it did not contain significant heavy metal contamination.

The physical structure of the biochar can be related to its sorption capacity (Downie *et al.* 2009). The BET surface area of the biochar (measured by N adsorption) was 409 m<sup>2</sup>/g, and the biochar had a micropore volume of 0.13 cm<sup>3</sup>/g. This relationship between surface area and micropore volume was found to lie on the trend line of biochar literature values compiled by Downie *et al.* (2009). Most of this surface area was contributed by

**Table 1. Chemical analysis of biochar, soil, and the 5 biochar/soil mixes before glasshouse trial**  
CEC, Cation exchange capacity; NA, not available

Analysis	Green waste biochar	Soil biochar				
		0%	1.1%	2.2%	4.4%	11%
EC (dS/m)	0.13	0.38	0.38	0.37	0.32	0.26
pH(CaCl <sub>2</sub> )	7.5	4.5	4.6	4.6	4.7	4.8
Bray #1 P (mg/kg)	6.3	510	530	510	500	520
Colwell P (mg/kg)	13	NA	NA	NA	NA	NA
Total N (%)	0.14	0.28	0.30	0.28	0.29	0.24
Total C (%)	78	2.1	3.4	4.0	5.7	8.6
NH <sub>4</sub> <sup>+</sup> -N (mg/kg)	<0.3	3.7	4.1	4.2	3.3	3.5
NO <sub>3</sub> <sup>-</sup> -N (mg/kg)	1.2	180	180	180	150	130
Exch. cations (cmol <sub>c</sub> /kg):						
Al	<0.03	0.082	0.067	0.069	0.044	0.047
Ca	2	4.4	4.4	4.5	4.4	4.3
K	0.63	0.63	0.64	0.64	0.65	0.65
Mg	0.15	1.1	1.1	1.1	1.1	1.1
Na	0.45	0.036	0.029	0.031	0.023	0.022
CEC	3.2	6.2	6.2	6.3	6.2	6.1
Total elements						
Al (%)	0.08	0.313	0.344	0.459	0.323	0.304
As (mg/kg)	<3	<3	<3	<3	<3	<3
B (mg/kg)	9.5	<1.9	<1.9	<1.9	<1.9	<1.9
Ca (%)	0.140	0.132	0.137	0.172	0.144	0.131
Cd (mg/kg)	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9
Co (mg/kg)	<1.2	<1.2	<1.2	1.56	<1.2	<1.2
Cr (mg/kg)	4.3	2.91	4.6	7.38	3.89	3.11
Cu (mg/kg)	3.1	20.8	20.2	24	20.3	19.4
Fe (%)	0.26	0.26	0.44	0.53	0.27	0.27
K (%)	0.055	0.0391	0.0404	0.0593	0.0418	0.0407
Mg (%)	0.040	0.020	0.020	0.091	0.021	0.021
Mn (mg/kg)	56	39.2	40.9	61.5	40.5	39.8
Mo (mg/kg)	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2
Na (%)	0.037	0.0021	0.0021	0.0037	0.0025	0.0033
Ni (mg/kg)	2.1	<1.3	<1.3	4.53	<1.3	<1.3
P (%)	0.0096	0.102	0.102	0.112	0.0999	0.0941
Pb (mg/kg)	<1.7	6.77	8.56	9.09	9.15	5.51
S (%)	0.0036	0.0235	0.0231	0.0259	0.023	0.022
Se (mg/kg)	<6.6	<6.6	<6.6	<6.6	<6.6	<6.6
Zn (mg/kg)	25	35.2	36.1	41.4	35.3	33.7



micropore area ( $329 \text{ m}^2/\text{g}$ ), with the average pore diameter being  $17.67 \text{ \AA}$ ; however, the material was also found through the adsorption experiment to have a significant external surface area of  $80 \text{ m}^2/\text{g}$ , indicating macropore structures. This was confirmed by the SEM analysis, which showed a highly porous surface structure with a prevalence of macropores in the  $5\text{--}10 \mu\text{m}$  range (Fig. 1).

The soil was acidic with pH 4.5 (in  $\text{CaCl}_2$ ),  $510 \text{ mg/kg}$  of available P, and  $184 \text{ mg/kg}$  of mineral N. It contained 2.1% total C and had a low effective CEC ( $6.2 \text{ cmol}_{(+)}/\text{kg}$ ). The particle size distribution of the soil was 88% sand, 8% silt, and 4% clay (USDA Method METH004.00). Chemical characteristics of soil and biochar are provided in Table 1.

#### Response of wheat and radish to urea N and biochar

The biomass production response of wheat to N was modified by increasing biochar application rates (Fig. 2). There was a

statistically significant increase in wheat biomass production with increasing N application rate ( $P < 0.001$ ) up to  $4.4\%$  w/w biochar amendment. At an amendment rate of  $11\%$  biochar, maximum biomass was produced at  $44 \text{ kg N/ha}$ ; however, none of the N treatments at this biochar rate had significantly different biomass production. At the highest rate of N ( $177 \text{ kg N/ha}$ ), a negative response to biochar was observed at  $>2.2\%$  biochar application rate. Increasing biochar rates had the greatest positive impact on biomass production at the lower rates of N addition. Maximum biomass production was found with the highest N application rate ( $177 \text{ kg N/ha}$ ) and  $2.2\%$  w/w biochar in soil.

A more consistent trend for biomass production was observed for radish (Fig. 3). Under all biochar rates, radish biomass increased with increasing N ( $P < 0.001$ ). Although the interaction between fertiliser and biochar was not statistically significant (at  $P = 0.5$ ), the biochar amendments tended to have the greatest growth response at the lower N fertiliser rates. The

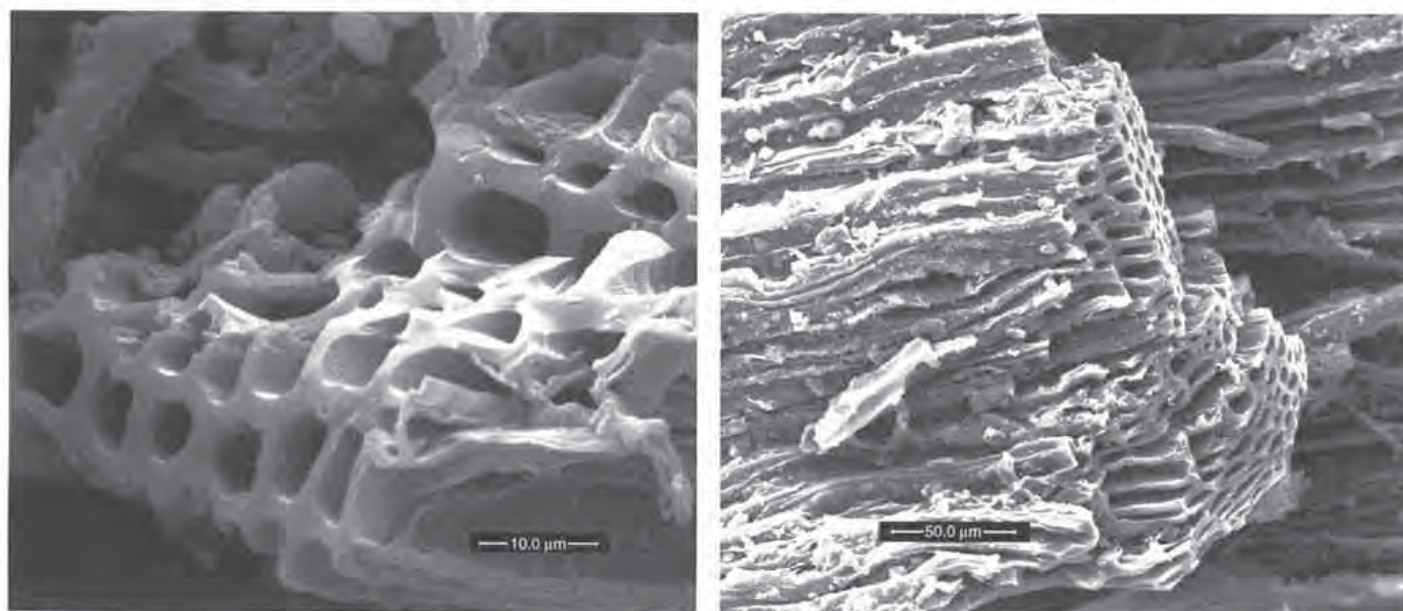


Fig. 1. Scanning electron micrograph showing green waste biochar at 2 magnifications.

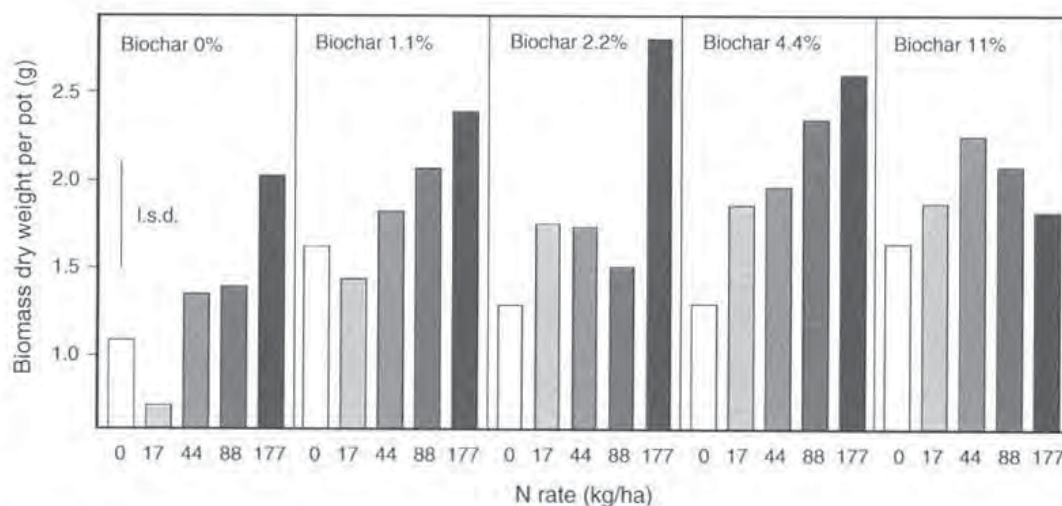


Fig. 2. Wheat biomass from different biochar and N application rates. Least significant difference ( $P = 0.05$ ) provided in the left-hand panel of the graph. Analysis of biomass production revealed a significant biochar  $\times$  N fertiliser interaction.



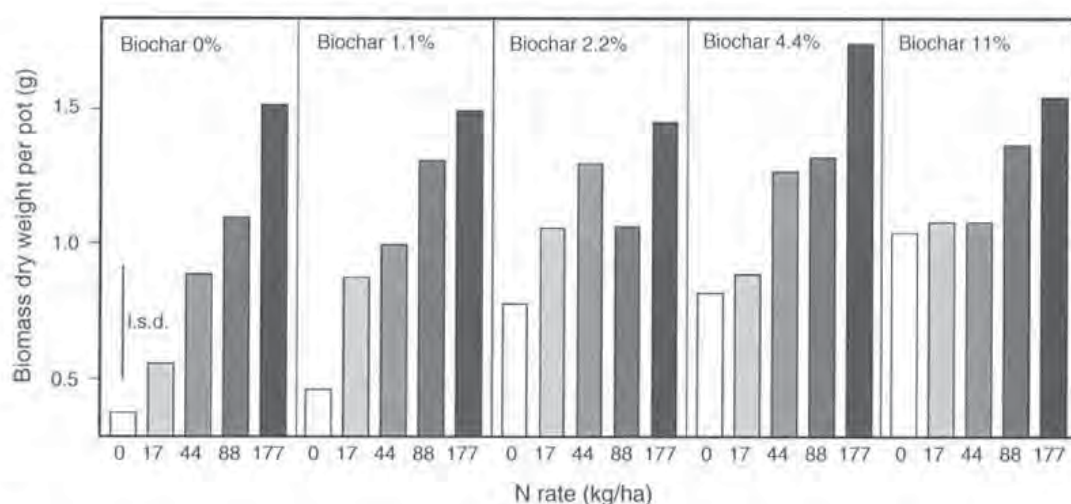


Fig. 3. Radish biomass from different biochar and N application rates. Least significant difference ( $P=0.05$ ) provided in the left-hand panel of the graph. Analysis of biomass production revealed a significant biochar  $\times$  N fertiliser interaction.

yield response to 177 kg N/ha of N was equal across biochar treatments. The 88 kg N/ha treatment demonstrated the influence of biochar addition more clearly; at 2.2% biochar, the biomass yield at only 17 kg N/ha was comparable to 88 kg N/ha with no biochar addition.

Measurement of N uptake into crop tissue could not be made on individual replicates, due to low volumes of plant material. However, N uptake for the bulked replicates of each treatment followed similar trends to biomass production. Nitrogen accumulation increased with increasing biochar concentrations at lower N application rates (Table 2). This effect was not as obvious for the higher N application rates. Similar trends were observed in both plant species.

#### *Influence of biochar and N fertiliser application on soil chemical and biological characteristics*

Application of biochar did not influence soil pH at the end of the glasshouse trial (Table 3); however, significant decreases in pH were observed with increasing N application (Table 4). A drop in pH of 0.43 units was observed between the 0 and highest N application rate. There was a significant increase in total soil C (from 2.1% total C up to 8.6%), consistent with the C content and rates of application of biochar (Table 1). The biochar,

Table 2. Nitrogen uptake (total N measured in above ground biomass as mg/pot) in wheat and radish across the 5  $\times$  biochar and 5  $\times$  N application rates

N applic. rate (kg/ha)	Mineral N applied (mg/pot)	Total mineral N in soil (mg/pot)	Biochar (%)				
			0	1.1	2.2	4.4	11
<i>Wheat</i>							
0	0	46	11	14	11	12	16
17	11	57	6.7	12	16	18	21
44	28	74	12	20	19	19	24
88	56	94	15	21	17	23	21
177	113	146	28	34	45	31	27
<i>Radish</i>							
0	0	46	5.7	6.0	11	11	17
17	11	57	7.3	12	12	12	15
44	28	74	12	14	18	17	15
88	56	94	15	21	18	21	22
177	113	146	27	30	34	26	28

however, influenced oxidisable C as determined by the Walkley–Black method only at the highest application rate. The lack of similarity between results obtained by total C and Walkley–Black C analysis is described in Kurth *et al.* (2006).

Table 3. Main effects of biochar on selected soil properties at the completion of the glasshouse trial averaged over N application

Biochar rate (%):	0	1.1	2.2	4.4	11	s.e.	l.s.d.
pH(CaCl <sub>2</sub> )	4.85	4.82	4.84	4.95	4.89	0.04	0.11
Total C (%)	2.25	2.50	2.93	3.83	6.61	0.28	0.79
Walkley–Black C (%)	1.92	2.05	1.99	1.95	2.12	0.05	0.13
Total N (%)	0.26	0.25	0.25	0.27	0.25	0.01	0.04
NH <sub>4</sub> <sup>+</sup> -N (mg/kg)	8.51	6.19	7.51	6.42	4.70	1.00	2.84
NO <sub>3</sub> <sup>-</sup> -N (mg/kg)	5.85	8.03	5.67	4.67	13.87	1.92	5.43
Bray P (mg/kg)	452	448	443	432	436	5.2	14.7
Total P (%)	0.10	0.11	0.11	0.09	0.09	0.001	0.004
EC (dS/m)	0.07	0.07	0.07	0.06	0.08	0.004	0.011
CEC (cmol <sub>c</sub> /kg)	4.90	5.04	4.96	4.86	4.79	0.07	0.20
Biomass C (mg C/kg)	0.25	0.20	0.24	0.18	0.31	0.03	0.09
FDA (μg fluorescein/g soil)	1.31	1.27	1.40	1.33	1.55	0.04	0.11



**Table 4.** Main effects of nitrogen on selected soil properties at the completion of the glasshouse trial averaged over biochar application

N rate (kg/ha):	0	17	44	88	177	s.e.	l.s.d.
pH(CaCl <sub>2</sub> )	5.06	4.98	4.93	4.75	4.63	0.04	0.11
Total C (%)	3.41	3.86	3.88	3.46	3.51	0.28	0.79
Walkley-Black C (%)	1.97	2.06	1.98	2.00	2.02	0.05	0.13
Total N (%)	0.25	0.25	0.25	0.29	0.25	0.01	0.04
NH <sub>4</sub> <sup>+</sup> -N (mg/kg)	6.52	6.60	7.79	6.52	5.90	1.00	2.84
NO <sub>3</sub> <sup>-</sup> -N (mg/kg)	3.62	3.78	2.89	11.33	16.46	1.92	5.43
Bray P (mg/kg)	425	434	439	447	466	5.2	14.7
Total P (%)	0.10	0.10	0.10	0.10	0.10	0.001	0.004
EC (dS/m)	0.06	0.07	0.06	0.08	0.08	0.004	0.011
CEC (cmol <sub>c</sub> /kg)	5.14	5.15	4.92	4.74	4.60	0.07	0.20
Biomass C (mg C/kg)	0.22	0.22	0.25	0.25	0.23	0.03	0.09
FDA (µg fluorescein/g soil)	1.36	1.36	1.34	1.39	1.42	0.04	0.11

Nitrogen addition (Table 4) did not affect either the total or oxidisable organic C content. At the completion of the study, the total N concentration in the soil was not influenced by either biochar or N addition; however, significant changes were observed in the soil mineral N fraction. The addition of 11% w/w biochar significantly reduced NH<sub>4</sub><sup>+</sup>-N in the soil compared with the control, while also resulting in the highest NO<sub>3</sub><sup>-</sup>-N levels in the soil. No significant changes were observed for the other biochar rates. Application of N fertiliser did not influence the accumulation of NH<sub>4</sub><sup>+</sup>-N in soil; however, significant increases in NO<sub>3</sub><sup>-</sup>-N were observed at the higher rates of N application (88 and 177 kg N/ha). Application of biochar resulted in lower available P in soil, whereas higher rates of N application resulted in greater P availability. Biochar did not influence CEC, but significant declines were observed with higher N application rates.

Biochar did not influence soil biomass C, although the highest rate of biochar application resulted in significant increases in soil microbial activity measured by the fluorescein diacetate method. Nitrogen had no influence on either of the soil biological indicators.

## Discussion

Many agricultural soils globally are deficient in one or more nutrients needed to support healthy and productive plant growth (Baligar *et al.* 2001). Acidity, alkalinity, salinity, erosion, anthropogenic processes, and farming practices have contributed to soil degradation and lowering of fertility across different agroecosystems. The application of biochar to soil has been shown to influence a wide range of soil limitations including low pH and high available Al (van Zwieten *et al.* 2010), compaction and soil structure (Chan *et al.* 2007), nutrient availability (Chan *et al.* 2008), bioavailability of organic (Yu *et al.* 2009) and inorganic (Hua *et al.* 2009; Namgay *et al.* 2010, this issue) contaminants, CEC and nutrient retention (Major *et al.* 2009; Singh *et al.* 2010a, this issue), production of greenhouse gases from soil (van Zwieten *et al.* 2009; Singh *et al.* 2010b), and organic matter decline (Lehmann *et al.* 2006; Kimetu *et al.* 2008).

A low-nutrient, high total C biochar was produced for this work to eliminate complications from endogenous nutrient in the

biochar amendment. The low liming value of this biochar did not alter soil pH, which can also influence other soil properties, notably P availability. The biochar was produced at a relatively high pyrolysis temperature of 600°C and contained a total C content of 78%. The resultant molar H/C ratio of 0.45 suggested high levels of aromaticity and thus stability in soil (Krull *et al.* 2009).

The soil used in this study has been farmed for >20 years for intensive vegetable production. The high N and P measured in the soil at the start of the trial are the result of historically large inputs of fertiliser by the farmer. Biomass production in this glasshouse trial was significantly greater when biochar was applied, and this effect was particularly noticeable at the lower N amendment rates (0, 17, and 44 kg N/ha). Similarly, it was shown that more N was taken up by the plants in the presence of biochar than the control treatment without biochar. There were no differences in tissue N concentrations. Nitrogen in wheat crop tissue was measured at anthesis for maximum N uptake assessment. Thus, this work has provided a clear example of increased N-use efficiency through the application of biochar to soil. Similarly, earlier work by Chan *et al.* (2007) has also indicated that low-nutrient biochars could increase fertiliser-use efficiency, but a range of N concentrations in soil was not available in that work. More pronounced impacts from biochar application, particularly at the lower N input rates, would have been expected had this soil had a lower background N level.

The growth curves for the radish reached a plateau at the higher N input levels. Chan *et al.* (2007) used a very low nutrient soil, and this phenomenon was not observed. In our research, it may be possible to reduce N fertiliser inputs by up to 90% (from 177 to 17 kg N/ha) and achieve the same crop response through the use of biochar. It should be noted, however, that this needs to be tested through to harvest. In the case of wheat, a negative response was observed at >4.4% biochar and 88 kg N/ha. It is possible that this is due to nitrate accumulation and toxicity (Karrou and Maranville 1993).

Analysis of the soils following the study revealed that the highest rate of biochar application (11% w/w) accumulated the greatest amount of NO<sub>3</sub><sup>-</sup>-N in the soil, with a concomitant reduction in NH<sub>4</sub><sup>+</sup>-N. However, this increased nitrification was not evident at lower biochar amendment rates. Increases in nitrification of supplied NH<sub>4</sub><sup>+</sup> following charcoal amendment



into nitrifier-deficient forest soils have been reported by DeLuca *et al.* (2006); the authors found that this response was lacking in grassland soil with naturally high rates of nitrifier activity.

The highest rate of biochar application in this study resulted in the greatest soil microbial activity. Similarly, Kolb *et al.* (2009) describes significant increases in microbial biomass with increasing charcoal, but reductions in mineral N in soil. Mineralisation of soil organic matter is governed by predictable factors, with  $\text{NO}_3^-$ -N as the end product (Olness *et al.* 2001). Crop production interrupts the natural balance through limiting C input into soil, accelerates mineralisation of N, and elevates levels of  $\text{NO}_3^-$ -N. Several factors have been shown to influence  $\text{NO}_3^-$ -N levels in soils: soil clay content, bulk density, organic matter content, pH, temperature, and rainfall. An optimal level of air-filled pore space directly influences the  $\text{NO}_3^-$  concentration, and maximum mineralisation occurs around pH 6.7 (Olness *et al.* 2001). The large macropore area (i.e. >50 nm) of the biochar and the influence of higher pH microsites associated with the biochar may have played a role in the N dynamics. It has previously been suggested that biochars from pine woody residues may have high pH microsites (Gundale and DeLuca 2006). It should be noted that the biochar did not influence the bulk soil pH.

Soil analysis revealed a strong trend towards increasing total C content of soil, but only minor increases in oxidisable organic C (by Walkley–Black method) were detected. Reports in the literature suggest good correlation between the Walkley–Black and dry combustion analytical methodologies (Dieckow *et al.* 2007), but soils used in these studies were unlikely to contain significant pools of black C. This study supports the notion that the Walkley Black method is inappropriate for determination of carbons with high degrees of aromaticity and stability in soil, and significant underestimation of organic C content in soil is possible.

It is anticipated that other soil properties would be influenced by this low mineral ash biochar once it is aged in soil; however, this short-term experiment does not facilitate oxidation and formation of reactive surfaces (Hammes and Schmidt 2009; Joseph *et al.* 2009). These surfaces are common in the biochars found in the *terra preta* soils of the Amazon (Cheng *et al.* 2006), and influence the chemical properties of these soils. Thus, biochar application to soil may have a long-term effect on N-use efficiency. The economic and environmental benefits from maintaining or enhancing productivity, while reducing N fertiliser inputs, could be significant and require more detailed investigation.

## Conclusions

As current cropping systems utilise <50% of N fertiliser applied to soil, technologies that increase N-use efficiency will result in significant economic and environmental outcomes. This research has described the application of a high C, low mineral ash biochar into historically heavily fertilised sandy soil used for vegetable production. Benefits of this addition on biomass production across a range of N application rates were studied. Significant increases in plant biomass production were observed with low rates of N application. This beneficial effect

was not evident at the higher rates of N application (in particular 177 kg N/ha) and in the case of wheat, a negative response was recorded with a combination of high N and biochar inputs. The biochar was shown to influence soil chemical characteristics, in particular available  $\text{NO}_3^-$ -N and total soil C.

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*Appendix E - Influence of biochars on flux of N<sub>2</sub>O and CO<sub>2</sub> from Ferrosol*



## Influence of biochars on flux of N<sub>2</sub>O and CO<sub>2</sub> from Ferrosol

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**Abstract.** Biochars produced by slow pyrolysis of greenwaste (GW), poultry litter (PL), papermill waste (PS), and biosolids (BS) were shown to reduce N<sub>2</sub>O emissions from an acidic Ferrosol. Similar reductions were observed for the untreated GW feedstock. Soil was amended with biochar or feedstock giving application rates of 1 and 5%. Following an initial incubation, nitrogen (N) was added at 165 kg/ha as urea. Microcosms were again incubated before being brought to 100% water-filled porosity and held at this water content for a further 47 days. The flooding phase accounted for the majority (<80%) of total N<sub>2</sub>O emissions. The control soil released 3165 mg N<sub>2</sub>O-N/m<sup>2</sup>, or 15.1% of the available N as N<sub>2</sub>O. Amendment with 1 and 5% GW feedstock significantly reduced emissions to 1470 and 636 mg N<sub>2</sub>O-N/m<sup>2</sup>, respectively. This was equivalent to 8.6 and 3.8% of applied N. The GW biochar produced at 350°C was least effective in reducing emissions, resulting in 1625 and 1705 mg N<sub>2</sub>O-N/m<sup>2</sup> for 1 and 5% amendments. Amendment with BS biochar at 5% had the greatest impact, reducing emissions to 518 mg N<sub>2</sub>O-N/m<sup>2</sup>, or 2.2% of the applied N over the incubation period. Metabolic activity as measured by CO<sub>2</sub> production could not explain the differences in N<sub>2</sub>O emissions between controls and amendments, nor could NH<sub>4</sub><sup>+</sup> or NO<sub>3</sub><sup>-</sup> concentrations in biochar-amended soils. A decrease in NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> following GW feedstock application is likely to have been responsible for reducing N<sub>2</sub>O emissions from this amendment. Reduction in N<sub>2</sub>O emissions from the biochar-amended soils was attributed to increased adsorption of NO<sub>3</sub><sup>-</sup>. Small reductions are possible due to improved aeration and porosity leading to lower levels of denitrification and N<sub>2</sub>O emissions. Alternatively, increased pH was observed, which can drive denitrification through to dinitrogen during soil flooding.

**Additional keywords:** nitrous oxide, soil properties, biochar, greenwaste, poultry litter, biosolids, papermill, slow pyrolysis, mechanism.

### Introduction

Nitrous oxide (N<sub>2</sub>O) is a potent greenhouse gas with global warming potential 298 times greater than the equivalent mass of CO<sub>2</sub> in the atmosphere (Forster *et al.* 2007). It accounted for almost one-quarter of Australia's agricultural emissions, or almost 4% of Australia's total greenhouse emissions in 2006 (DAFF 2009). Anthropogenic sources of N<sub>2</sub>O contributed 3 GT CO<sub>2</sub>e (CO<sub>2</sub> equivalents), around 8% of global emissions in 2004 with agriculture being responsible for 42% of this total (Denman *et al.* 2007).

Nitrogen enters soil primarily through the application of fertilisers, biological N fixation, addition of organic material, and the excreta of animals. Independent of the source of N, IPCC (2007) assign a value of 1% conversion of soil nitrogen to N<sub>2</sub>O, although values greater than this have been recorded in some agricultural systems. For example, up to 21% of applied N in a sugarcane crop in northern New South Wales, Australia, was converted into N<sub>2</sub>O (Denmead *et al.* 2008), equivalent to 45.9 kg N<sub>2</sub>O-N/ha/year. It has been estimated that 0.76 Mt of synthetic N was applied in Australia in 2007 (FIFA 2008); this is compared

to an input of 2.4–3.5 Mt from N fixation associated with legume crops and pasture (GRDC 2006).

Nitrous oxide is formed in soil through 3 key biological mechanisms: nitrification, nitrifier denitrification, and denitrification (Wrage *et al.* 2005). Denitrification is often discussed as the main pathway for N<sub>2</sub>O production (Opdyke *et al.* 2009; Senbayram *et al.* 2009), occurring primarily in moist soils. The key processes controlling production of N<sub>2</sub>O are, however, not well understood (Hernandez-Ramirez *et al.* 2009; Yao *et al.* 2009). Factors that significantly influence emissions of N<sub>2</sub>O from farmed soil can include: N application rate (Jarecki *et al.* 2009); the form of N that has been applied (Thornton *et al.* 1996; Venterea *et al.* 2005); crop type; soil organic C content; pH and texture (Dalal *et al.* 2003); soil aeration and water content (Ball *et al.* 2008; Beare *et al.* 2009); gas diffusivity (Andersen and Petersen 2009); and redox potential (Hernandez-Ramirez *et al.* 2009).

A range of management options have been proposed to reduce emissions of N<sub>2</sub>O from soil. These include matching N application to crop demand (Burton *et al.* 2008), providing



organic amendments to soil to decrease mineral N availability (Yao *et al.* 2009), increasing soil aeration by tillage (Ball *et al.* 2008; Gregorich *et al.* 2008), and application of nitrification inhibitors which decrease  $\text{NO}_3^-$  in soil (Zaman *et al.* 2009). Nitrification inhibitors may also allow for lower fertiliser application rates as N loss from farming systems can be reduced (Linzmeier *et al.* 2001).

Attempting to reduce  $\text{N}_2\text{O}$  emissions when applying feedlot manure to Vertosols, Dalal *et al.* (2009) tested the concurrent application of low-nutrient green waste compost for regulating N release and  $\text{N}_2\text{O}$  emission. Significant increases in  $\text{N}_2\text{O}$  emissions were observed from application of manure alone, but in combination with the low-nutrient green waste compost, reductions in emissions to levels similar to the control were observed. The authors suggested the compost decreased the amount of mineral N (either as  $\text{NH}_4^+$  or  $\text{NO}_3^-$ ) in the manure-amended soil.

More recently, biochar application to soil has been suggested as a means of reducing  $\text{N}_2\text{O}$  emissions (Yanai *et al.* 2007; van Zwieten *et al.* 2009), although data supporting these observations are limited. Biochar is a form of black carbon derived from the pyrolysis of biomass (Lehmann *et al.* 2006). Biochar is protected from rapid microbial degradation, enabling the carbon stored in biochar to remain for hundreds of years (Lehmann *et al.* 2006, 2009). This effectively removes C from the labile pool, providing an additional benefit for climate change mitigation.

In this experiment, the effects of 5 contrasting biochars and 1 feedstock material on  $\text{N}_2\text{O}$  and  $\text{CO}_2$  flux from a Ferrosol were investigated. The soil was unamended (control), or amended with 1 or 5% (w/w) biochar or greenwaste feedstock, and incubated in microcosms under controlled environmental conditions which included a 47-day period when the soils remained flooded.

## Materials and methods

### Biochar production

Biochars were produced by Pacific Pyrolysis (formerly BEST Energies Australia) using a semi-continuous 40 kg/h pilot unit at Somersby, NSW. Biochars from biosolids (BS), poultry litter (PL), and papermill waste (PS) were produced at a highest treatment temperature (HTT) of 550°C and a heating rate 5–10°C/min. Greenwaste biochar (GW) was produced at 2 temperatures with HTT 350°C and heating rate 5–10°C/min (GW350), and HTT 550°C and heating rate 5–10°C/min (GW550). Biochar residence time at HTT was 45 min. Biochars were sieved to below 2 mm before analysis and application to soils.

### Soil and microcosm set-up

A Ferrosol was sourced from a dairy pasture at Wollongbar Primary Industries Institute (28°50'S, 153°25'E) in north-eastern New South Wales. Soil was sieved to 2 mm and thoroughly homogenised. Microcosms consisted of 5-L glass jars with gas-tight lids. Each microcosm contained 1.5 kg (dry weight) of soil/biochar mix repacked to a density around 1 g/cm<sup>3</sup>, resulting in a soil depth of 100 mm. The rates were 1 and 5% biochar (w/w dry material), equivalent to field application rates of 10 and 50 t/ha,

as the bulk density of the soil was 1.02 g/cm<sup>3</sup>. Each soil by biochar combination was replicated in triplicate and allocated positions in a controlled temperature room set at a constant 22°C in the dark. Moisture contents of the soils were maintained close to 65–70% water-filled porosity by mass balance until day 90 of the trial, when the soils were flooded to 90–100% water-filled porosity. Milli-Q water was used in both flooding and nutrient additions. Nitrogen was added (as dissolved urea) at an equivalent 165 kg N/ha at day 60 of the trial.

Subsamples of soil were carefully taken using a stainless-steel microcorer 2.5 cm in diameter by 8 cm deep. Three cores were taken per microcosm and homogenised; 100 g (wet weight) was kept for analysis. Surplus soil was carefully returned to the holes. Soil was gently collapsed around the hole following each sampling period. Samples were collected on days 14, 28, 84, and 132 of the incubation. Sampling at day 84 corresponded to post N addition and pre-flooding, while day 132 was post-flooding.

### Gas analysis

Gas samples were taken in each phase of the incubation at 1 h then 1, 2, 3, 4, 7, 14, and 21 days after each 'trigger' event (i.e. initiation of the incubation, N addition, flooding). Microcosms were incubated with lids off. The lids were sealed exactly 1 h before sampling. Preliminary testing confirmed that the gases were accumulating linearly well beyond this incubation period (data not shown). Greenhouse gas samples were collected from the microcosms using a 25-mL gas-tight syringe (SGE, 25MDR-LL-GT), and introduced into pre-evacuated 12-mL Exetainer<sup>®</sup> vials with grey silicon septa (Labco, UK). Samples were analysed on an Agilent 7890A gas chromatograph (GC) fitted with a Gilson (GX 271) auto sampler. The system has 2 channels leading to  $\mu$ -ECD and FID detectors.  $\text{N}_2\text{O}$  was analysed by  $\mu$ -ECD. The sample was loaded onto a 1000- $\mu$ L sample loop, and then injected onto a 1-m Porapak Q pre column. Gases were then passed onto a 2-m Porapak Q column for further separation. The pre-column was back-flushed to remove moisture after the analytes had passed onto the analytical column.  $\text{CO}_2$  and  $\text{CH}_4$  were analysed by FID. Sample was loaded onto a 500- $\mu$ L sample loop, and then injected onto a 1-m Porapak Q pre column, a 2-m Porapak Q column, then a 1-m molecular sieve column to achieve further separation of gases.  $\text{CO}_2$  was bypassed around the molecular sieve column. Both  $\text{CO}_2$  and  $\text{CH}_4$  were passed through a catalytic methaniser before detection. RSDs (based on 7 replicate injections) for  $\text{N}_2\text{O}$  and  $\text{CO}_2$  were <2%. For each batch of samples, a range of standards, controls, and blanks were included for QC purposes.

The flux rate,  $F_{\text{N}_2\text{O}}$ , was calculated using Eqns 1 and 2. All  $\text{N}_2\text{O}$  flux rates were corrected in order of the actual air temperature during the measurement and recorded as [ $\mu\text{gN}_2\text{O-N m}^2/\text{h}$ ]:

$$F_{\text{N}_2\text{O}} = \frac{b \times V_{\text{CH}} \times \text{MW}_{\text{N}_2\text{O-N}} \times 60 \times 10^6}{A_{\text{CH}} \times \text{MV}_{\text{corr}} \times 10^9} \quad (1)$$

where  $A_{\text{CH}}$  is basal area of the measuring chamber [ $\text{m}^2$ ];  $b$  is increase in concentration [ppb/min];  $\text{MW}_{\text{N}_2\text{O-N}}$  is molecular weight of  $\text{N}_2\text{O-N}$  [28 g/mol];  $\text{MV}_{\text{corr}}$  is temperature-corrected molecular volume [ $\text{m}^3/\text{mol}$ ];  $V_{\text{CH}}$  is volume of the measuring chamber [ $\text{m}^3$ ].



$$MV_{\text{corr}} = 0.02241 \times \left( \frac{273.15 + T}{273.15} \right) \quad (2)$$

where  $MV_{\text{corr}}$  is as defined;  $T$  is air temperature during the measurement [°C]; 0.02241 m<sup>3</sup> is the molar volume of an ideal gas at 1 atm, 273.15 K (Aylward and Finlay 1974).

#### Chemical analyses and quality assurance

All soil, biochar, and plant tissue chemical analyses were undertaken in a NATA (National Association of Testing Authorities, Australia) facility accredited to ISO17025. Soil or biochar (200 g) was dried at 40°C and passed through a 2-mm sieve, homogenised, and subsampled. Total C and N in soil, biochar, and plant samples was measured by Dumas combustion using an Elementar vario MAX CN analyser with combustion chamber set at 900°C and oxygen flow rate of 125 mL/min. Details for the following methods are found in Rayment and Higginson (1992). In summary, oxidisable organic C was measured using the Walkely and Black wet oxidation by dichromate-sulfuric acid mixture (method 6A1). The pH was measured in 0.01 M CaCl<sub>2</sub> (1:5) (method 4B2). Cations and cation exchange capacity (CEC) were assessed by compulsive exchange using 1 M NH<sub>4</sub>OAc (method 15E1). Available orthophosphate-P was tested in soil using Bray#1 extraction (method 9E2). Available orthophosphate-P was also tested in biochar using Colwell bicarbonate extraction (method 9B1). Nitrate and ammonia were assessed using 2 M KCl extract and automated colourimetric procedures (method 7C2). Liming value is reported as carbonate equivalent (method 19A1).

#### Biometrical analysis

Estimates of total gas production were obtained by modelling the observed patterns of response and then interpolating production over the observation period. Each phase of the experiment (pre-incubation, post N addition, and flooding) was treated independently because of information free time lags between final observation in one phase and first observation in the next and because of the dissimilar response patterns observed for each phase.

The relationship between gas production and time was modelled by cubic smoothing splines as described by Verbyla *et al.* (1999). In brief, the models used were:

$$Y = \mathbf{X}b + \mathbf{Z}u + e$$

The term  $Y$  indicates the vector of gas emissions from all jars and occasions. The matrix  $\mathbf{X}$  defines fixed effects and has columns defining a straight-line relationship between emissions and time for each soil. The vector  $b$  contains the corresponding slopes and intercepts. The matrix  $\mathbf{Z}$  defines random effects and includes columns to fit a straight line relationship between emissions and time for each jar as well as columns to define a cubic spline basis for each jar and treatment. The vector  $u$  contains the corresponding random effects. The vector  $e$  contains residuals which are assumed normally distributed with mean zero and covariance matrix  $\mathbf{R}$ . A block diagonal covariance structure was applied to  $\mathbf{R}$  in order to accommodate differing levels of variation from each soil.

The models were used to predict emissions at hourly increments for the duration of each phase. The predictions were summed to estimate total emissions from each soil. Variance of the estimates was calculated by summing the covariance matrix of the predictions. One of the microcosms under the 1% BS amendment yielded nitrous oxide levels 10-fold or higher than the levels from any other microcosm in the study. These values were highly influential and could not be explained under the experimental methods. Observations from this microcosm were not included in the statistical analysis.

Soil traits were summarised by fitting a linear model which had terms to estimate the effects of the amendment, phase, and their interaction. Variation due to microcosms was included as random effects. The model was used to estimate the average response from each soil and phase.

All analyses were conducted by use of the ASReml package (Butler *et al.* 2007) in the R environment (R Development Core Team 2009).

## Results

### Characterisation of biochar

The high temperature GW550 biochar had the highest C content of 75% and an N content of 0.24% (Table 1). The same feedstock pyrolysed at 350°C (GW350) had a lower total C content of 62% and a slightly lower total N content of 0.21%. The PL biochar had a C content of 42%, the PS biochar contained 38% total C, while the BS biochar had the lowest C content of 21%. The PS biochar had the highest liming value of 18% CaCO<sub>3</sub> equivalency despite having a pH of 6.8. The PL biochar had a liming equivalency of 8.8% and a more alkaline pH of 8.9. The GW350, GW550, and BS biochars and GW feedstock also contributed to a liming effect.

Molar H/C ratios of the different biochars indicated that the PS biochar is likely to remain the most stable in soil, while the GW350 had the lowest level of aromaticity and its turnover time in soil is likely to be the shortest. The GW550 had a lower molar H/C ratio (0.36) than the GW350 biochar (0.78). The GW feedstock had a molar H/C ratio of 1.35, similar to unburnt fuel products such as cellulose and lignin (Krull *et al.* 2009). The molar H/C ratio of the biosolids feedstock was 1.7 (data not shown).

### Initial soil analyses

Analysis of the soils before incubation (Table 2) shows changes to the chemical properties following amendment. All amendments resulted in an increase in total C content of the soil. Soil initially had 4.9% total C, but this increased to 12% total C with 5% GW550 biochar. The increase in C content was consistent with the C contents and input rates of the various amendments applied to the soil.

Increases from 0.47 to 0.74% in total N were evident when both PL and BS biochars were added at 5%. There were only small changes in total N for the other amendments. Likewise, PL and BS biochars gave large increases in total P, increasing from 0.095% through to 0.27% for the PL and 0.67% for the BS biochar at 5% application. As the PL biochar contained high levels of K (2.8%), concomitant increases in K content of the soils were evident for both application rates. The PL and BS



Table 1. Characterisation of biochar used in trials

	GW feedstock	GW350	GW550	BS	PL	PS
Total C (%)	44	62	75	21	42	38
Molar H/C ratio	1.35	0.78	0.36	0.54	0.48	0.33
Total N (%)	0.09	0.21	0.24	2.2	2.6	2.5
Total P (%)	0.004	0.056	0.037	5.7	2.4	0.56
Total K (%)	0.02	0.098	0.063	0.19	2.8	0.41
Colwell P (mg/kg)	19	49	72	1400	3700	840
NH <sub>4</sub> <sup>+</sup> -N (mg/kg)	5.0	0.95	0.32	20	9.4	3.3
NO <sub>3</sub> <sup>-</sup> -N (mg/kg)	1.4	<0.2	0.22	0.81	0.45	<0.2
pH(CaCl <sub>2</sub> )	3.2	4.9	7.3	7.9	8.9	6.8
Acid-neutralising capacity (CaCO <sub>3</sub> equivalents)	2.9	8.4	7.5	1.7	8.8	18
<i>Other elements</i>						
Total Al (%)	0.005	0.16	0.07	1.1	0.25	0.8
Total As (mg/kg)	<5	<5	<5	<3	110	<3
Total B (mg/kg)	<4	<4	<4	36	64	10
Total Ca (%)	0.04	0.23	0.12	5.5	4	1.1
Total Cd (mg/kg)	<0.2	<0.2	<0.2	<0.9	<0.9	<0.9
Total Co (mg/kg)	<0.4	1.4	<0.4	10	2.7	3.4
Total Cr (mg/kg)	0.6	14	5.2	48	190	14
Total Cu (mg/kg)	0.7	8.2	3.6	360	310	79
Total Fe (%)	0.03	0.34	0.14	23	0.37	0.53
Total Mg (%)	0.01	0.13	0.029	1.1	0.69	0.31
Total Mn (mg/kg)	14	75	23	790	550	190
Total Mo (mg/kg)	<0.3	<0.3	<0.3	8.1	2.2	1.9
Total Na (%)	0.009	0.08	0.03	0.38	0.61	0.14
Total Ni (mg/kg)	<0.7	5.2	1.2	27	11	5.6
Total Pb (mg/kg)	<2	<2	<0.2	34	<1.7	6.4
Total S (%)	0.006	0.008	0.003	2.6	0.42	0.18
Total Se (mg/kg)	<4	<4	<4	<6.6	<6.6	<6.6
Total Zn (mg/kg)	4.0	76	52	890	550	190

biochar amendments provided large increases in available soil P measured using the Bray#1 method. Control soil had quite low available P of 7.5 mg/kg, but this was increased to 69 mg/kg with 1% PL biochar and 320 mg/kg with 5% PL application. Likewise, BS biochar increased available P up to 19 and 43 mg/kg at 1% and 5%.

The control soil had the highest NH<sub>4</sub><sup>+</sup>-N, at 13 mg/kg, with all of the amendments reducing ammonium slightly. The control soil contained 56 mg/kg NO<sub>3</sub><sup>-</sup>-N initially, and this was reduced to 1.3 and 0.47 mg/kg with the GW feedstock at 1% and 5%, respectively. The GW and PS biochar amendments did not influence available nitrate. Increases in NO<sub>3</sub><sup>-</sup>-N were, however, evident for both the PL and BS biochars. These biochar amendments also gave large increases in Zn and Na in the soil. None of the amendments influenced arsenic (<3 mg/kg), boron (<1.9 mg/kg), cadmium (<0.9 mg/kg), molybdenum (<1.2 mg/kg), lead (<1.7 mg/kg), or selenium (<6.6 mg/kg) (data not shown).

#### N<sub>2</sub>O emissions

The observed and predicted emissions of N<sub>2</sub>O over the 3 incubation phases are shown in Fig. 1. Following mixing of the amendments into the soil, there were low emissions of N<sub>2</sub>O from soil. The second phase of the incubation involved surface application of solubilised urea equivalent to applying 165 kg N/ha; there was no significant emission activity following

application of urea to the soil. However, significant emission activity was observed in the final phase of the incubation, when the soil was flooded. Rates of up to 8000 µg N<sub>2</sub>O-N m<sup>2</sup>/h were observed in the control during the flooding phase.

Assessing the cumulative emissions over the individual phases, Fig. 2 shows that negligible emissions arose from the control directly following amendment (the control was treated identically to the other amendments but no organic materials were incorporated). All of the amendments at 1% resulted in significantly greater emissions than 5% amendment, except for GW feed and BS biochar. The highest emission over this period was observed for the 1% GW350 biochar (193 mg/m<sup>2</sup> of N<sub>2</sub>O-N). GW550 biochar gave significantly lower emissions of N<sub>2</sub>O-N during this phase than the equivalent application rate of the lower temperature GW biochar.

Emissions of N<sub>2</sub>O remained low following the application of solubilised urea (Fig. 3). The highest cumulative emission of 46 mg/m<sup>2</sup> of N<sub>2</sub>O-N over the period was found for GW feedstock addition at 1%. GW feedstock at 5% released 28 mg/m<sup>2</sup> of N<sub>2</sub>O-N while the control released 13 mg/m<sup>2</sup> of N<sub>2</sub>O-N. The biochar amendments released a maximum of 8 mg/m<sup>2</sup> of N<sub>2</sub>O-N; some treatments including BS 5% and PL 1% resulted in small negative fluxes of N<sub>2</sub>O-N, -0.8 to -0.9 mg/m<sup>2</sup>. Emissions from the biochar treatments were significantly different from the control and GW feed treatments, except for the low rate GW350 and both PS rates.



Table 2. Chemical characterisation of soil mixtures following amendment

	Control	GW feed 1%	GW feed 5%	GW350 1%	GW350 5%	GW550 1%	GW550 5%	PL 1%	PL 5%	PS 1%	PS 5%	BS 1%	BS 5%
Total C (%)	4.9	5.8	11	6.7	11	7.0	12	5.5	9.1	5.6	7.3	5.1	6.6
Total N (%)	0.47	0.46	0.45	0.44	0.45	0.48	0.45	0.51	0.74	0.47	0.47	0.52	0.74
Total P (%)	0.095	0.094	0.092	0.093	0.085	0.098	0.089	0.11	0.27	0.098	0.11	0.20	0.67
Total K (%)	0.026	0.026	0.029	0.028	0.031	0.026	0.041	0.07	0.29	0.035	0.034	0.033	0.053
Bray#1 P (mg/kg)	7.5	7.2	9.8	8.4	9.1	10	11	69	320	13	20	19	43
NH <sub>4</sub> <sup>+</sup> -N (mg/kg)	13	9.6	10	10	8.1	7.6	7.0	6.0	6.2	5.2	4.9	7.5	10
NO <sub>3</sub> <sup>-</sup> -N (mg/kg)	56	1.3	0.47	66	40	75	40	98	130	64	59	94	100
EC (dS/m)	0.13	0.047	0.059	0.15	0.11	0.16	0.088	0.39	1.2	0.35	0.53	0.35	0.86
pH(CaCl <sub>2</sub> )	4.2	4.3	4.3	4.3	4.4	4.2	4.5	4.9	6.2	6.1	6.8	4.8	5.9
<i>Exchangeable cations (cmol(+) / kg)</i>													
Al	0.62	0.42	0.50	0.45	0.46	0.66	0.28	0.044	<0.03	<0.03	<0.03	0.093	<0.03
Ca	4.5	4.9	5.0	5.0	4.4	4.5	4.8	6.6	8.9	13	19	7.5	14
K	0.18	0.19	0.26	0.22	0.26	0.21	0.31	1.6	6.2	0.31	0.69	0.26	0.42
Mg	0.68	0.78	0.90	0.78	0.69	0.78	0.79	1.7	4.2	1.0	1.1	1.1	1.7
Na	0.081	0.091	0.12	0.092	0.13	0.092	0.12	0.55	2.1	0.14	0.32	0.25	0.80
CEC	6.1	6.4	6.8	6.5	5.9	6.2	6.3	10	21	14	21	9.2	17
<i>Other elements</i>													
Total Fe (%)	8.4	8.5	7.6	8.3	7.5	8.3	7.4	7.9	7.5	8.1	8.1	8.6	9.6
Total S (%)	0.061	0.060	0.058	0.061	0.054	0.061	0.054	0.066	0.090	0.064	0.071	0.11	0.29
Total Ca (%)	0.11	0.11	0.11	0.10	0.097	0.10	0.12	0.23	0.63	0.36	1.0	0.27	0.73
Total Zn (mg/kg)	33	33	33	34	35	32	35	43	83	34	46	54	120
Total Na (%)	0.0052	0.0053	0.0060	0.0057	0.0068	0.0051	0.0084	0.017	0.065	0.0066	0.014	0.014	0.045
Total Al (%)	6.7	6.6	6.1	6.4	5.9	6.4	5.9	6.4	6.0	6.4	6.3	6.4	5.9
Total Cu (mg/kg)	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	5.6	36	<0.9	4.5	10	52
Total Mg (%)	0.025	0.026	0.026	0.026	0.026	0.025	0.038	0.039	0.090	0.032	0.051	0.048	0.13
Total Mn (mg/kg)	350	330	330	330	320	380	310	370	360	340	340	370	400

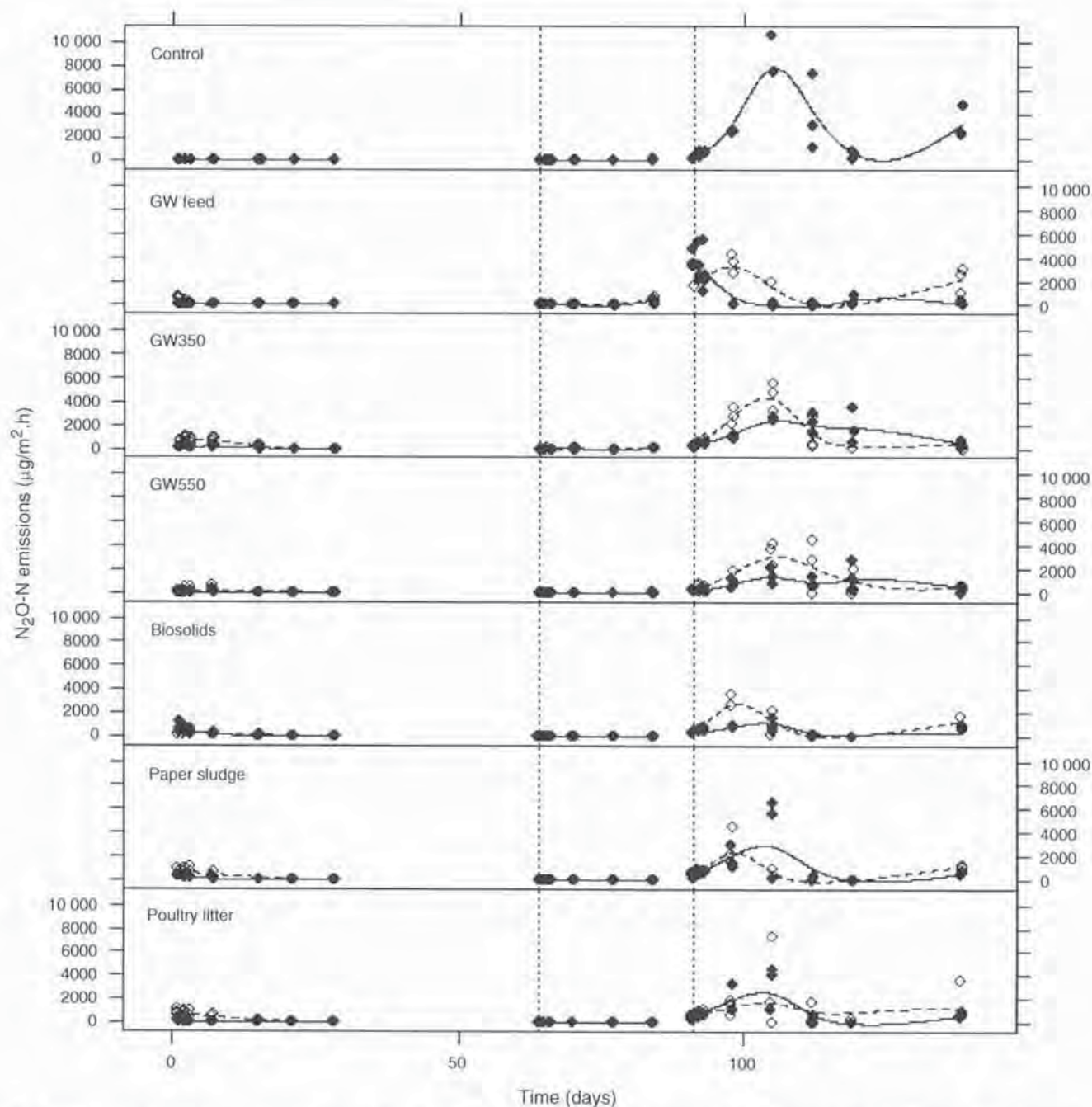
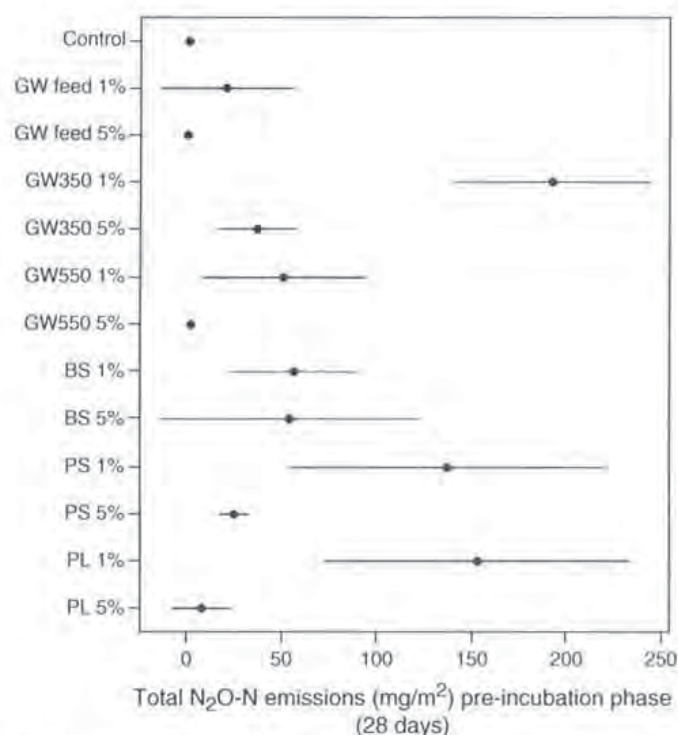


Fig. 1. Observed and predicted emissions of  $\text{N}_2\text{O}$ . The graphs show responses from the nominated char type at 1% (hollow symbols, dashed lines) and 5% (solid symbols and lines) during the 3 experimental phases (indicated by the vertical dotted lines): start of incubation, N addition, flooding.

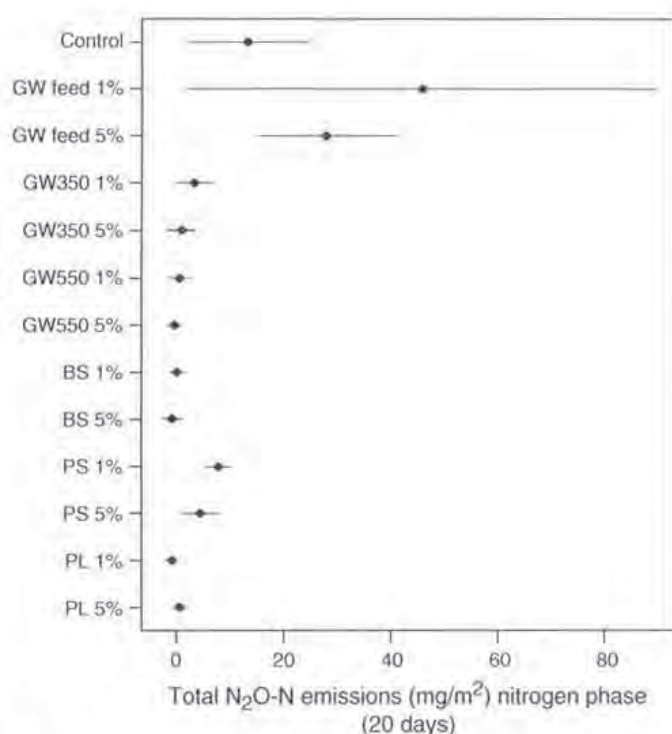
The flooding phase (Fig. 4) accounted for the majority of emissions from all treatments. This phase was maintained for 47 days. Emission data were integrated over the first 28 days. After this time, the control soil in particular behaved unexpectedly, with emissions rising again after the initial peak. The highest cumulative emission was measured in the control, where  $3165 \text{ mg/m}^2$  of  $\text{N}_2\text{O-N}$ , or 15.1% of the applied N, was released (Table 3). The GW feedstock significantly reduced emissions down to  $1470$  and  $636 \text{ mg/m}^2$  of  $\text{N}_2\text{O-N}$  for 1% and 5% amendments, respectively, equal to 8.6 and 3.8% of applied N (Table 3). The GW350 biochar was the least effective biochar in reducing emissions, resulting

in  $1625$  and  $1705 \text{ mg/m}^2$  of  $\text{N}_2\text{O-N}$  for 1% and 5% amendments. GW550 biochar reduced emissions to  $1503$  and  $1029 \text{ mg/m}^2$  of  $\text{N}_2\text{O-N}$  for 1% and 5% amendment, respectively. Amendment with PL biochar reduced emissions to  $1313$  and  $984 \text{ mg/m}^2$   $\text{N}_2\text{O-N}$ , and PS biochar to  $786$  and  $1099 \text{ mg/m}^2$  of  $\text{N}_2\text{O-N}$ , for 1% and 5% amendments. BS biochar at 1% amendment resulted in a cumulative release of  $992 \text{ mg/m}^2$  of  $\text{N}_2\text{O-N}$ , while 5% BS biochar gave the smallest emission of  $518 \text{ mg/m}^2$   $\text{N}_2\text{O-N}$  or 2.2% of the applied N. All treatments significantly lowered emissions of  $\text{N}_2\text{O}$  compared with the control, but treatments were not significantly different from each other.





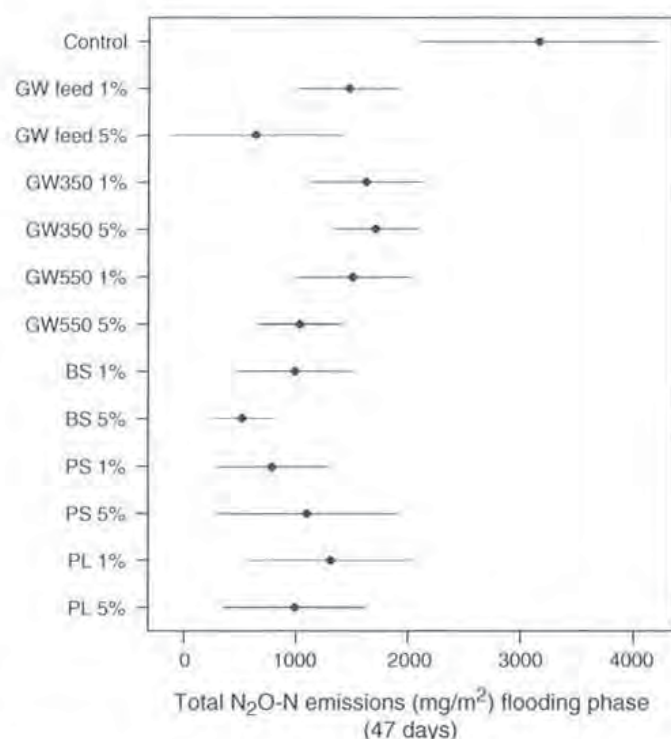
**Fig. 2.** Total nitrous oxide production following amendment with organic materials. Estimates are indicated by points. Horizontal bars span the estimates  $\pm 2$  s.e.



**Fig. 3.** Total nitrous oxide production following urea application (165 kg N/ha). Estimates are indicated by points. Horizontal bars span the estimates  $\pm 2$  s.e.

### $\text{CO}_2$ emissions

The observed and predicted emissions of  $\text{CO}_2$  over the 3 incubation phases are shown in Fig. 5. Most of the release of



**Fig. 4.** Total nitrous oxide production following flooding. Estimates are indicated by points. Horizontal bars span the estimates  $\pm 2$  s.e.

$\text{CO}_2$  occurred with the GW feedstock amendment. In the initial phase following amendment (Fig. 6), the control soil released a cumulative 35 g/m<sup>2</sup> of  $\text{CO}_2$ . This increased to 272 and 233 g/m<sup>2</sup> of  $\text{CO}_2$  for the GW feedstock amendments at 1% and 5%, respectively; these values were significantly higher than with the other amendments. The only other notable emission was found for the PL biochar at 5%, where 67 g/m<sup>2</sup> of  $\text{CO}_2$  was released. Following amendment by N (Fig. 7), the control soil released a further 30 g/m<sup>2</sup> of  $\text{CO}_2$  over the 20-day incubation period. The GW feedstock released 87–97 g/m<sup>2</sup> of  $\text{CO}_2$  over the same period. All of the biochar amendments released less  $\text{CO}_2$  than the control during this phase of the study. The PS amendment at 5% released a cumulative 3 g/m<sup>2</sup> of  $\text{CO}_2$ . During the flooding phase (Fig. 8) the GW feed again resulted in higher  $\text{CO}_2$  emissions. The control released 70 g/m<sup>2</sup> of  $\text{CO}_2$ , while the GW feedstock at 5% resulted in emissions of 405 g/m<sup>2</sup> of  $\text{CO}_2$ . The GW550 biochar and the PS biochar tended to release the least  $\text{CO}_2$  during this phase.

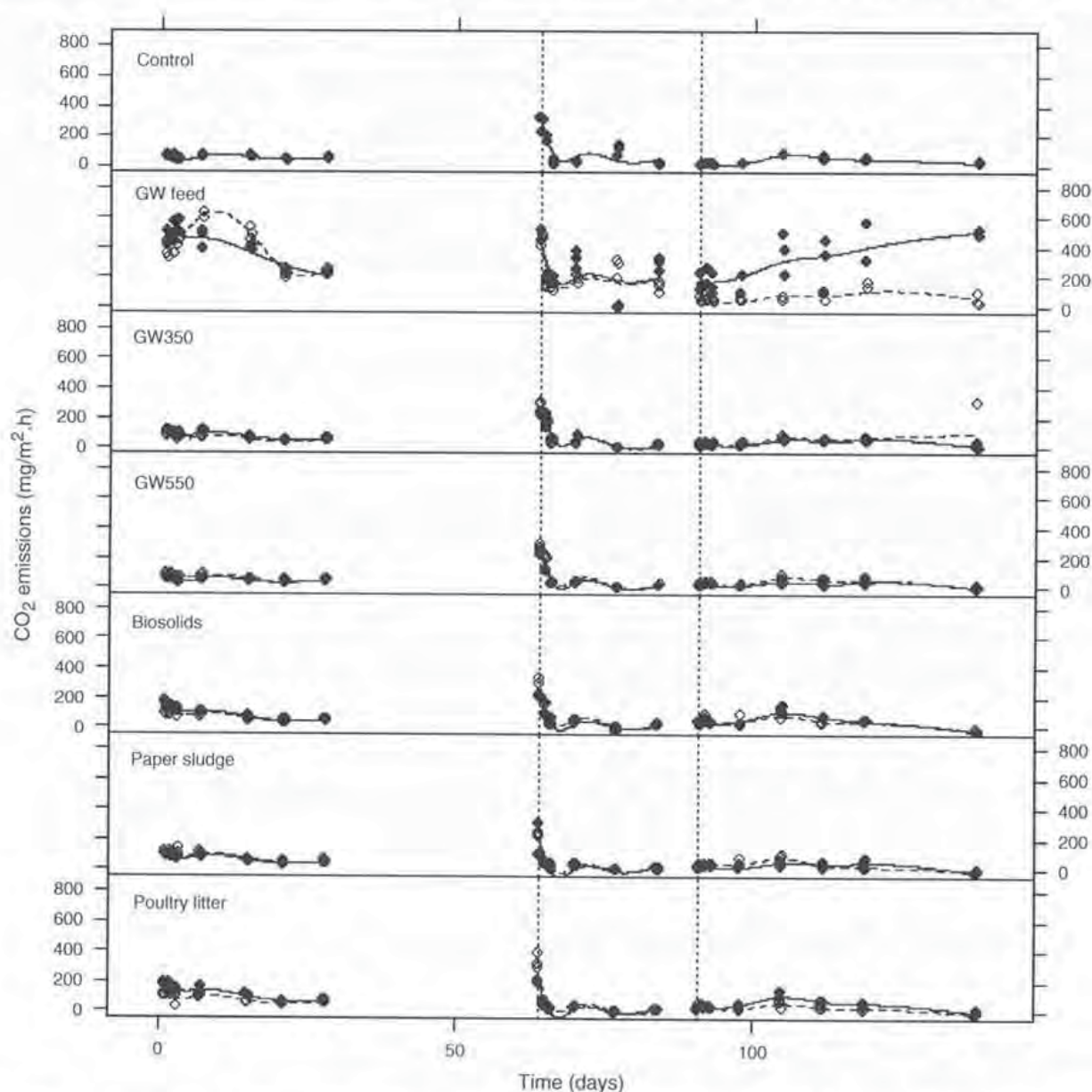
### Analyses of soil during incubation

Soil chemical properties including  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N, pH, CEC, and Bray#1 P were assessed at days 14, 28, 84, and 132 of the incubation. Day 84 corresponded with the period following N addition and before flooding, while day 132 was at the completion of the flooding phase. Water-filled porosity was maintained at 65–70% until the flooding phase, when it was increased to 100%. There was a small amount of free water at the surface of all microcosms. At day 14, all treatments other than GW350 at 1% had significantly lower  $\text{NH}_4^+$ -N concentrations than the control (Table 4). Significant increases in  $\text{NH}_4^+$ -N occurred following urea application, but lower amounts were

**Table 3.** Percentage of N lost as N<sub>2</sub>O from the soil

	% Mineral-N lost following amendment	% N lost following urea application	% N lost following flooding	Total (% initial and added N)
Control	0.1	0.1	15.1	15.2
GW feedstock 1%	2.3	0.3	8.6	9.0
GW feedstock 5%	0.6	0.2	3.8	3.9
GW350 1%	3.0	0.0	8.0	9.0
GW350 5%	0.8	0.0	8.5	8.7
GW550 1%	0.9	0.0	7.2	7.5
GW550 5%	0.1	0.0	5.6	5.6
BS 1%	1.0	0.0	4.5	4.8
BS 5%	1.3	0.0	2.2	2.5
PS 1%	3.9	0.0	3.8	4.5
PS 5%	0.1	0.0	5.1	5.2
PL 1%	3.0	0.0	6.0	6.7
PL 5%	0.0	0.0	3.9	4.0

found in the GW550 biochar at 5% and both amendment rates for the BS, PS, and PL biochars. Following flooding, there was a decrease in NH<sub>4</sub><sup>+</sup>-N concentration in all microcosms. GW550 at 1% had an NH<sub>4</sub><sup>+</sup>-N concentration statistically similar to the control, while all other amendments were lower than the control. Nitrate concentrations were significantly lower in the GW feedstock amendments at all sampling times except directly following urea application (Table 5), when values were similar. The GW feedstock amendment at 5% had significantly less nitrate than the amendment at 1%. Nitrate concentrations in all of the GW biochar amendments and the PS amendments were similar to those found in the control. Amendment with 5% BS and 5% PL biochars resulted in higher nitrate concentrations initially, and following flooding. Following urea application, all biochar amendments had similar nitrate concentrations. Flooding soil decreased available-P in the control (Table 6), and this trend was evident for all of the



**Fig. 5.** Observed and predicted emissions of CO<sub>2</sub>. The graphs show responses from the nominated char type at 1% (hollow symbols, dashed lines) and 5% (solid symbols and lines) during the 3 experimental phases: start of incubation, N addition, flooding.



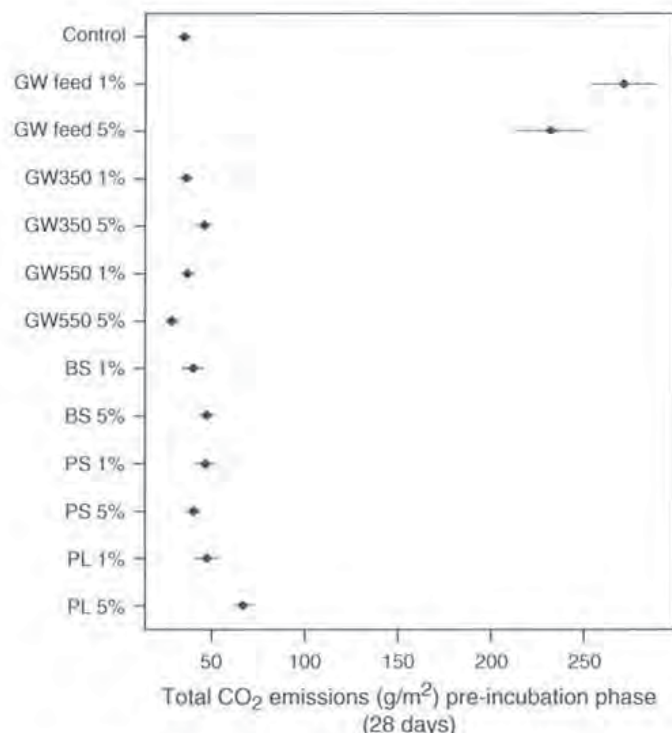


Fig. 6. Total carbon dioxide production following amendment with organic materials. Estimates are indicated by points. Horizontal bars span the estimates  $\pm 2$  s.e.

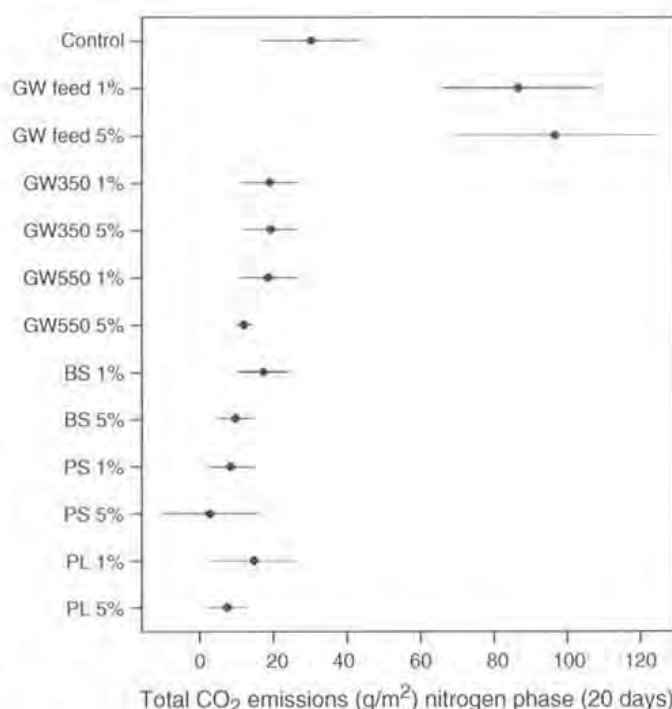


Fig. 7. Total carbon dioxide production following urea application (165 kg N/ha). Estimates are indicated by points. Horizontal bars span the estimates  $\pm 2$  s.e.

amendments. The largest decrease in available P was found for the GW feedstock amendments, where concentrations fell to 2.1 and 1.5 mg/kg for the 1% and 5% amendments, respectively. The highest available-P concentrations were found for amendments with 5% PL biochar and 5% BS biochar.

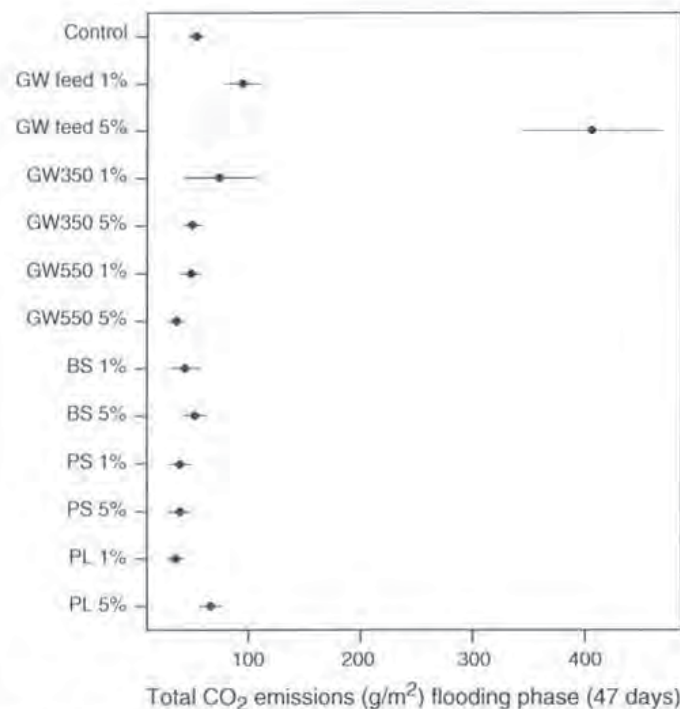


Fig. 8. Total carbon dioxide production following flooding. Estimates are indicated by points. Horizontal bars span the estimates  $\pm 2$  s.e.

There was a small but significant decline in CEC in the control following application of urea and the flooding phase (Table 7). Although the application of GW feedstock and GW biochars did not have a significant influence on CEC, these amended soils did not experience a drop in CEC during the flooding phase. Amendments with the BS, PS, and PL biochars all significantly increased soil CEC at day 14, with a higher application rate of 5% giving significantly higher CEC than amendment with 1%. Except for PS amendment at 1%, all of these biochar amendments significantly increased CEC during the flooding phase. Soil pH was not influenced by amendment with GW feedstock or GW biochars, except for amendment with GW550 at 5% (Table 8), where a small but significant increase of 0.3 units occurred. The GW feedstock and GW biochar amendments tended to result in small increases in pH following flooding. The PS biochar at 5% had the strongest influence on soil pH, increasing it to 7. This pH was maintained throughout the incubation trial. The PL biochar provided the next significant increase in soil pH, with 5% amendment resulting in pH 6.3. The BS biochar also significantly increased pH up to 5.8 at 5% amendment.

#### CH<sub>4</sub> emissions

Methane was measured throughout the trial; however, concentrations were very low, and in some cases, small negative fluxes were observed (data not shown).

#### Discussion

Five biochars produced from slow pyrolysis were utilised in this study. The feed stocks were materials that may be considered waste, or may present problems when used in their native state. These included greenwaste, poultry litter, papermill sludge, and



**Table 4. Changes in ammonium-N during the incubation**

Values are on natural log scale for statistical inference (average l.s.d. 0.48, average s.e. 0.17); values in parentheses are transformed to the original scale for information. Day 0 values are from single analysis of bulked samples

Sampling day:	0	14	28	84	132
Control	(13)	2.42 (11.7)	2.92 (19.3)	5.54 (266.4)	3.45 (32.9)
GW feed 1%	(9.6)	2.23 (9.7)	2.60 (14.0)	5.19 (186.8)	2.71 (15.7)
GW feed 5%	(10)	1.67 (5.6)	2.11 (8.6)	5.67 (301.7)	2.83 (17.6)
GW350 1%	(10)	1.35 (4.0)	1.74 (5.9)	5.28 (205.6)	2.73 (16.0)
GW350 5%	(8.1)	1.88 (6.8)	2.17 (9.1)	5.50 (254.8)	2.73 (16.0)
GW550 1%	(7.6)	1.30 (3.8)	1.76 (6.0)	5.46 (244.8)	3.04 (21.7)
GW550 5%	(7.0)	1.25 (3.6)	1.65 (5.4)	4.75 (120.2)	2.18 (9.2)
BS 1%	(6.0)	1.39 (4.2)	1.70 (5.7)	4.49 (92.5)	2.15 (8.9)
BS 5%	(6.2)	1.93 (7.2)	1.99 (7.6)	3.90 (51.2)	2.12 (8.7)
PS 1%	(5.2)	1.32 (3.9)	1.71 (5.8)	4.49 (92.6)	2.00 (7.7)
PS 5%	(4.9)	1.59 (5.1)	1.78 (6.2)	3.58 (37.4)	2.11 (8.6)
PL 1%	(7.5)	1.52 (4.8)	1.85 (6.7)	4.39 (83.7)	2.28 (10.2)
PL 5%	(10)	1.63 (5.3)	1.75 (6.0)	3.84 (48.5)	1.78 (6.2)

**Table 5. Changes in nitrate-N during the incubation**

Values are on natural log scale for statistical inference (average l.s.d. 0.61, average s.e. 0.22); values in parentheses are transformed to the original scale for information (mg NO<sub>3</sub>-N/kg dry soil)

Sampling day:	0	14	28	84	132
Control	(56)	4.30 (78.9)	4.42 (89.1)	5.90 (392.4)	5.42 (243.2)
GW feed 1%	(1.3)	-0.52 (0.6)	-0.95 (0.4)	5.14 (182.9)	4.20 (71.4)
GW feed 5%	(0.47)	-1.20 (0.3)	-1.90 (0.2)	5.40 (238.5)	0.52 (1.8)
GW350 1%	(66)	4.34 (82.2)	4.38 (86.0)	5.71 (324.4)	5.72 (327.0)
GW350 5%	(40)	4.23 (73.7)	4.30 (79.5)	5.77 (345.9)	5.76 (341.4)
GW550 1%	(75)	4.42 (89.5)	4.51 (98.1)	5.52 (269)	5.71 (325.7)
GW550 5%	(40)	3.73 (44.7)	3.66 (41.7)	5.79 (352.2)	5.72 (329.1)
BS 1%	(98)	4.75 (123.7)	4.79 (129.8)	5.89 (388.6)	6.10 (479.8)
BS 5%	(130)	4.96 (153.4)	4.99 (157.2)	6.08 (470.6)	6.35 (614.8)
PS 1%	(64)	4.49 (95.7)	4.54 (100.5)	5.91 (396.5)	5.80 (354.0)
PS 5%	(59)	4.70 (117.8)	4.73 (121.6)	6.03 (445)	6.00 (434.2)
PL 1%	(94)	4.84 (135.9)	4.76 (125.2)	5.92 (400.0)	6.12 (486.7)
PL 5%	(100)	5.28 (210.8)	5.25 (203.9)	6.17 (515.4)	6.16 (507.7)

**Table 6. Changes in Bray#1 P during the incubation**

Values are on natural log scale for statistical inference (average l.s.d. 0.22, average s.e. 0.08); values in parentheses are transformed to the original scale for information (mg/kg)

Sampling day:	0	14	28	84	132
Control	(7.5)	2.09 (8.2)	2.00 (7.4)	2.32 (10.2)	1.72 (5.6)
GW feed 1%	(7.2)	1.93 (6.9)	1.79 (6.0)	2.15 (8.6)	0.74 (2.1)
GW feed 5%	(9.8)	2.22 (9.3)	1.92 (6.9)	2.53 (12.7)	0.37 (1.5)
GW350 1%	(8.4)	2.11 (8.3)	2.05 (7.9)	2.28 (9.8)	0.99 (2.7)
GW350 5%	(9.1)	2.25 (9.6)	2.29 (9.9)	2.48 (12.1)	1.87 (6.5)
GW550 1%	(10)	2.29 (9.9)	2.37 (10.7)	2.51 (12.4)	1.57 (4.8)
GW550 5%	(11)	2.48 (12.1)	2.54 (12.7)	2.71 (15.1)	1.97 (7.2)
BS 1%	(69)	2.98 (19.8)	3.11 (22.5)	3.13 (23.2)	1.40 (4.1)
BS 5%	(320)	3.61 (37.3)	3.78 (44.0)	3.66 (39.3)	2.28 (9.9)
PS 1%	(13)	2.39 (11)	2.71 (15.2)	2.61 (13.7)	1.50 (4.5)
PS 5%	(20)	2.54 (12.7)	2.79 (16.4)	2.75 (15.8)	1.03 (2.8)
PL 1%	(19)	4.28 (73.2)	4.34 (77.7)	4.42 (83.9)	3.56 (35.4)
PL 5%	(43)	5.70 (302.3)	5.76 (319.0)	5.78 (325.9)	5.36 (215.1)

biosolids. These feed stocks produced biochars with varying properties. For example, the GW550 biochar had a total C content of 75%, while the BS biochar had only 21% total C content. The lower H/C ratios of the GW550 and PS biochars

suggests increased aromaticity and maturation (Krull *et al.* 2009) compared with the low temperature GW biochar, and the BS and PL biochar. The molar H/C ratios also related to the potential residence time in soil, with structures protected from microbial



**Table 7. Changes in CEC during the incubation**

Values are on natural log scale for statistical inference (average l.s.d. 0.06, average s.e. 0.02); values in parentheses are transformed to the original scale for information (cmol (+)/kg)

Sampling day:	14	28	84	132
Control	1.78 (5.9)	1.84 (6.3)	1.68 (5.4)	1.68 (5.4)
GW feed 1%	1.81 (6.1)	1.87 (6.5)	1.64 (5.1)	1.76 (5.8)
GW feed 5%	1.90 (6.7)	1.93 (6.9)	1.75 (5.8)	1.83 (6.3)
GW350 1%	1.85 (6.4)	1.89 (6.6)	1.72 (5.6)	1.83 (6.3)
GW350 5%	1.77 (5.9)	1.82 (6.2)	1.66 (5.3)	1.81 (6.1)
GW550 1%	1.80 (6.0)	1.89 (6.6)	1.59 (4.9)	1.75 (5.7)
GW550 5%	1.82 (6.2)	1.87 (6.5)	1.70 (5.5)	1.86 (6.4)
BS 1%	2.28 (9.8)	2.28 (9.7)	2.23 (9.3)	2.47 (11.8)
BS 5%	2.91 (18.3)	2.83 (17.0)	2.95 (19.2)	3.3 (27.1)
PS 1%	2.59 (13.3)	2.54 (12.7)	2.48 (11.9)	2.59 (13.3)
PS 5%	3.14 (23.0)	3.09 (22.0)	3.32 (27.6)	3.56 (35.1)
PL 1%	2.40 (11.0)	2.40 (11.0)	2.34 (10.4)	2.57 (13.1)
PL 5%	3.14 (23.0)	3.14 (23.0)	3.05 (21.2)	3.28 (26.7)

**Table 8. Changes in pH(CaCl<sub>2</sub>) during the incubation**

Average l.s.d. 0.16, average s.e. 0.06

Sampling day:	14	28	84	132
Control	4.2	4.4	4.3	4.3
GW feed 1%	4.4	4.5	4.4	4.7
GW feed 5%	4.3	4.5	4.5	4.7
GW350 1%	4.3	4.5	4.4	4.5
GW350 5%	4.4	4.4	4.5	4.4
GW550 1%	4.3	4.4	4.4	4.3
GW550 5%	4.5	4.7	4.3	4.6
BS 1%	4.8	4.8	4.7	5.0
BS 5%	5.8	5.7	5.9	6.0
PS 1%	5.9	5.6	5.6	5.6
PS 5%	7.0	6.9	7.0	7.0
PL 1%	5.0	4.8	4.8	5.1
PL 5%	6.3	6.1	6.0	6.4

degradation. There was a large decrease in molar H/C ratios from the GW feedstock and the BS feedstock to their respective biochars. The higher molar H/C ratio of the BS feedstock of 1.7 suggests that this material would be available for rapid degradation in soil. This is reflected in the elevated CO<sub>2</sub> emissions that were measured relative to the control and biochar treatments.

The biochars contained low concentrations of mineral N compared with the unamended soil, which had 56 mg/kg of NO<sub>3</sub><sup>-</sup>-N and 13 mg/kg of NH<sub>4</sub><sup>+</sup>-N. The highest mineral N content was found in the BS biochar, which had a total of almost 21 mg/kg combined NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>-N. The PL biochar had 3700 mg/kg of available-P, and the BS 1400 mg/kg. Available-P concentrations in this range have been previously reported for poultry biochars (Chan *et al.* 2008). The biochars were also tested for a range of potential contaminants. Copper and zinc concentrations in the BS and PL biochars would have them classified as Grade B, if Australian biosolids guidelines were applied (Natural Resource Management Ministerial Council 2005). It should be noted, however, that biochars are unlikely to be produced from these pure feed stock materials, due to negative energy balance in the case of BS, and the

availability of material in the case of PL. A more likely scenario would be the mixing of these feed stocks with lower nutrient, higher energy materials such as green waste or wood chip. Additionally, biochar is anticipated to be used at much lower rates than biosolids application to soils (10–20 t/ha for v. 100–200 t/ha (wet weight, biosolids)). Biochar application would also most likely be a single application.

The amendments produced some large changes in the soil chemical properties at the commencement of the trial. For example, the greenwaste feedstock with a C:N ratio of 188:1 almost completely immobilised NO<sub>3</sub><sup>-</sup>. This N immobilisation occurs when biomass with high C:N ratios is added to soils (Burgos *et al.* 2006), but later mineralisation is possible when the substrate breaks down. As the PL and BS biochars contained mineral N, it was expected that mineral N concentrations would initially increase in soils with these amendments. This is supported by the measured available-N, notably KCl-extractable NO<sub>3</sub><sup>-</sup> (Tables 4 and 5). The PL, PS, and BS biochars gave large increases in soil pH and CEC. Hence, it is evident that amendment with biochars from different feed stocks resulted in soils with a wide range of chemical characteristics.

It is well established that organic materials such as sewage sludge and poultry manure additions to soil result in N<sub>2</sub>O emissions sometimes far greater than equivalent amounts of chemical fertiliser (Jones *et al.* 2007; Hayakawa *et al.* 2009), especially following rainfall. In fact, emissions from sewage sludge amendment were 26 times greater than ammonium nitrate fertiliser. Results from our studies clearly demonstrate that if these organic amendments are processed via slow pyrolysis, they do not pose the same greenhouse gas risk as untreated organic material. Indeed, the biochars produced from the BS feed stocks were the most effective in reducing overall emissions of N<sub>2</sub>O compared with the control soil. The control soil that received an equivalent 165 kg N (in the form of urea) released 15.2% of this N as N<sub>2</sub>O, while amendment of the soil with 5% BS biochar resulted in only 2.5% of the N being converted into N<sub>2</sub>O. This is an 84% decrease in emissions. Likewise, the PL biochar reduced emissions to 4.0% of applied and available N. Generally, the higher rate of amendment resulted in greater reduction of N<sub>2</sub>O release. Figure 1 clearly demonstrates that the majority of emissions of N<sub>2</sub>O occur during the flooding phase when the water-filled porosity was close to 100%, and the benefits of the amendments are most obvious during this period. Scheer *et al.* (2008) observed in the field that fertilisation in combination with wet conditions was the major cause of N<sub>2</sub>O emissions, accounting for up to 2.6% of applied N. Rudaz *et al.* (1991) also demonstrated that wetting soil accounts for significant N<sub>2</sub>O emissions. Singh *et al.* (2010) observed in microcosm studies that the greatest peak of N<sub>2</sub>O formation occurred immediately following the first wetting cycle.

All of the amendments (other than 1% GW350) had lower NH<sub>4</sub><sup>+</sup> levels in soil at the end of the flooding period. However, results for NO<sub>3</sub><sup>-</sup> were more complex. The control soil had 243 mg/kg of NO<sub>3</sub><sup>-</sup>-N, which was reduced significantly by N draw-down, from application of the high C:N ratio GW feedstock amendments. The GW and PS biochars were not significantly different from the control, displaying either moderate immobilisation of N, or stimulation of nitrification activity in the system. The high mineral biochars, PL and BS



biochar, displayed either higher N sorption capacity, or greater stimulation of nitrification activity resulting in higher levels of soil  $\text{NO}_3^-$ . DeLuca *et al.* (2006) showed that biochar is capable of stimulating nitrifier activity. This was generally observed in soils with low initial nitrifier activity, not agricultural soils. In any case, our data do not allow discrimination between adsorption of  $\text{NO}_3^-$  and nitrification. The differences in  $\text{N}_2\text{O}$  emissions in our study could not be explained on the basis of mineral N in soil alone.

It has been shown that increased metabolic activity through increased available carbon can lead to decreased oxygen in the soil, favouring enhanced denitrification (Miller *et al.* 2008). In our study, however, treatment with GW feedstock did not result in additional  $\text{N}_2\text{O}$  production, even though metabolic activity as seen by  $\text{CO}_2$  emissions was significantly greater than the control and biochar amendments. Immediately following N addition, a sharp increase in respiration was observed; however, this can be explained by the expected  $\text{CO}_2$  evolution from urea hydrolysis. Assuming 100% hydrolysis,  $29 \text{ g CO}_2/\text{m}^2$  will be generated from the urea applied to the microcosms. This accounts for 97% of the  $\text{CO}_2$  generated in the control soil in phase 2 of the incubation. GW feed treatments released additional  $\text{CO}_2$ , consistent with the labile form of carbon in these treatments. However, this increase in activity did not influence emission of  $\text{N}_2\text{O}$ . The maximum emissions of  $\text{N}_2\text{O}$  in the control soil occurred during the flooding period when  $\text{CO}_2$  emissions were  $<100 \text{ mg CO}_2/\text{m}^2\cdot\text{h}$ . In contrast, the GW feedstock had emissions of  $100\text{--}600 \text{ mg CO}_2/\text{m}^2\cdot\text{h}$  during this period, and significantly lower emissions of  $\text{N}_2\text{O}$  than the control.

Biochar application to soil can alter soil physical properties (Downie *et al.* 2009). Chan *et al.* (2007) observed that application of greenwaste biochar at rates  $>50 \text{ t/ha}$  ( $\sim 5\%$ ) can result in significant decreases in soil tensile strength, while Asai *et al.* (2009) demonstrated increases in saturated hydraulic conductivity following biochar amendment in the field. By increasing soil porosity using biochars with high surface areas (Downie *et al.* 2009), it is likely that the amendments in this study altered aeration in the soil as well as redox potential. We hypothesise that biochar amendment influenced the soil physical structure, increasing air content and therefore reducing levels of denitrification.

Soil pH has a major influence on both  $\text{N}_2\text{O}$  production and  $\text{N}_2\text{O}/\text{N}_2$  ratio of emissions (Clough *et al.* 2004). Work by Clough *et al.* (2004) has shown that when soil is at field capacity, pH values  $>5.9$  result in lower  $\text{N}_2\text{O}$  flux than lower pH values. It was also shown that in saturated soils, the  $\text{N}_2\text{O}/\text{N}_2$  ratio decreased with increasing pH values, thus forcing denitrification through to dinitrogen. In the current study, amendment with the PL, BS, and PS biochars resulted in significant increases in soil pH, results also observed by van Zwieten *et al.* (2010), while also having significantly higher  $\text{NO}_3^-$  concentrations in the soil. Soil  $\text{NO}_3^-$  concentrations are generally linked to higher emissions of  $\text{N}_2\text{O}$  (Gillam *et al.* 2008) but do not influence denitrification reactions. We hypothesise that biochar amendment provided a liming effect in soil and, thus, during the flooded phase, encouraged denitrification to proceed to dinitrogen. This would require  $\delta\text{N}^{15}$  studies to confirm.

It is likely that in agricultural systems, the higher  $\text{NO}_3^-$  concentrations found in the PL, BS, and PS biochar-amended soils would have been taken up by plants. This is especially likely as these amendments increased CEC, in particular available Ca and K, which would encourage plant uptake of  $\text{NO}_3^-$  (Chan *et al.* 2007).

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*Appendix F – Effect of biochar on soil carbon storage, fertility and  
productivity in subtropical pasture*

# Effect of biochar on soil carbon storage, fertility and productivity in subtropical pasture

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**Keywords:** biochar, soil carbon, agricultural emissions, P availability, pasture productivity

## Abstract

This study provides timely evidence of the impacts of biochar in a subtropical pasture, where very high inputs of fertiliser and lime are required to maintain productivity. Biochars from beef feedlot manure [FM] and municipal greenwaste [GW] were soil incorporated at 10t ha<sup>-1</sup> and tested for their capacity to influence storage of C in soil, pasture productivity and soil fertility. The biochars differed in their chemical properties with FM and GW biochars having a carbon content of 44 and 76% with molar H/C ratios of 0.51 and 0.71, and liming values of 13 and 5.6% respectively. Significant accumulation of soil C occurred over the 3-year trial period in the biochar amended plots. Soil initially contained 4.7% C which increased to between 5.1- 5.4% following amendment with biochar. With GW biochar and farmer-practice fertiliser rates, soil C increased to 6.5% after 3 years. No significant increases were detected for non -biochar amended controls. The FM biochar gave significant increases (almost double) in plant available P in both the fertilised and unfertilised plots 3 years following trial establishment. FM biochar provided significant increases in yield of annual ryegrass, but this was not evident for the GW biochar. There was no significant difference in soil microbial biomass between treatments.

## 1 Introduction

2 Emerging research on the manufacture and agronomic application of biochar suggests that this  
3 technology has the potential to effectively meet both the productivity and greenhouse gas (GHG)  
4 abatement challenge for agricultural systems (Lehmann & Joseph, 2009). Biochar is a high carbon  
5 material produced from a range of processes including slow pyrolysis. The properties of biochar  
6 depend principally on the type of feedstock used and the production conditions such as temperature  
7 and residence time (Glaser *et al.*, 2002; Downie *et al.*, 2009).

8  
9 Biochar has the potential to increase nutrient availability when applied to soils. This increase in  
10 soil nutrient availability results directly from the addition of nutrients in the biochar and indirectly  
11 from increased nutrient retention and microbial biomass in the soil (Lehmann *et al.*, 2003). In the  
12 glasshouse, Chan *et al.*, (2007, 2008) and Van Zwieten *et al.*, (2010) have shown that biochar  
13 derived from different biomass feedstocks can significantly improve plant growth, increase  
14 nutrient use efficiency and improve soil quality. Blackwell *et al.*, (2010) in dryland wheat studies  
15 found that applying banded wood derived biochar at around 1 t ha<sup>-1</sup> with P fertiliser resulted in  
16 grain yield increases up to 40%. Yield increases were, however, associated with low soil available  
17 P sites and for those sites which had experienced drought stress. Similarly, Yamato *et al.*, (2006)  
18 reported increased yields of maize and peanut when bark charcoal was applied with NPK fertiliser  
19 to an infertile but not to a fertile soil.

20  
21 Cool season forage for grazing dairy cattle in the subtropical dairy region of eastern Australia is  
22 based on annual ryegrass (*Lolium multiflorum*) pastures. These intensively grazed pastures are  
23 highly productive when irrigated and high rates of NPK fertiliser are regularly applied. Lowe *et al.*,  
24 (2005), for instance, recommends that 50-85 kg N ha<sup>-1</sup>month<sup>-1</sup> be applied to annual ryegrass  
25 following grazing so as to achieve 90% maximum yield, irrespective of soil type. The growing

season usually extends from May to November which means a total N application between 300-510 kg ha<sup>-1</sup>.

Much of the subtropical dairy region in northern NSW is conducted on naturally acidic red ferrosols which supported tropical rainforests before clearing in the late 1800s (Moody, 1994). When these tropical rainforests were replaced by dairy pastures soil fertility declined not only as a result of a decrease in organic matter and nutrient removal in forage but also because of an increase in acidity exacerbated by the frequent application of N fertiliser at high rates (Nicolls *et al.*, 1953). As a consequence, it is common practice to periodically apply lime to these pasture soils in order to ameliorate the acidification associated with high N use and to sustain pasture productivity (Fulkerson *et al.*, 1993).

The use of N fertiliser to drive crop and pasture growth has been identified as a significant source of N<sub>2</sub>O emissions from soil (Snyder *et al.*, 2009). Urea is the main form of N fertiliser applied to annual ryegrass pastures in this subtropical environment. The direct CO<sub>2</sub> and N<sub>2</sub>O emissions from urea application to soils are estimated to be 3 t CO<sub>2</sub>-e urea t<sup>-1</sup> (De Klein *et al.*, 2006). As well, additional emissions arise during fertiliser manufacture and transport (Wood & Cowie, 2004).

The application of lime to offset the acidifying effects of urea also results in GHG emissions as CO<sub>2</sub> is released from soil during the chemical dissolution of lime. Using the IPCC default value of 12% for lime, applying 1 t lime to soil has the potential to directly emit 0.44 t CO<sub>2</sub>-e yr<sup>-1</sup> (De Klein *et al.*, 2006). Also, liming acid soils can increase soil microbial activity which may decrease soil carbon (Chan & Heenan, 1996).



The availability of P for plant uptake is highly dependent on the physical and chemical properties of the soil. In dairy pastures, P fixation in soils can amount to 5-25 kg ha<sup>-1</sup>yr<sup>-1</sup> depending on the soil type and productivity (Tillman, 1995) or representing between 50-80% of applied P (Richardson *et al.*, 2009) resulting in low P-uptake efficiency. Although ferrosols generally have high total P content the plant-available P is low due to its complexation with Al and Fe oxides, clays and organic matter (Moody, 1994). In order to avoid potential yield reductions caused by low soil P availability the fertiliser P requirement for annual ryegrass pastures on this soil type is 15-20 kg ha<sup>-1</sup>yr<sup>-1</sup> above the general recommendation (Havilah *et al.*, 2002; Lippke *et al.*, 2006).

The subtropical dairy production system is thus characterised by a high demand for manufactured fertilisers and soil additives, and a corresponding level of both direct and indirect GHG emissions. New production technologies for this system will need to demonstrate not only the capacity to improve yield and fertiliser use efficiency but also reduce net GHG emissions.

The aim of this study was to assess, in a subtropical environment, the benefit of applying biochar and lime to an acid soil by comparing differences in soil carbon storage, soil fertility, biomass production and nutrient uptake. The implications of the results to the GHG emissions from this farming system are discussed.

## **Materials and methods**

### *Site*

A field study was conducted on a highly permeable red ferrosol derived from basalt (Isbell, 1996) at the Wollongbar Primary Industries Institute (28°50'S, 153°25'E; elevation 140 m), Wollongbar, New South Wales, Australia from November 2006 for a period of 3 years. The monthly rainfall

and the mean monthly maximum and minimum ambient temperatures for the annual ryegrass growth periods are shown in Fig 1.

#### *Biochar types*

The biochars were derived from either beef feedlot manure (FM) or municipal greenwaste (GW) and were produced by Pacific Pyrolysis P/L using a continuous 300 kg h<sup>-1</sup> pilot slow-pyrolysis unit located at Somersby, NSW. Both biochars were produced at a highest treatment temperature of 550°C and at a heating rate of 5-10°C min<sup>-1</sup>.

#### *Experimental design and treatments*

Twelve treatments were derived as factorial combinations of fertiliser, lime and biochar. Fertiliser levels were F<sub>0</sub> = 0 and F<sub>1</sub> = annual rates of 22 and 50 kg ha<sup>-1</sup> yr<sup>-1</sup> of P and K applied as molybdenum (Mo) superphosphate and muriate of potash, respectively. In the F<sub>1</sub> treatment, 46 kg N as urea ha<sup>-1</sup> was applied 6 times during the ryegrass growing season for a total of 276 kg ha<sup>-1</sup> yr<sup>-1</sup>. Lime levels were L<sub>0</sub> = 0 and L<sub>1</sub> = 5 t ha<sup>-1</sup> of superfine agricultural lime (Ca 37.7%, 94.1% as CaCO<sub>3</sub>; neutralising value 94%; fines>90%). Biochar levels were C<sub>0</sub> = 0, C<sub>1</sub> = FM biochar and C<sub>2</sub> = GW biochar, both applied at 10 t ha<sup>-1</sup> fresh weight.

Plots (4 m x 5 m) were laid out in a randomised complete block design with three replicates. In November 2006, the lime and biochars were surface applied to the appropriate treatment plots and immediately incorporated to a depth of 100-150 mm using a rotary hoe. The experimental area was then direct-drilled to forage peanut (*Arachis pinto* cv. Amarillo), a perennial tropical legume, at a seeding rate of 100 kg ha<sup>-1</sup>. Following sowing 250 kg ha<sup>-1</sup> Mo superphosphate was applied to all plots. The NPK fertiliser treatment plots received N fertiliser after each ryegrass harvest, approximately monthly while the P and K fertilisers were applied as split dressings on 13 June/7

December 2007 and then 10 July/4 December 2008. No fertiliser was applied following the last ryegrass harvest in 2008.

#### *Pasture management*

In April 2007 and 2008, cv. Warrior, a tetraploid annual ryegrass, was broadcast at 35 kg ha<sup>-1</sup> onto the established forage peanut pasture which had been mown to a height of 5 cm above ground level. Following an initial establishment of 6 weeks, annual ryegrass was the dominant pasture species from late May until December of each year, at which time the forage peanut became dominant. The pasture was harvested when the ryegrass plant had 2.5- 3 leaves per tiller since this stage has been found to be optimal in terms of forage yield and quality (Fulkerson and Donaghy, 2001).

#### *Sampling and analyses*

Annual ryegrass dry matter (DM) yield At each harvest date the entire plot was cut with a rotary mower to 5 cm above ground level, the cut biomass weighed and a subsample taken and dried in a forced-draught oven at 80°C for 24 h to determine dry matter (DM) yield. No assessment of biomass production was made on the warm season forage peanut with a summer to early autumn growing season in this subtropical environment.

Nutrient uptake In September 2007 leaf material from the harvested oven-dried subsample was ground to pass through a 1 mm sieve to determine N, P, K, Ca, Mg, and Na concentration.

Total leaf N concentration was measured by Dumas combustion using an Elementar™ vario MAX CN analyser with combustion chamber set at 900°C and oxygen flow rate of 125 mL min<sup>-1</sup>, based on the SPAC 11 (Horneck & Miller, 1998). Leaf P and metal concentration was determined using

a Perkin Elmer Optima 5300 DV inductively coupled plasma atomic emission spectrometry (ICP-AES) (USEPA, 2000) following microwave digestion (SPAC Method 8) of the plant material.

Soil and biochar properties In April 2007, December 2007, December 2008 and October 2009 three soil cores (50 mm diameter) to 75 mm depth were taken from each plot, air-dried, composited and passed through a 1 mm sieve prior to analysis. Soil and biochar chemical analyses were undertaken in a NATA (National Association of Testing Authorities, Australia) facility accredited to ISO17025.

Total C and N were measured by Dumas combustion using an Elementar vario MAX CN analyser with combustion chamber set at 900 °C and oxygen flow rate of 125 mL·min<sup>-1</sup>. The pH was measured in 0.01 M CaCl<sub>2</sub> (1:5) according to method 4B2 (Rayment and Higginson 1992). Cations and CEC were assessed using exchange into 1 M NH<sub>4</sub>OAc described in method 15E1 (Rayment and Higginson 1992). P was tested using Bray #1 extraction as described in method 9E2 (Rayment and Higginson 1992) and available orthophosphate phosphorus by Colwell bicarbonate extraction, described in method 9B1 (Rayment and Higginson 1992). Soil phosphate buffering index (PBI) was determined according to method 9I2 (Rayment & Higginson 1992). Liming value measured as carbonate equivalent was determined using method 19A1 (Rayment and Higginson 1992). The acid extractable elements and metals were determined according to USEPA 6010 using a Varian 720-EC ICP-OES, Inductively Coupled Plasma, Optical Emission Spectrometers (ICP-OES). Molar H/C ratio was determined by Bureau Veritas International Trade Australia using Australian Standard Method AS 1038.6.1 under a NATA quality control system. At the completion of the experiment soil bulk density was measured using a bulk density core (ring height 62 mm, ring diameter 73 mm, ring volume 259.5 cm<sup>3</sup>) to 60 mm depth.

Table 1 shows the analyses for a composite of the unamended soils at the test site and the characteristics of the applied biochars.

Soil biological properties In April 2007, December 2007 and December 2008 three soil cores (50 mm diameter) to 150 mm depth were taken at random from each plot, composited and immediately refrigerated at 4°C before being tested for soil microbial biomass carbon (MBC) and soil microbial activity using the fluorescein diacetate hydrolysis method (FDA).

For MBC, duplicate samples of soil (10 g oven-dried equivalent at field collected moisture) were weighed into 50 ml centrifuge tubes, adjusted using Type 1 water to 80% water filled porosity (Forster 1998) and incubated for 2 days at 23°C. MBC was determined using the chloroform fumigation extraction method (Vance *et al.*, 1987).

Estimates of microbial activity were based on the ability of several enzymes, produced by bacteria or fungi, to cleave fluorescein diacetate (FDA), thereby, releasing fluorescein, which can be measured flurometrically (Fontvieille *et al.*, 1991). A more detailed description is given in Bell *et al.*, (2006).

#### Statistical analysis

A baseline mixed linear model predicted all observations as a function of the factors and all their interactions. Experimental blocks were included as a source of random error. For traits that were measured repeatedly over time, additional terms to describe the response to seasons and all interactions with factors were included as well as an additional random factor to estimate variation within plots. The model included the same variance for winter unfertilised treatments.



An analysis of variance table was derived from each model to provide hypothesis tests of nil effect due to each term. The models were also used to provide estimates of the average response under each treatment and season when required.

## Results

### *Characteristics of biochar*

Results of chemical analysis of homogenous biochar samples (Table 1) showed FM biochar had a pH of 9.7, compared to 7.8 for GW biochar. Both biochars contributed a liming value to soil with FM and GW biochar around 13 and 6 %, respectively, that of  $\text{CaCO}_3$ . FM biochar had higher total N content (0.61 %) compared to GW biochar (0.22 %). GW biochar had a higher C content than FM biochar (76 and 44 %, respectively), while FM biochar had considerably higher levels of exchangeable cations, in particular, Ca and K than GW biochar.

The ultimate analysis (Australian Standards 1038.6.3.3 method) revealed that the molar H/C ratio of the GW feedstock and FM feedstock was 1.40 and 1.38 respectively. This indicates the disproportional loss of hydrogen as the carbon formed more stable, conjugated aromatic structures, with resulting molar H/C ratio of 0.71 and 0.51 for GW and FM biochar, respectively. With regards to metals, both biochars met Australian standards according to current guidelines for composts and soil conditioners (Dorahy *et al.*, 2007).

### *Annual ryegrass DM yield*

The main factors, fertiliser, lime and biochar, as well as season were significant ( $p < 0.05$ ) predictors of annual ryegrass DM yield as were various lower order interactions. In general, the

1 FM biochar plots were higher yielding than the GW biochar and nil biochar plots. The addition of  
2 lime also improved yields (Figure 2 and 3).

3  
4 Over 24 months the addition of the FM biochar with fertiliser and lime achieved the highest total  
5 yield of 16787 kg DM ha<sup>-1</sup> which was 934 and 877 kg DM ha<sup>-1</sup> above the GW biochar and nil  
6 biochar with fertiliser and lime, respectively. Likewise, without fertiliser but with lime the highest  
7 total yield of 8905 kg DM ha<sup>-1</sup> was achieved by the addition of the FM biochar and this was 161  
8 and 1166 kg DM ha<sup>-1</sup> higher than the GW biochar and nil amendments, respectively.

9  
10 Applying fertiliser significantly ( $p<0.05$ ) increased DM yield in winter and spring. The addition of  
11 lime and FM biochar provided further significant increases, although this varied with season.

### 12 13 *Nutrient uptake*

14 The FM biochar with fertiliser and lime increased the uptake of P and K although this was  
15 statistically significant ( $p<0.05$ ) for P only (Table 2). The GW biochar increased the uptake  
16 of Na only when fertiliser was applied. Without fertiliser, the FM biochar generally  
17 increased the uptake of all minerals compared to the GW and nil biochar. The addition of  
18 fertiliser significantly increased the uptake of all nutrients whereas liming increased the  
19 uptake of P and Ca only.

### 20 21 *Changes in soil properties*

22 Over 3 years, there was no significant ( $p>0.05$ ) change in soil C in the nil-biochar treatments  
23 (Table 3). Initial soil C was 4.7% and this remained unchanged with either fertiliser or lime  
24 amendments up to 36 months following pasture establishment. Total C increased by the  
25 application of biochar as can be seen at 6 months following the application of amendments. GW

biochar increased soil C initially to a greater extent than FM biochar. Significant ( $p<0.05$ ) accumulation in of soil C occurred from analysis at 6 months to analysis at 36 months in all GW biochar treatment plots. The greatest accumulation (from 5.4 to 6.5%) occurred with fertiliser and without lime. Generally, treatment plots that included FM biochar resulted in a lower C accumulation than those treatment plots that included GW biochar. The addition of lime did not significantly ( $p>0.05$ ) increase C compared to the nil lime.

In general, there was little or no difference between treatments in total soil N. Over the study period total soil N increased by 0.04% over all treatments from around 0.46 to 0.50%.

At the conclusion of the study the soil C:N was 11.9, 11.2 and 9.7 for the GW biochar, FM and nil biochar treatments, respectively. These soil C:N ratios are in the lower range for a ferrosol and are indicative of high N availability (Spain et. al 1983).

The addition of FM biochar reduced soil acidity and this was still evident at 36 months. At 36 months with fertiliser and lime the FM biochar treatment had significantly ( $p=0.05$ ) higher pH than nil biochar with fertiliser and lime treatment (pH 4.9 vs pH 4.6). There was, however, no significant ( $p>0.05$ ) difference in pH between the GW biochar with fertiliser and lime and the nil biochar with fertiliser and lime (Table 4).

At 6 months, liming significantly ( $p<0.05$ ) increased the soil pH by 0.9 units from 4.6 to 5.6. By 36 months, however, the pH for the lime treated plots decreased to 4.8. The application of fertiliser generally decreased soil pH over the study period and this decline in pH was greater in the fertiliser with lime treatments than the fertiliser without lime treatments.

1 In the absence of fertiliser and lime, the FM biochar significantly ( $p>0.05$ ) increased soil available  
2 P at all sampling periods up to 3 years following application (Table 5). Adding lime generally  
3 reduced P availability and more so in the FM biochar plots. The GW biochar treatments did not  
4 improve soil available P compared to the nil biochar treatments.

5  
6 At 12 months the phosphorous buffer Index (PBI) of soil was in the order nil biochar > GW  
7 biochar > FM biochar with mean ( $\pm$  s.e.) values  $483 \pm 2$ ,  $469 \pm 7$  and  $454 \pm 7$ , respectively.  
8 Although both biochars decreased the PBI and hence the soil P buffer capacity, all treatment values  
9 were high (Moody & Cong 2008).

10  
11 There were no significant ( $p>0.05$ ) differences in soil  $\text{NH}_4\text{-N}$  between treatments within years  
12 although soil  $\text{NH}_4\text{-N}$  varied between years. While there were differences in available soil  $\text{NO}_3\text{-N}$   
13 between years it was only at 6 months that there were significant ( $p>0.05$ ) differences in  $\text{NO}_3\text{-N}$   
14 levels between treatments.

15  
16 At 6 months, the FM biochar soil  $\text{NO}_3\text{-N}$  ( $22.3 \text{ mg kg}^{-1}$ ) was significantly ( $p>0.05$ ) higher than for  
17 either the GW biochar ( $7.5 \text{ mg kg}^{-1}$ ) or nil biochar ( $7.6 \text{ mg kg}^{-1}$ ) treatments. However, by 12  
18 months soil  $\text{NO}_3\text{-N}$  level in the FM biochar decreased to  $10.4 \text{ (mg kg}^{-1})$  whereas there was no  
19 change in  $\text{NO}_3\text{-N}$  in either the GW or nil biochar.

20  
21 Without lime the FM biochar treatments had higher exchangeable Ca and Mg and ECEC at the  
22 completion of the study. At 36 months, the FM biochar without lime had a ECEC value of  $6.0$   
23  $\text{cmol(+) kg}^{-1}$  dominated by Ca and Mg, compared to  $4.8 \text{ cmol(+) kg}^{-1}$  for nil biochar without lime  
24 (Table 6). In general, there was no difference between the GW biochar and the nil biochar

treatment plots for exchangeable cations and ECEC. Liming decreased exchangeable Al and significantly increased exchangeable Ca with a resultant increase in ECEC compared to nil lime.

At 36 months the bulk density of soil to 60 mm depth was in the order nil biochar > GW biochar > FM biochar with mean ( $\pm$  s.e.) values  $0.99 \pm 0.01$ ,  $0.98 \pm 0.00$  and  $0.95 \pm 0.02$  ( $\text{tm}^{-3}$ ), respectively. These bulk density values are very favourable for root growth and reflect the already relatively high soil C levels.

### *Soil biological properties*

Applying lime but not fertiliser or biochar affected MBC. At 6 months limed plots had significantly ( $p < 0.05$ ) higher MBC than nil lime plots ( $0.97$  vs.  $0.83$   $\text{mg g}^{-1}$  dry-weight-equivalent soil, respectively). After 2 years MBC was still significantly ( $p < 0.05$ ) higher with lime than without ( $1.44$  vs.  $1.23$   $\text{mg g}^{-1}$  dry-weight-equivalent soil, respectively). There were, however, larger differences between years (Year 1,  $0.90 \pm 0.03$  vs. Year 2,  $1.34 \pm 0.05$   $\text{mg/g}$  dry-weight-equivalent soil) in this study than between treatment effects within years.

The main effects, lime, biochar and fertiliser, were not significant ( $p > 0.05$ ) for soil enzyme activity within years and there were no significant interactions. The FDA means ( $\pm$  s.e.) were  $10.58 \pm 0.33$ ,  $4.76 \pm 0.24$  and  $3.24 \pm 0.13$  ( $\mu\text{g fluorescein g dry soil}^{-1} \text{ min}^{-1}$ ) at 6, 12 and 24 months, respectively.

## **Discussion**

Annual ryegrass DM response to biochar was positive and consistent over the study period although the extent of the response varied with the properties of the biochar. The DM response to lime was more variable with, generally, a smaller response in Year 1 than Year 2. The productivity



of annual ryegrass was substantially lower without fertiliser, irrespective of the addition of lime and/or biochar.

The yield response increased in the following order: fertiliser>FM biochar > lime > GW biochar. Applying the FM biochar with fertiliser was additive increasing ryegrass yield by 9% in the first year and further to 16% in the second year. The additive benefit of animal-sourced biochars with fertiliser has previously been reported by Chan *et al.*, (2008) in a glasshouse study using a poultry litter biochar at 10 t/ha; although the N fertiliser rate applied was twice that of our study. We found, however, there was no positive yield response to fertiliser with the GW biochar at 10 t ha<sup>-1</sup>. Only high rates of GW biochar (> 50 t ha<sup>-1</sup>) have resulted in an enhanced yield response with fertiliser in a glasshouse study by Chan *et al.*, (2007). This further supports evidence that biochars will vary in their response depending on their nature and application rate.

Adding biochar in a tropical environment has been shown to increase nutrient availability and subsequent nutrient uptake by plants (Glaser *et al.*, 2002; Lehmann *et al.*, 2003; Lehmann & Rondon, 2006). Similar to the yield response, nutrient uptake was higher using the FM biochar compared to the GW biochar and as Chan *et al.*, (2007) found the GW biochar required 5 times the rate used in our study to improve nutrient uptake. Similarly, Steiner *et al.*, (2007) observed a large enhancement in grain yield in rice (*Oryza sativa* L.) and sorghum (*Sorghum bicolor* L.) where charcoal with NPK fertiliser were applied to an acidic, highly weathered tropical soil with an associated greater nutrient availability remaining in the charcoal-amended soil.

The magnitude of the production response from liming ryegrass pasture soils can vary between seasons and years and is dependent on the initial soil pH and soil type (Edmeades *et al.*, 1984; Wheeler and O'Connor 1998; Crawford and Gourley 2001). In our study the lime increased

ryegrass yields by around 7% whereas Edmeades *et al.*, (1984) found that of 126 ryegrass trials in New Zealand liming increased yields by 8 to 11%. In Australia, applying lime to ryegrass pastures has been inconsistent with yield increases ranging from 5 to 33% with considerable variation found between years (Fulkerson *et al.*, 1993; Crawford & Gourley, 2001).

Whereas the GW biochar had a very low liming value the FM biochar had a liming value equivalent to 1.3 t lime ha<sup>-1</sup> when applied at 10 t ha<sup>-1</sup> and this appears to have been sufficient to slow the rate of acidification by 0.3 pH units when fertiliser and lime were applied. However, when Van Zwieten *et al.*, (2010) applied a biochar derived from paper mill waste with a much higher liming value (33%) at 10 t ha<sup>-1</sup> to a ferrosol the soil pH (CaCl<sub>2</sub>) increased by 1.5 units. On acidic soils there are clear benefits from applying biochars with higher liming values.

Currently, liming guidelines recommend that 2 kg lime be applied per kg N as urea (Lines-Kelly 2004). In a subtropical environment 350 to 595 kg N ha<sup>-1</sup> as urea is applied annually to annual ryegrass pastures and this would require 700 to 1190 kg lime ha<sup>-1</sup>year<sup>-1</sup> to maintain soil pH (Lowe *et al.*, 2005; Haby & Robinson, 1997). As expected, incorporating lime at 5 t ha<sup>-1</sup> was shown in our study to be an effective ameliorant in offsetting the acidifying effects of applying frequent high rates of N fertiliser as urea. It remains a necessary and on-going input into this pasture system.

Applying lime to the ferrosol used in our study generally decreased plant-available P in the soil although plant P uptake was found to have increased with liming. In a review Haynes (1982) reported on conflicting findings in which liming an acid soil increased, decreased or had no effect on available soil P or P plant content. Our findings highlight the complexity of the lime-phosphorous-acid soil-plant interaction and the difficulty in predicting soil P behaviour and hence improving P fertiliser efficiency in acid soils.

On the other hand, incorporating the FM biochar but not the GW biochar showed a substantial increase in plant-available P which was maintained throughout the study. The FM biochar substantially improved soil available P at 6 months compared to the nil biochar. At 36 months the difference in soil available P was even more pronounced. Further the FM biochar treated plots had a lower PBI index than the nil biochar soil and this may have contributed to a higher P availability. Applying a poultry litter biochar which had a high P content Chan *et al.*, (2008) showed that soil available P increased with application rate and even at 10 t ha<sup>-1</sup>, the lowest rate applied, soil P was 70% higher than in the unamended soil. Schefe *et al.*, (2007) in an incubation study found that lignite applied as a soil amendment decreased total P sorption relative to either lime or compost. Lignite like biochar is high in aromatic C compounds. However, the underlying mechanism by which the FM biochar with a substantially higher innate P content maintained a constant higher available P is yet to be defined. It is possible that soil P availability could be influenced by specific adsorption of orthophosphate onto the biochar surface (Beaton *et al.*, 1960)

The soil C initially increased from pre-treatment levels as expected from the addition of C in the biochar. Expected soil C levels from adding biochar were calculated using the biochar total C content, application rate and assuming mixing to 150 mm and a bulk density 0.99 t m<sup>-3</sup> for the ferrosol in this study. These calculated estimates would predict an increase to 4.99 and 5.21% for the FM and GW biochar, respectively. These estimated soil C values compare favourably with the soil C values measured at 6 months after application of 5.15 (s.e.  $\pm$  0.05) and 5.27 (s.e.  $\pm$  0.05) % for the FM and GW biochar, respectively.

Although the increase in C due to the biochar application is expected to be long-term, possibly even hundreds or thousands of years as suggested by Lehmann *et al.*, (2006), the effects of this

biochar application on other soil C fractions is still not well understood. Wardle *et al.*, (2008) observed a positive priming effect following charcoal addition to a forest leaf litter, resulting in significantly greater microbial activity and a subsequent more rapid loss of carbon in the litter fraction. Lehmann & Sohi (2008) who comment on these effects also suggest increased mineralisation of labile components in the biochar due to this priming effect may lead to a loss of C in the litter/charcoal fraction. Novak *et al.*, (2010) also observed increased mineralisation of fresh ground switchgrass (*Panicum virgatum* L.) which had been added to soil in combination with biochar. Results from our study, however, revealed a significant C accumulation in soil under pasture in the biochar amended field soils. Although the reason for these increases in soil C were not fully explored, it is possible that enhanced root growth resulted in greater deposition of C in the soil (Chan *et al.*, 2010). Likewise, Major *et al.*, (2010) found greater CO<sub>2</sub> emissions from non-biochar sources when biochar was added to native savanna soils. The authors speculated that the greater CO<sub>2</sub> emissions were a result of higher primary productivity in the biochar amended field plots. An alternative explanation for the stabilization of this otherwise decomposable SOC could be its sorption to mineral and organic soil surfaces, occlusion with aggregates, and deposition in pores or other locations inaccessible to decomposers and extracellular enzymes (Jastrow *et al.*, 2007). It is well understood that biochar when applied to soil can significantly alter the soil pore-size distribution and surface area (Downie *et al.*, 2009).

The change in ECEC was more affected by the addition of lime and its subsequent effect on exchangeable Ca than by the addition of biochar. Incorporated soil biochar particles are known to undergo surface oxidation and interactions with soil constituents forming reactive surfaces enabling an increase in ECEC (Hammes & Schmidt, 2009). However, although the biochars were thoroughly incorporated into soil there was no improvement in ECEC by the addition of either

biochar. This suggests that the biochar reaction rates may not be as rapid as reported in other studies (Hammes & Schmidt, 2009).

Microbial biomass carbon (MBC) is used to indicate nutrient turnover rate and release with soil moisture, temperature and pH being the most important factors influencing microbial biomass (Dalal, 1998; Wardle, 1992). Applying lime to reduce soil acidity in our study increased MBC by 17% although previous reports of increases in MBC by applying lime to low pH pastoral soils was in the order of 25-40% (Adams & Adams, 1983; White *et al.*, 2000; Sarathchandra *et al.*, 2001). Under the warm moist conditions of a subtropical environment a high annual rate of nutrient cycling would be expected along with high MBC compared to cooler drier environments. MBC reported in previous pastoral soils in more temperate climates were substantially lower than in our study. In pasture soils of the warm temperate north-west and cool temperate south-west slopes of NSW MBC was approximately 0.54 mg g<sup>-1</sup> and 0.43 mg g<sup>-1</sup>, respectively (White *et al.*, 2000; Banu *et al.*, 2004; Lodge & King, 2004) whereas in our study MBC averaged 1.12 mg g<sup>-1</sup>.

Similar to MBC, microbial enzyme activity (as measured by the fluorescein diacetate hydrolysis method) showed considerable year to year variation in our study although level of activity was much higher (6.2 µg fluorescein g dry soil<sup>-1</sup>min<sup>-1</sup>) than that found in pastoral soils in of the warm temperate north-west and cool temperate south-west slopes of NSW (1.3 and 2.6 µg fluorescein g dry soil<sup>-1</sup>min<sup>-1</sup>, respectively) (Lodge *et al.*, 2004). The higher soil enzyme activity in our study can be attributed to the presence of high levels of soil C in a warmer, wetter subtropical environment.

Recent studies have shown that the addition of biochars can stimulate the activity of soil microorganisms as well as providing a suitable habitat for them (Thies & Rillig, 2009). However, in our study the addition of biochar irrespective of their properties did not enhance either the size



of the microbial biomass C or the microbial enzyme activity in the soil although values in the control were clearly high. In a glasshouse study, Chan *et al.*, (2007) using GW biochar produced under different pyrolysis conditions observed significant differences in MBC but could not offer an explanation for these differences. Van Zwieten *et al.*, (2010) also in a glasshouse observed differences in enzyme activity between soil types and plant species in biochar amended soil.

N fertiliser application practices for annual ryegrass in a subtropical environment is based on the most effective rate and frequency of application so as to maximise growth while minimising any losses to nitrate leaching and ammonia volatilisation. Nevertheless, this pasture system imposes a significant cost to the environment in terms of GHG emissions from the application of urea and lime. With annual N applications between 300 and 510 kg ha<sup>-1</sup> which then requires 600 to 1020 kg lime ha<sup>-1</sup> yr<sup>-1</sup> based on guidelines (Lines-Kelly 2004) to offset soil acidification this system has the potential to cause emissions of between an estimated 1.89 to 3.68 t CO<sub>2</sub>-e ha<sup>-1</sup>yr<sup>-1</sup> (De Klein *et al.*, 2006).

Three years after biochar was applied total soil C in the FM and GW biochar treatments ranged between 0.6% and 1.4% higher than the nil biochar treated soil. This is equivalent to approximately 4.4 to 10.3 t C ha<sup>-1</sup> or 16 to 38 t CO<sub>2</sub>-e ha<sup>-1</sup>, respectively accounting for the bulk density of the soil. This is a significant amount in comparison to the direct annual emissions from urea and lime use (assuming reapplication every 5 years) in this experiment, estimated to be around 1.8 t CO<sub>2</sub>-e emissions ha<sup>-1</sup> y<sup>-1</sup> from urea and a 0.44 t CO<sub>2</sub>-e emission ha<sup>-1</sup>yr<sup>-1</sup> from liming (using estimates from De Klein *et al.*, 2006), a total of 2.24 t CO<sub>2</sub>-e ha<sup>-1</sup> yr<sup>-1</sup>. Integrating biochar into high input agricultural systems could be effective in assisting governments to meet their GHG emission target while also providing agronomic benefits. Sohi *et al.*, 2009 and Lehmann, 2009 have also discussed the potential for stable biochars to be included in emission offsets. It must be

stressed here that the different biochars resulted in varying offsets and varying crop and soil fertility responses, so individual case studies will need to be tested to confirm these benefits.

## Conclusion

This study has demonstrated the capacity of 2 contrasting biochars, one derived from feedlot manure and the other from greenwaste, to accumulate a significant C store in the soil surface of a ferrosol under pasture over a 3-year time frame. The net accumulation of C in the soil profile to 75 mm following biochar addition is likely to have been due to a combination of increased biomass input to the soil as a result of increased productivity with fertiliser, and stabilization of C due to the added porosity provided by the biochars. The increase in C storage in the pasture soil offset emissions associated with N and lime application. It was evident from this study that the higher C biochar produced from greenwaste was more appropriate for C storage purposes, while the lower C, higher nutrient feedlot manure biochar was more appropriate for agronomic application. In the absence of lime application, the feedlot manure biochar resulted in significant increases in plant available P in soil, both in the presence and absence of applied P fertiliser. This may provide a strategy for maintaining plant available P when fertiliser costs or access to P fertiliser becomes limited.

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## Captions for figures and tables

**Fig. 1** Mean monthly rainfall (mm) (■) and mean maximum (■) and minimum (▲) temperature (°C) for April to December 2007 and 2008 at Wollongbar.

**Fig. 2** Annual ryegrass yield (kg DM/ha) without fertiliser (F<sub>0</sub>), nil lime (L<sub>0</sub>) (◇) or lime (L<sub>1</sub>) (◆) and nil biochar (C<sub>0</sub>), FM biochar (C<sub>1</sub>) or GW biochar (C<sub>2</sub>) for winter 2007 and 2008 and for spring 2007 and 2008. The vertical bars span  $\pm 2x$  s.e.

**Fig. 3** Annual ryegrass yield (kg DM/ha) with fertiliser (F<sub>0</sub>), nil lime (L<sub>0</sub>) (◇) or lime (L<sub>1</sub>) (◆) and nil biochar (C<sub>0</sub>), FM biochar (C<sub>1</sub>) or GW biochar (C<sub>2</sub>) for winter 2007 and 2008 and for spring 2007 and 2008. The vertical bars span  $\pm 2x$  s.e.

**Table 1** Chemical analysis of the ferrosol, FM and GW biochars.

**Table 2** Plant uptake of nutrients by annual ryegrass after 21 days of regrowth in September, Year 1 following the application of nil NPK fertiliser (F<sub>0</sub>) or NPK fertiliser (F<sub>1</sub>), nil lime (L<sub>0</sub>) or lime (L<sub>1</sub>) and nil biochar (C<sub>0</sub>), FM biochar (C<sub>1</sub>) or GW biochar (C<sub>2</sub>).

**Table 3** Total soil N and C subject to nil NPK fertiliser (F<sub>0</sub>) or NPK fertiliser (F<sub>1</sub>), nil (L<sub>0</sub>) or lime (L<sub>1</sub>) and to nil biochar (C<sub>0</sub>), FM biochar (C<sub>1</sub>) or GW biochar (C<sub>2</sub>) at 6 months and 36 months.

**Table 4** Soil pH following the application of nil NPK fertiliser (F<sub>0</sub>) or NPK fertiliser (F<sub>1</sub>), nil lime (L<sub>0</sub>) or incorporated lime (L<sub>1</sub>) and nil biochar (C<sub>0</sub>), FM biochar (C<sub>1</sub>) or GW biochar (C<sub>2</sub>) at 6 months, 24 months and 36 months.

**Table 5** Soil P (Bray) subject to nil NPK fertiliser (F<sub>0</sub>) or NPK fertiliser (F<sub>1</sub>), nil (L<sub>0</sub>) or incorporated lime (L<sub>1</sub>) and to nil biochar (C<sub>0</sub>), FM biochar (C<sub>1</sub>) or GW biochar (C<sub>2</sub>) at 6 months, 12 months, 24 months and 36 months.

**Table 6** Exchangeable cations and ECEC subject to nil NPK fertiliser (F<sub>0</sub>) or NPK fertiliser (F<sub>1</sub>), nil (L<sub>0</sub>) or incorporated lime (L<sub>1</sub>) and to nil biochar (C<sub>0</sub>), FM biochar (C<sub>1</sub>) or GW biochar (C<sub>2</sub>) at 36 months.

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**table 1**  
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Soil test	Ferrosol	FM biochar	GW biochar	Units
Total C	4.7	44	76	%
EC		1.6	0.14	dS m <sup>-1</sup>
pH(CaCl <sub>2</sub> )	4.7	9.7	7.8	
Acid neutralising capacity		13	5.6	% CaCO <sub>3</sub>
P-Bray1	12	73	6	mg kg <sup>-1</sup>
P- Colwell	49			mg kg <sup>-1</sup>
Phosphate buffer index	489			
Total N		0.22	0.61	%
NH <sub>4</sub> <sup>+</sup> -N		<0.3	<0.3	mg kg <sup>-1</sup>
NO <sub>3</sub> <sup>-</sup> -N		<0.2	0.33	mg kg <sup>-1</sup>
Exchangeable cations				
Al	0.47	0.03	0.03	cmol(+) kg <sup>-1</sup>
Ca	5.23	3.70	0.46	cmol(+) kg <sup>-1</sup>
K	0.49	5.60	0.40	cmol(+) kg
Mg	0.76	2.70	0.06	cmol(+) kg <sup>-1</sup>
Na	0.18	1.30	0.22	cmol(+) kg <sup>-1</sup>
Mn	<0.01			cmol(+) kg <sup>-1</sup>
ECEC	7.14	13.33	1.17	cmol(+) kg <sup>-1</sup>
Calcium		1.5	0.17	%
Iron		1.9	0.45	%
Potassium		2.1	0.078	%
Magnesium		0.72	0.088	%
Sodium		0.36	0.052	%
Phosphorus		0.78	0.014	%
Sulfur		0.048	0.0078	%
Arsenic		<3	<3	mg kg <sup>-1</sup>
Boron		20	7.6	mg kg <sup>-1</sup>
Cadmium		<0.9	<0.9	mg kg <sup>-1</sup>
Cobalt		5.9	<1.2	mg kg <sup>-1</sup>
Chromium		43	12	mg kg <sup>-1</sup>
Copper		21	4.6	mg kg <sup>-1</sup>
Manganese		420	78	mg kg <sup>-1</sup>
Molybdenum		2.6	<1.2	mg kg <sup>-1</sup>
Nickel		19	7.5	mg kg <sup>-1</sup>
Lead		<1.7	<1.7	mg kg <sup>-1</sup>
Selenium		<6.6	<6.6	mg kg <sup>-1</sup>
Zinc		120	33	mg kg <sup>-1</sup>

**table 2**  
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NPK fertiliser	Lime	Biochar	N	P	K	Ca	Mg	Na
						(kg ha <sup>-1</sup> )		
F <sub>0</sub>	L <sub>0</sub>	C <sub>0</sub>	21.0	3.8	30.7	4.1	1.6	1.3
F <sub>0</sub>	L <sub>0</sub>	C <sub>1</sub>	22.6	4.3	38.8	3.4	1.7	0.8
F <sub>0</sub>	L <sub>0</sub>	C <sub>2</sub>	18.0	2.8	24.7	2.8	1.2	0.6
F <sub>0</sub>	L <sub>1</sub>	C <sub>0</sub>	19.3	3.3	28.4	3.7	1.3	1.0
F <sub>0</sub>	L <sub>1</sub>	C <sub>1</sub>	22.9	4.6	38.8	4.8	1.8	1.0
F <sub>0</sub>	L <sub>1</sub>	C <sub>2</sub>	20.6	4.3	32.3	4.5	1.6	0.7
F <sub>1</sub>	L <sub>0</sub>	C <sub>0</sub>	56.3	4.4	61.0	7.4	2.9	2.8
F <sub>1</sub>	L <sub>0</sub>	C <sub>1</sub>	60.0	4.6	60.5	6.4	2.9	2.2
F <sub>1</sub>	L <sub>0</sub>	C <sub>2</sub>	56.1	4.4	57.5	7.2	3.1	5.8
F <sub>1</sub>	L <sub>1</sub>	C <sub>0</sub>	59.2	5.0	62.4	8.6	2.9	2.2
F <sub>1</sub>	L <sub>1</sub>	C <sub>1</sub>	57.9	6.7	79.8	10.0	3.6	2.9
F <sub>1</sub>	L <sub>1</sub>	C <sub>2</sub>	58.0	5.2	58.2	8.5	3.1	4.3
l.s.d. ( <i>p</i> =0.05)			6.7	1.7	19.6	2.7	0.8	2.0



**table 3**  
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NPK fertiliser	Lime	Biochar	Total N%		Total C%	
			6 mths	36 mths	6 mths	36 mths
F <sub>0</sub>	L <sub>0</sub>	C <sub>0</sub>	0.46	0.50	4.7	4.8
F <sub>0</sub>	L <sub>0</sub>	C <sub>1</sub>	0.44	0.50	5.1	5.5
F <sub>0</sub>	L <sub>0</sub>	C <sub>2</sub>	0.44	0.51	5.2	5.9
F <sub>0</sub>	L <sub>1</sub>	C <sub>0</sub>	0.45	0.49	4.6	4.7
F <sub>0</sub>	L <sub>1</sub>	C <sub>1</sub>	0.47	0.50	5.2	5.5
F <sub>0</sub>	L <sub>1</sub>	C <sub>2</sub>	0.45	0.49	5.3	6.0
F <sub>1</sub>	L <sub>0</sub>	C <sub>0</sub>	0.48	0.51	4.8	5.1
F <sub>1</sub>	L <sub>0</sub>	C <sub>1</sub>	0.47	0.50	5.2	5.7
F <sub>1</sub>	L <sub>0</sub>	C <sub>2</sub>	0.47	0.52	5.4	6.5
F <sub>1</sub>	L <sub>1</sub>	C <sub>0</sub>	0.46	0.51	4.7	4.9
F <sub>1</sub>	L <sub>1</sub>	C <sub>1</sub>	0.44	0.49	5.1	5.5
F <sub>1</sub>	L <sub>1</sub>	C <sub>2</sub>	0.45	0.50	5.1	5.7
l.s.d. ( <i>p</i> =0.05)			0.03	0.03	0.4	0.4

**table 4**  
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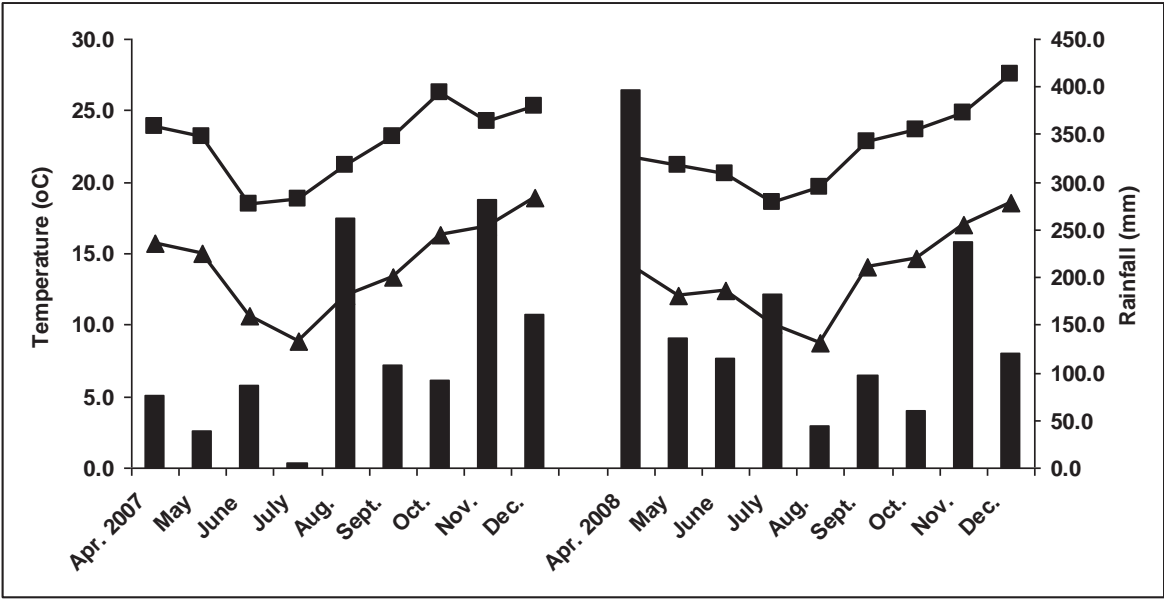
NPK fertiliser	Lime	Biochar	Soil pH		
			6 mths	24 mths	36 mths
F <sub>0</sub>	L <sub>0</sub>	C <sub>0</sub>	4.6	4.6	4.2
F <sub>0</sub>	L <sub>0</sub>	C <sub>1</sub>	4.7	4.7	4.4
F <sub>0</sub>	L <sub>0</sub>	C <sub>2</sub>	4.5	4.6	4.2
F <sub>0</sub>	L <sub>1</sub>	C <sub>0</sub>	5.7	5.4	4.9
F <sub>0</sub>	L <sub>1</sub>	C <sub>1</sub>	5.6	5.5	5.0
F <sub>0</sub>	L <sub>1</sub>	C <sub>2</sub>	6.0	5.4	5.0
F <sub>1</sub>	L <sub>0</sub>	C <sub>0</sub>	4.5	4.5	4.0
F <sub>1</sub>	L <sub>0</sub>	C <sub>1</sub>	4.7	4.7	4.2
F <sub>1</sub>	L <sub>0</sub>	C <sub>2</sub>	4.6	4.5	4.1
F <sub>1</sub>	L <sub>1</sub>	C <sub>0</sub>	5.5	5.3	4.6
F <sub>1</sub>	L <sub>1</sub>	C <sub>1</sub>	5.6	5.5	4.9
F <sub>1</sub>	L <sub>1</sub>	C <sub>2</sub>	5.3	5.5	4.5
l.s.d.( <i>p</i> =0.05) = 0.3					

**table 5**  
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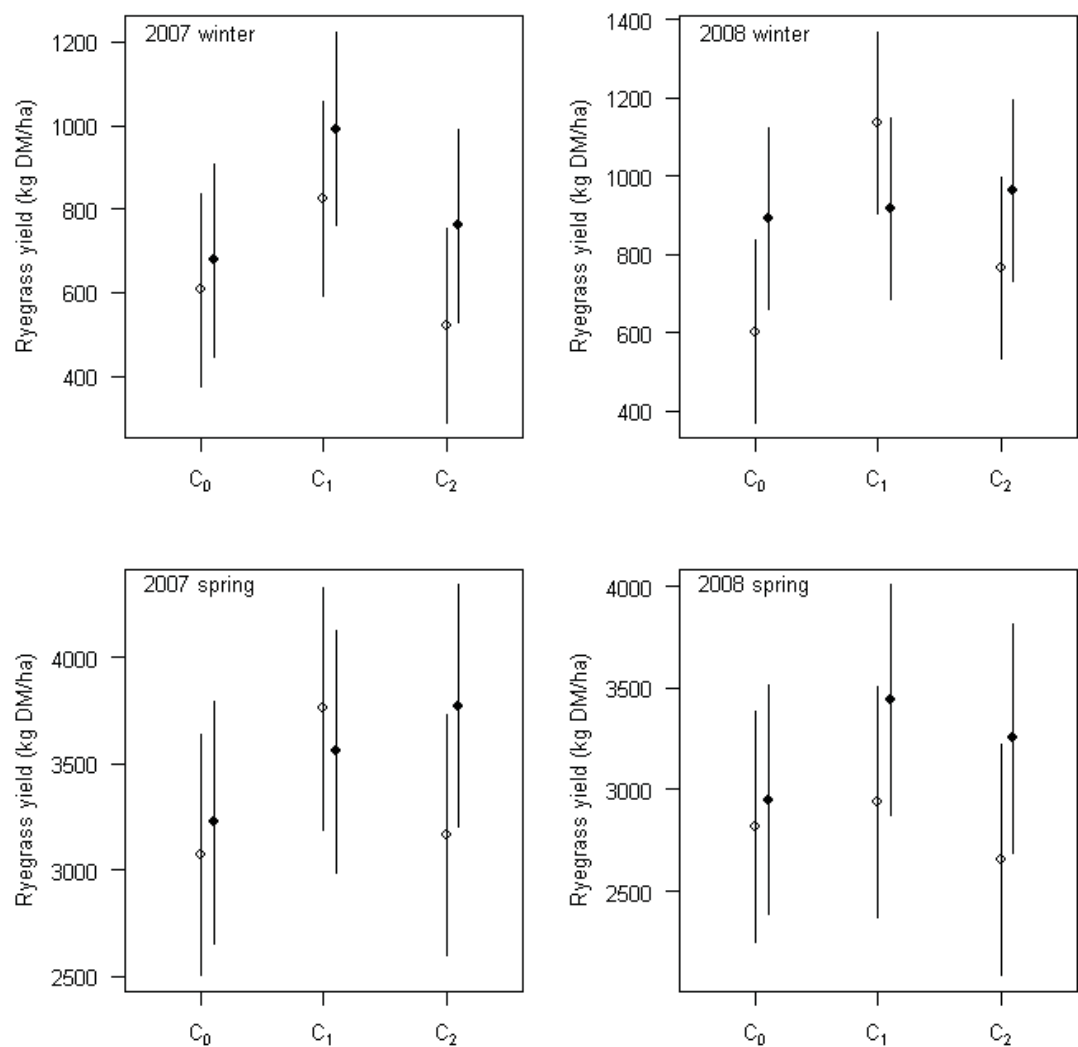
NPK fertiliser	Lime	Biochar	Soil P (mg/kg)			
			6 mths	12 mths	24 mths	36 mths
F <sub>0</sub>	L <sub>0</sub>	C <sub>0</sub>	15.0	8.5	7.4	6.9
F <sub>0</sub>	L <sub>0</sub>	C <sub>1</sub>	22.0	12.3	14.3	13.0
F <sub>0</sub>	L <sub>0</sub>	C <sub>2</sub>	12.7	8.0	8.0	6.7
F <sub>0</sub>	L <sub>1</sub>	C <sub>0</sub>	12.6	6.8	8.1	6.6
F <sub>0</sub>	L <sub>1</sub>	C <sub>1</sub>	17.0	8.9	7.6	10.1
F <sub>0</sub>	L <sub>1</sub>	C <sub>2</sub>	12.7	6.9	6.8	6.4
F <sub>1</sub>	L <sub>0</sub>	C <sub>0</sub>	16.0	8.7	11.3	8.3
F <sub>1</sub>	L <sub>0</sub>	C <sub>1</sub>	20.3	13.3	15.0	16.0
F <sub>1</sub>	L <sub>0</sub>	C <sub>2</sub>	16.0	8.9	11.1	11.0
F <sub>1</sub>	L <sub>1</sub>	C <sub>0</sub>	14.0	6.8	8.3	11.3
F <sub>1</sub>	L <sub>1</sub>	C <sub>1</sub>	16.2	8.9	11.4	11.7
F <sub>1</sub>	L <sub>1</sub>	C <sub>2</sub>	14.0	7.3	10.2	14.3
l.s.d. ( $p=0.05$ ) = 4.1						

**table 6**  
[Click here to download table: Table 6.doc](#)

NPK fertiliser	Lime	Biochar	Exchangeable cations at 36 mths					
			Al	Ca	K	Mg	Na	ECEC
			cmol(+)/kg					
F <sub>0</sub>	L <sub>0</sub>	C <sub>0</sub>	0.0	4.1	0.2	0.7	0.20	5.2
F <sub>0</sub>	L <sub>0</sub>	C <sub>1</sub>	0.0	4.9	0.2	1.1	0.22	6.5
F <sub>0</sub>	L <sub>0</sub>	C <sub>2</sub>	0.1	4.1	0.2	0.8	0.22	5.4
F <sub>0</sub>	L <sub>1</sub>	C <sub>0</sub>	0.0	7.7	0.2	0.8	0.22	8.9
F <sub>0</sub>	L <sub>1</sub>	C <sub>1</sub>	0.0	7.8	0.2	1.1	0.26	9.4
F <sub>0</sub>	L <sub>1</sub>	C <sub>2</sub>	0.0	8.2	0.2	1.0	0.31	9.7
F <sub>1</sub>	L <sub>0</sub>	C <sub>0</sub>	0.1	3.2	0.2	0.6	0.17	4.3
F <sub>1</sub>	L <sub>0</sub>	C <sub>1</sub>	0.1	4.2	0.2	0.8	0.16	5.5
F <sub>1</sub>	L <sub>0</sub>	C <sub>2</sub>	0.1	4.0	0.2	0.7	0.19	5.2
F <sub>1</sub>	L <sub>1</sub>	C <sub>0</sub>	0.0	6.7	0.2	0.8	0.19	7.9
F <sub>1</sub>	L <sub>1</sub>	C <sub>1</sub>	0.0	8.2	0.2	0.9	0.25	9.6
F <sub>1</sub>	L <sub>1</sub>	C <sub>2</sub>	0.0	6.1	0.2	0.8	0.21	7.3
l.s.d. ( <i>p</i> =0.05)			0.3	1.7	0.1	0.2	0.05	1.6

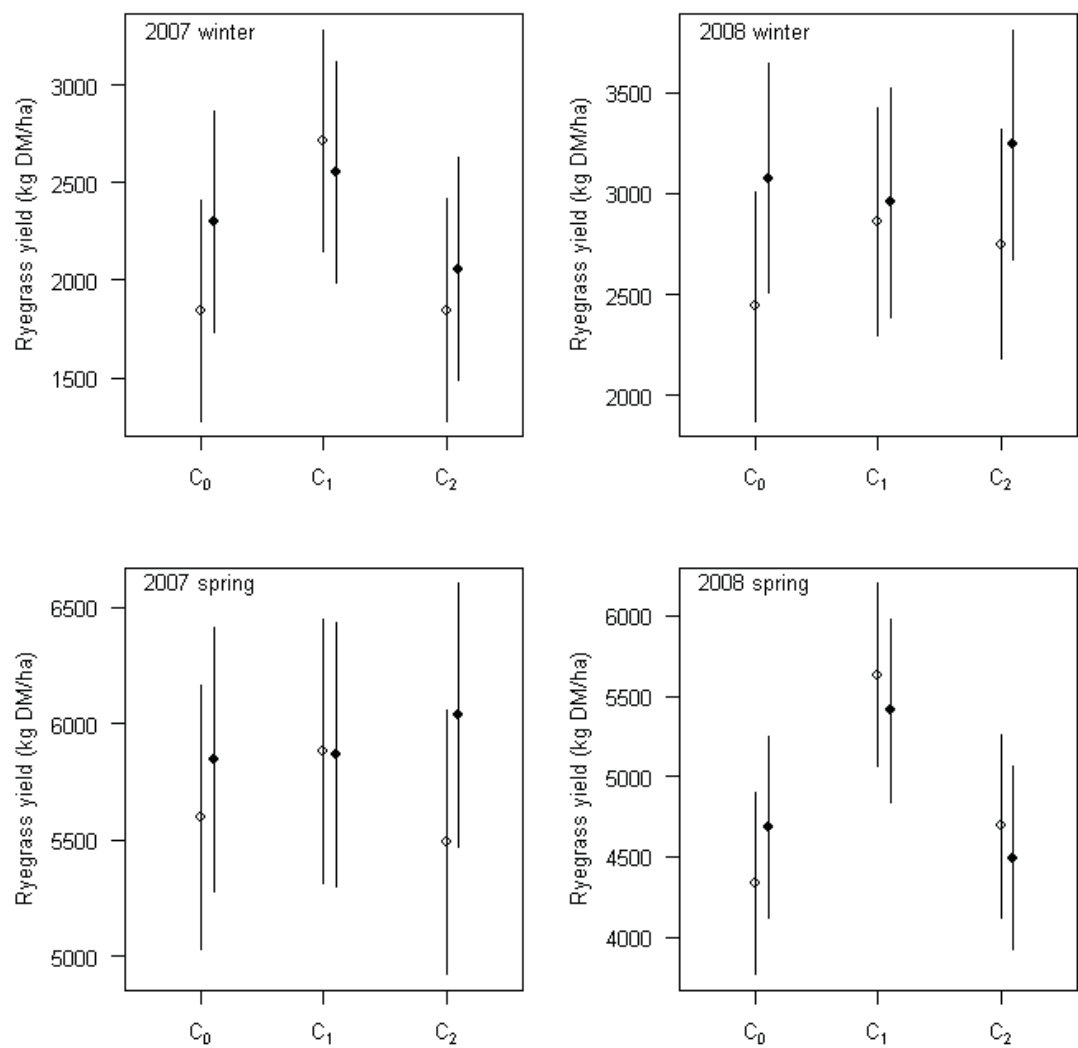






line figure 3

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*Appendix G - Biochars in soil for climate mitigation and adaptation*

## Chapter 15

# Biochar in Soil for Climate Change Mitigation and Adaptation

David Waters, Lukas Van Zwieten, Bhupinder Pal Singh, Adriana Downie, Annette L. Cowie, and Johannes Lehmann

### 15.1 Introduction

Global environmental change, including land degradation, loss of biodiversity, changes in hydrology and changes in climate patterns resulting from enhanced anthropogenic emission of greenhouse gases, will have serious consequences for world food security, particularly affecting the more vulnerable socio-economic sectors (Ericksen et al. 2009; Lal 2010). The World Bank suggests that at least a doubling of cereal yields and a 75% increase in meat production by 2030 are required to maintain the current level of nutrition globally (Fresco 2009). This poses a quandary. To significantly increase food production when large areas of agricultural lands will be adversely affected by climate change or converted into

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forestry for C sinks may not be possible unless new technologies and sustainable practices are rapidly adopted. The application of biochar to agricultural soils may play a crucial role in global climate change mitigation through the reduction of greenhouse gas production and the sequestering of atmospheric carbon in soils (Gaunt and Cowie 2009; Lehmann 2007; McCarl et al. 2009; McHenry 2009; Read 2009). The agronomic benefits of biochar in soils (Chan et al. 2007; Steiner et al. 2008a, b) could assist in the adaptation of agriculture to meet rising demands for food and fibre. Furthermore, improving soil health with biochar application may increase resilience of agricultural systems and enable the continuation of farming on marginal lands. Application of biochar to soil has been shown to have many advantages including enhanced soil health characteristics, reduced metal contamination risks and consequently increased plant growth (Chan et al. 2007; Namgay et al. 2010; Reichenauer et al. 2009); as well as reduced greenhouse gas emissions from soil (Singh et al. 2010a; Van Zwieten et al. 2009; Yanai et al. 2007).

The competing and often conflicting demands of land use primarily stem from growing populations requiring housing and food, coupled with community desires for greater allocation of land to ecological reserves and the increasing production of energy crops to displace greenhouse gas emitting fossil fuels (Koomen et al. 2005; Simon and Wiegmann 2009). In addition to the challenge of a changing climate, the increasing claim for this scarce land use resource will force the necessity for greater productivity from less land, meaning farmers will need to undertake activities that result in significant yield increases. Land managers from more developed countries have historically had greater access to technological innovations and training, thereby improving the productivity of agricultural systems compared with those from developing countries. With the escalating effects of climate change technological adaptation will become increasingly vital to sustainably augment production systems globally (Bryan et al. 2009; Jones and Thornton 2009).

“Black carbon” (BC), a heterogeneous mix of carbonaceous materials formed from the incomplete combustion of biomass (Hammes et al. 2008; Schmidt and Noack 2000), is found in the most stable pool of soil organic carbon (SOC) (i.e. the component that resists microbial decomposition and mineralisation to CO<sub>2</sub>). This BC may be derived from natural events such as biomass burning in wildfires (producing charcoal, consisting of partly charred organic matter through to completely carbonised submicron particles of soot) or through human activities (referred to as biochar).

Biochar can be manufactured through the pyrolysis of biomass (Lehmann and Rondon 2006), which condenses aliphatic carbon into more stable aromatic carbon, while releasing combustible gases (H<sub>2</sub>, CH<sub>4</sub>, CO) that can be used to heat the kiln with surplus for bioenergy. Rudimentary biochar production systems have been used for over 2,000 years, and when applied to soils biochar has demonstrated sustained productivity increases. A well-known example of ancient soil amendment with charcoal is the Terra Preta – dark earth-soils of the Amazon. These low fertility tropical soils were amended in pre-Columbian times by indigenous Amerindians through the addition of carbonised organic matter, believed to be from their cooking hearths (Glaser et al. 2001).



Modern biochar production uses a range of technologies including fast pyrolysis, gasification and/or carbonisation (Bridgwater 2003). These processes can be applied at different scales from small cooking stoves often used in developing countries through to more advanced industrial systems which include full gas recovery for integrated bioenergy production (Brown 2009). The sustainability credentials of each of these systems including efficiency of resource utilisation, emissions control, life cycle greenhouse gas balance and environmental sustainability need to be assessed on a case-by-case basis. The production process will influence the properties of the biochar and therefore the way it behaves and interacts in a soil (Downie et al. 2009; Glaser et al. 2002; Joseph et al. 2010; Novak et al. 2009; Singh et al. 2010a). To date agronomic benefits from biochar application have been demonstrated for biochars produced from a limited range of production systems (mainly small industrial scale, demonstration-level, pyrolysis or gasification units involving co-production of biochar, bio-oil and/or syngas) and applied to limited soil/plant systems. However, further research is required to quantify the impacts of biochar produced from a range of small (including mobile units) to large industrial scale biochar production systems and conditions, and then applied to contrasting soil/plant systems.

The global potential for annual sequestration of atmospheric CO<sub>2</sub> through biochar application has been estimated at the billion-tonne scale (Gt/year) under present day scenarios (Laird et al. 2009). The greenhouse gas mitigation potential from the application of biochar to agricultural systems may vary widely with variation in biomass feedstock, production technologies, product utilisation methods and environmental conditions.

## 15.2 Biochar Properties for Soil Health and Climate Change

### 15.2.1 Biochar Stability

The stability of organic matter in soils is determined by its ability to resist microbial and/or chemical decomposition, through chemical transformations and physical interactions with soil minerals (Lehmann et al. 2007; Rasse et al. 2006; Skjemstad et al. 1996). BC, as either charcoal or biochar, has a predominantly condensed aromatic structure that is known to be highly resistant to microbial decomposition (Baldock and Smernik 2002). Additionally, interactions of biochar with soil minerals could further increase stability of biochar in soil (Brodowski et al. 2006), further contributing to long-term carbon sequestration (Lehmann et al. 2009), while also adding to the health and production outcomes of soil systems.

Published studies have reported soil residence time of charcoal and biochars in timescales ranging from decades to centuries to millennia (Cheng et al. 2008b; Hamer et al. 2004; Hammes et al. 2008; Kuzyakov et al. 2009; Major et al. 2010; Skjemstad et al. 1996; Titiz and Sanford 2007; Zimmerman 2010). The stability of

biochar depends on the type of biomass feedstock, charring conditions (temperature, heating time), biochar particle size, and edaphic and climatic conditions under which biochar oxidises (Kuzyakov et al. 2009; Lehmann et al. 2009; Nguyen and Lehmann 2009; Nguyen et al. 2010; Singh and Cowie 2008, 2010; Zimmerman 2010). In general, the proportion of aryl-C to aliphatic-C in biochar increases with increasing charring or pyrolysis temperature (Baldock and Smernik 2002; McBeath and Smernik 2009; Nguyen et al. 2010). The lability and density of the biomass feedstock and its mineral content may also influence the decomposition rate of biochar in soil (Nguyen et al. 2010; Singh and Cowie 2008, 2010).

Spectroscopic and surface chemistry analyses have proven useful to evaluate biochar–mineral interactions and oxidation status of biochar along a decomposition continuum (Cheng et al. 2006, 2008b; Liang et al. 2008). However, these approaches do not quantify turnover time, necessary to evaluate the residence time of biochar in soil. The rate of biochar decomposition may vary according to the stability of the oxidisable component, i.e. initial rapid decomposition of surface-oriented labile components of the biochar particle (e.g. aliphatic-C) followed by slow decomposition of condensed aromatic-C, which dominates the core structure of biochar. This warrants long-term studies to accurately estimate the mean residence time of biochar in soil (Kuzyakov et al. 2009; Nguyen and Lehmann 2009). Furthermore, biochars can potentially stimulate decomposition of native soil organic matter (i.e. humic and labile components) possibly by enhancing microbial activity (Hamer et al. 2004; Wardle et al. 2008). However, application of biochar may also lead to a decline in the decomposition of other organic matter components, through the possible enhancement of soil aggregation (Liang et al. 2010). The “priming effect” of biochar on organic matter decomposition in soil needs to be accounted for to determine the magnitude of biochar decomposed. Carbon isotope methods ( $\delta^{13}\text{C}$ , or  $^{14}\text{C}/^{13}\text{C}$  labelling) can be used to identify sources of C decomposed in biochar–soil systems (Kuzyakov et al. 2009). These methods can be relatively easy to manage in the laboratory, providing optimal conditions for biochar decomposition. However, in the field, presence of plant roots, rhizosphere processes and variable environmental conditions provide challenges to identifying C sources with a limited number of isotopes (Major et al. 2010).

### ***15.2.2 Nutrient and Liming Values of Biochar***

Some biochars are a potential source of nutrients (Table 15.1). The nutrient content of biochar is largely determined by biomass feedstocks (Gaskin et al. 2008; Singh et al. 2010b; Table 15.1). Feedstocks with higher nutrient contents such as animal manures will produce biochars with greater nutrient value, compared with plant feedstocks (Singh et al. 2010b). Pyrolysis temperature also affects nutrient value: for example, analysis of two biochars produced under different temperatures (400 and 500°C) from the same poultry litter feedstock revealed a higher N percentage (3.47%) and lower P percentage (3.01%) for the lower temperature product

**Table 15.1** Nutrient content of selected biochars

Biochar source	N (%)	P (%)	K (%)	Ca (%)	CEC (cmol/kg)	C (%)	pH water	C:N	EC (dS/m)	Production temperature	References
Green wastes	0.18	0.07	0.82	<0.01	24	36	9.4 <sup>a</sup>	200	3.2	450°C	Chan et al. (2007)
Poultry litter	2	2.5	—	—	—	38	9.9 <sup>a</sup>	19	5.6	450°C	Chan et al. (2008)
Poultry litter	3.47	3.01	5.11	4.27	61.1	39.2	10.1	11.3	—	400°C	Gaskin et al. (2008)
Poultry litter	3.09	3.59	5.86	5.04	38.3	39.2	9.74	12.7	—	500°C	Gaskin et al. (2008)
Bark of <i>Acacia mangium</i>	1.04	—	—	—	37.14	39.8	7.4	38	—	260–360°C	Yamato et al. (2006)
Paper mill sludge and wood (1:1)	0.48	—	0.22	6.2	9.0	50	9.4	104	—	550°C	Van Zwieten et al. (2010a)
Paper mill sludge and wood (1:2)	0.31	—	1.0	11.0	18.0	52	8.2	168	—	550°C	Van Zwieten et al. (2010a)
Soybean cake	7.82	—	—	—	—	58.81	—	7.5	—	550°C	Uzun et al. (2006)
<i>Pinus ponderosa</i> bark	<0.01	<0.01	—	—	34.5	71.5	4.81	—	1.12	350°C	Gundale and DeLuca (2007)
Cow manure/ <i>Pinus</i> spp. (3:1)	1.2	0.3	1.9	1.0	—	73.3	9.4	61	—	500°C	Kolb et al. (2009)
<i>Pinus taeda</i> chips	0.255	0.015	0.145	0.171	7.27	73.9	7.55	290	—	400°C	Gaskin et al. (2008)
<i>Pinus taeda</i> chips	0.223	0.014	0.145	0.185	5.03	81.7	8.3	366	—	500°C	Gaskin et al. (2008)
<i>Eucalyptus deglupta</i> wood	0.57	0.06	—	—	4.7	82.4	7.00	144	—	350°C	Rondon et al. (2007)
<i>Eucalyptus saligna</i> wood	0.22	0.03	0.27	0.98	—	85.1	9.4	387	—	400–500°C	Kimetu et al. (2008)
<i>Eucalyptus saligna</i> wood	0.26	0.02	0.24	2.13	3.48	83.6	8.82	322	0.32	550°C	Singh et al. (2010a)
<i>Tectona grandis</i> , <i>Pterocarpus macrocarpus</i>	0.3	—	3.1	4.4	10.7	87	7.5	290	—	Earth mound	Asai et al. (2009)

<sup>a</sup>pH measured in 1:5 soil/0.01 M CaCl<sub>2</sub> extract

compared with the higher temperature product (3.09% and 3.59% respectively, Table 15.1) (Gaskin et al. 2008). Furthermore, the concentration of C and N may increase with increasing pyrolysis temperature in plant-based biochars, but the C and N concentrations may decrease with increasing pyrolysis temperature for mineral-rich feedstocks, such as manure or papermill sludge, because less-volatile elements, including P, K, Ca and Mg, are concentrated as the volatiles are lost (Gaskin et al. 2008; Singh et al. 2010b). However, information on forms and bioavailability of nutrients present in biochars is scarce, and some research has shown that feedstock type and pyrolysis temperature can significantly influence bioavailable fraction of nutrients in biochars (Gaskin et al. 2008; Singh et al. 2010b).

Many biochars have a neutral to alkaline pH value (Table 15.1) and can provide some benefit in neutralising acidic soils. Van Zwieten et al. (2010a) reported liming values of 33 and 29% for two papermill waste biochars (compared to carbonate). Singh et al. (2010b) found that the  $\text{CaCO}_3$  equivalence of biochars increased with increasing pyrolysis temperature.

### 15.2.3 Surface Charge Properties

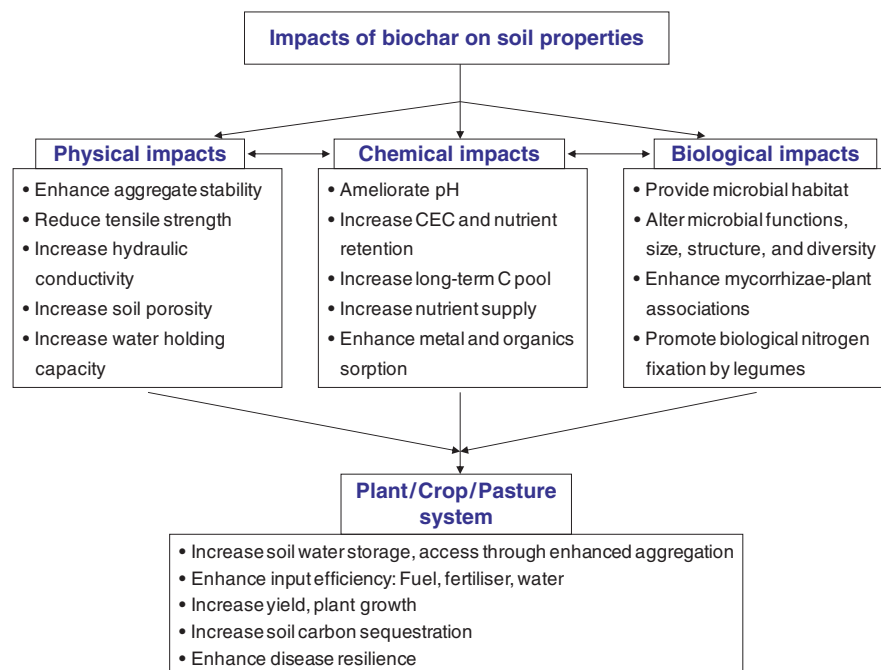
Cation exchange capacity (CEC) is a measure of the ability of a substrate to retain positively charged ions through electrostatic forces. Biochar has been associated with the enhancement in CEC of some amended soils (Glaser et al. 2001; Van Zwieten et al. 2010a), thereby increasing the availability and retention of plant nutrients in soil and potentially increasing nutrient use efficiency. However, biochars from different feedstocks and produced under differing pyrolysis conditions may differ in surface charge properties. Furthermore, the method for determining CEC of biochars is far from standardised, and methods applied to soils may not be appropriate to biochars (Singh et al. 2010b). Of the two biochars from the same peanut hull biomass, the biochar produced at 500°C had a lower CEC (4.63 cmol/kg) compared with that produced at 400°C (14.2 cmol/kg) (Gaskin et al. 2008). The reduction in surface functional groups was suggested as the cause of lower CEC in the biochar produced at higher temperatures. The decline in the acidic functional groups on biochar surfaces has been reported to be greatest between 300 and 400°C (Guo and Rockstraw 2007). Liang et al. (2006) reported that the high charge density (CEC/specific surface area) of “aged” biochar resulted from oxidation of the particles and adsorption of organic matter to biochar surfaces. An increase in the charge density on biochar surfaces as biochar interacts with soil over time (e.g. Cheng et al. 2008a) could be responsible for enhanced cation retention and consequently reduced leaching from amended soils (Singh et al. 2010a). However, more research on the chemical interactions of differing biochars and soils, as well as the implications for soil nutrient retention, is needed.

### 15.3 Impacts of Biochar on Soil Health and Plant Growth

Biochar application can potentially influence a number of physical, chemical and biological properties of soil due to the inherent characteristics of biochar, and properties that develop over time through oxidation of biochar surfaces and interaction with plant–soil–microbial components. Some potential impacts of biochar application on soil health, soil carbon dynamics, nutrient use efficiency and plant growth are described below, and the benefits to plant–soil systems are summarised in Fig. 15.1.

#### 15.3.1 Soil Physical Health

Increases in SOC contents often contribute to enhanced soil aggregate stability (e.g. Albiach et al. 2001; Chan et al. 2003; Neufeldt et al. 2002) which can result from interactions of carbon functional groups and clay mineral surfaces (Lehmann et al. 2008). Evidence suggests a close interaction between biochar particles and clay mineral surfaces, which may aid in the occlusion of biochar particles within newly formed soil aggregates (Brodowski et al. 2006; Liang et al. 2008). Implications that



**Fig. 15.1** Potential impacts of biochar application to plant–soil systems



biochar may contribute to the physical stabilisation of other soil organic matter, through aggregation (Liang et al. 2008), could also suggest an enhanced soil structure.

Biochar has also been associated with the enhancement of other soil physical properties such as soil water retention, saturated hydraulic conductivity and porosity. A study of available soil moisture in three soil types (sand, loam, clay) with 15, 30 and 45% wood biochar additions reported increases in the sandy soils, no change in the loam and a decrease in the clay soil (Tryon 1948). Similarly, Glaser et al. (2002) reported an 18% increase in field capacity for high BC Anthrosol soils compared to low BC surrounding soils, and attributed this to the increased surface area and porous structure of the char particle. In a study of soils under charcoal kilns in Ghana, saturated hydraulic conductivity and total porosity were increased and bulk density decreased compared to adjacent field soils (Oguntunde et al. 2008). Biochar was reported to enhance saturated hydraulic conductivity and water-holding capacity in upland rice production in Northern Laos (Asai et al. 2009), indicating a greater potential for efficient water use and improved soil productivity. The improvement in aggregation, water retention, saturated hydraulic conductivity and porosity from different biochar-amended soils could lead to better plant water use efficiency and consequently more resilient plant systems, and needs greater investigation.

### ***15.3.2 Soil Chemical Health***

The addition of biochar to soils can have a positive effect on soil chemical processes. Studies of the Terra Preta soils in the Amazon Basin have revealed significantly higher CEC per unit of SOC, attributed to the high level of “aged” biochar-like carbon in the Anthrosol soils (Glaser et al. 2001; Liang et al. 2006). In a pot trial, two papermill biochars (10 t/ha) increased the CEC and pH of a Ferralsol; however, there was no effect on a calcarosol (Van Zwieten et al. 2010a). The addition of a pecan biochar to a sandy Norfolk soil at rates of 1 and 2% did not change the soil’s inherent CEC, although soil pH was raised more than one unit over the two incubation periods (Novak et al. 2009). These latter authors suggested minimal surface oxidation due to high pyrolysing temperatures may be the reason for the unchanged CEC.

Increased retention of plant available nutrients in soils as a result of biochar application could have significant agronomic and environmental benefits. Increased retention of inorganic nutrients such as ammonium and potassium within the soil profile may reduce fertiliser requirements. Furthermore, reducing nutrient losses from leaching may slow soil acidification (Helyar et al. 1990) and eutrophication of waterways. Although mechanisms for increasing soil nutrient retention have recently been explored (Liang et al. 2006; Major et al. 2009), greater understanding of the impacts of biochar on different soil types and in different climatic conditions is still required.

### 15.3.3 Soil Biological Health

Many studies have reported a positive response of soil micro-organisms to biochar amendments (O'Neill et al. 2009; Pietikäinen et al. 2000; Steiner et al. 2008a; Thies and Rillig 2009; Warnock et al. 2007; Zackrisson et al. 1996), although overall soil productivity outcomes from these interactions are mostly undocumented. Microbe/biochar interactions could include the attraction of microbes to the products of biochar adsorption such as other organic matter fractions, soil mineral components and nutrients, and extracellular enzymes (Thies and Rillig 2009).

Several studies have reported increased N mineralisation and nitrification through biological processes with charcoal amendment in forest soils (Berglund et al. 2004; DeLuca et al. 2002; MacKenzie et al. 2008). It has been suggested that the adsorption of phytotoxic phenolic compounds by charcoal in forest soils reduces the inhibition of nitrifying micro-organisms in these soils (Berglund et al. 2004; MacKenzie and DeLuca 2006; Zackrisson et al. 1996), or reduces the presence of organic compounds that could stimulate N immobilisation (DeLuca et al. 2006). In agricultural soils, N mineralisation and nitrification may be reduced by biochar addition due to either N immobilisation by N-poor and labile biochar (i.e. a high C/N ratio), or adsorption of ammonium (Lehmann et al. 2006). A study on the effect of a manure-pine biochar in four soils from Wisconsin reported enhanced microbial biomass and activity, as well as decreased extractable N with increasing biochar rates in the three agricultural soils (Kolb et al. 2009). However, Kolb et al. (2009) recorded the highest extractable N in the coniferous forest soil with the highest biochar rates. Pietikäinen et al. (2000) reported that charcoal adsorbed up to 42% of dissolved organic carbon from a litter extract, which consequently attracted and harboured micro-organisms.

Biochar may enhance the symbiotic associations of mycorrhizal fungi (MF) and terrestrial plants. Demonstrations of the positive response of plant growth and nutrient availability as a result of enhanced MF colonisation following BC additions in soils have been reported (Makoto et al. 2010). Root growth and aboveground biomass of *Larix gmelinii* (Gmelin larch) both increased with applied BC alone, and were greatest when BC was applied with MF. Phosphorus concentration in needles of the larch seedlings was also highest from the application of biochar with MF, indicating increased plant uptake, due to the utilisation of phosphate by the MF and seedling root/BC contact. A trial of maize amended with Acacia bark charcoal in Indonesia recorded increases in plant root mass and colonisation rates of MF (Yamato et al. 2006). A review of biochar–mycorrhizal interactions reported numerous positive responses, such as increases in soil nutrient availability and enhanced disease resistance, but also noted that a few studies reported a negative effect on MF with biochar addition, possibly from a reduction in plant available nutrients (Gaur and Adholeya 2000; Warnock et al. 2007).

Biochar has also been implicated in the enhancement of biological N<sub>2</sub> fixation (BNF) of *Phaseolus vulgaris* (Rondon et al. 2007). This study reported a BNF increase of 49% and 78% with 30 and 60 g/kg biochar additions, respectively.

However, a 90 g/kg biochar application increased BNF only by 30% above the control due to lower total biomass production and plant N uptake. Rondon et al. (2007) stated that greater boron and molybdenum availability were the main reasons for the increase in BNF. While some evidence exists for the improvement of plant–soil systems from BC/microbe interactions, this field of research is currently largely unexplored.

#### 15.3.4 Turnover of SOC

Biochar addition to soils may influence the net carbon balance of systems. A stepwise increase in total soil carbon due to direct biochar addition is expected (Chan et al. 2007; Novak et al. 2009; Van Zwieten et al. 2010a). For example, a study of incubations of a Norfolk loamy sand amended with four rates of pecan shell biochar (0, 0.5, 1.0 and 2.0%) revealed increases in total SOC with increasing biochar rates (Novak et al. 2009). In a pot trial of *Raphanus sativus* with the addition of two poultry manure biochars (10, 25, 50 t/ha), total SOC increased compared to the controls (Chan et al. 2008). Furthermore, Liang et al. (2010) reported a greater incorporation of added plant carbon (sugarcane residue) into the intra-aggregate fraction in the *terra preta* soils as compared to the control soil (oxisol), indicating enhanced stabilisation of added carbon in the soil enriched with biochar-like organic matter. Additionally, in the studied *terra preta* soils, biochar-like carbon was found to reside primarily in organo-mineral (heavy) rather than free (light) fractions (Liang et al. 2010). However, another study reported that 72–75% of the light fraction of organic matter in an agricultural soil in Ontario was BC from the previously burnt C<sub>3</sub> forest, and that the turnover of the light fraction with BC was 2.5 times slower than without BC (Murage et al. 2007), suggesting a net reduction in the turnover rate of the light fraction in the presence of BC. In a cropping trial from Brazil, the loss of SOC over 20 months was reduced from biochar-amended soils (4–8% C) in comparison to soils amended with chicken manure, compost, or non-amended control plots (27, 27, and 25% C loss) (Steiner et al. 2007). In a study of historical charcoal blast furnace sites across the eastern half of the USA (Cheng et al. 2008b), organic carbon in the BC-containing soils was more stable, with a lower labile fraction and longer half-life of the recalcitrant component, compared to adjacent non-BC soils.

However, as noted previously in the stability section (Sect. 15.2.1), the overall increase of SOC due to biochar addition may sometimes be partly offset or even negated by the increased turnover of native/labile C (Hamer et al. 2004; Steinbeiss et al. 2009; Wardle et al. 2008). A 10-year study of mesh bags mixed with biochar and humus in a boreal forest site recorded a greater loss of carbon mass, compared with mesh bags of biochar or humus alone (Wardle et al. 2008). However, it was unclear as to the exact source of the carbon losses, or to their specific fate (i.e. leaching or emission). These losses occurred predominantly in the first year of mesh mixing and in the absence of a mineral component and soil profile; so there is some

uncertainty as to the effect of biochar on humus in this instance (Lehmann and Sohi 2008). Another study investigating the influence of biochar on decomposition rates of litters of different quality mixed in a cambisol found no difference in the rate of decay between separate and combined mixtures of these substrates over 240 days of incubation (Abiven and Andreoli 2010). Clearly, further research is needed to generalise the effect of biochar on decomposition of relatively labile forms of organic carbon in soil and to advocate the role of biochar in offsetting global CO<sub>2</sub> emissions (Woolf et al. 2010).

The complexity of interactions between biochar and soil, and consequences of these for carbon sequestration, appear to revolve around the type of biochar, its degree of ageing and the extent of interaction with minerals and organic matter components in soil (Brodowski et al. 2005; Liang et al. 2008). It may well be that as biochar ages in a soil, increasing interactions with soil mineral components may help protect the labile and recalcitrant components of biochar from further biotic and abiotic oxidation. The occlusion of biochar particles within soil mineral aggregation has also been demonstrated in a study of a long-term agricultural field experiment in Germany (Brodowski et al. 2006). It was suggested that biochar could act as a binding agent in micro-aggregation. Further studies involving the identification and influence of specific biomass feedstocks and biochar production conditions to the mechanisms of biochar–soil interactions, as well as processes leading to stabilisation of biochar and other forms of organic matter in biochar-amended soil, are needed to assess the overall influence of biochar on the net soil carbon balance. In particular, the biochemical (e.g. microbial activity, aromaticity) and physicochemical (aggregation, sorption) factors affecting turnover of various forms of SOC need further investigation.

### 15.3.5 Nutrient Use Efficiency

There have been several reports of increases in fertiliser use efficiency with the addition of biochar to soils. A glasshouse study of the agronomic response of wheat, soybean and radish to the application of paper mill waste biochar in a ferrosol and calcarosol, revealed an increase in biomass of wheat (250% of fertilised control), as well as soybean and radish, with fertiliser plus biochar in the ferrosol (Van Zwieten et al. 2010a). The authors reported significantly increased N uptake for the wheat treatment and suggested an improvement in fertiliser use efficiency. However, the results of biochar and fertiliser amendments in the calcarosol were variable, with increased soybean growth but reduced wheat and radish growth. In an upland rice production system in Northern Laos, treatments with wood biochar reported higher grain yields and improved response to fertiliser treatments (Asai et al. 2009), although the authors noted that the positive yield response was dependent on adequate soil nitrogen. In another study, the application of a low nutrient biochar derived from timber increased the retention of N in soil and increased uptake of N into crop biomass (Steiner et al. 2008a, b).

When biochar amendments are combined with fertilisers, the effect is often synergistic, most likely due to increased plant nutrients and nutrient use efficiency from greater retention (Hossain et al. 2010). In a cropping trial in Brazil, wood charcoal and NPK fertiliser together significantly improved plant growth and doubled grain production of *Oryza sativa* and *Sorghum bicolor*, compared with NPK fertiliser alone (Steiner et al. 2007). These authors also reported higher plant available nutrients for following crops, despite the greater nutrient export from the higher plant yields of the biochar-amended plots. In a pot trial of *R. sativus*, a combination of 50 or 100 t/ha addition of green waste biochar and N fertiliser increased dry matter by approximately two times, compared with the N fertiliser treatment only, and 3.7 times compared to the biochar treatment only (Chan et al. 2007).

#### 15.3.6 Plant Growth and Yield

The production of plant biomass through photosynthesis removes CO<sub>2</sub> from the atmosphere, and therefore any increase in plant biomass (carbon stock) due to biochar additions in soil systems will contribute to the mitigation of rapidly rising atmospheric CO<sub>2</sub> levels. Specifically, biochar either increases plant nutrient availability or enhances the soil environment (e.g. CEC, soil pH, aeration) and therefore may indirectly contribute to enhanced plant growth (e.g. Chan et al. 2008; Lehmann et al. 2003; Steiner et al. 2007; Zackrisson et al. 1996).

Some studies have reported increased plant nutrient availability and crop yield with the addition of BC alone. In a cropping trial (*Vigna unguiculata* and *O. sativa*) in Amazon Basin archaeological Anthrosol soils with high carbon levels and Ferralsols with added wood biochar, significantly increased phosphorus, calcium, manganese and zinc availability was found, with a 38–45% increase in biomass of the two crops in the Anthrosol (Lehmann et al. 2003). In a *Zea mays* trial of degraded cropping soils in Western Kenya, the authors noted that the application of biochar doubled crop yield, and furthermore suggested that the improvement could not be explained by biochar nutrient availability alone (Kimetu et al. 2008). Hence, despite the low nutrient status of some biochars, biochars generally appear to increase nutrient availability through increased ion retention in soils (Liang et al. 2006; Tryon 1948) and therefore potentially enhance plant yields. Biochar applications produced from manures may directly contribute high levels of nutrients to soils. Chan et al. (2008) reported yield increases of *R. sativus* with the application of 10, 25 and 50 t/ha of poultry manure biochar alone.

However, there have been variable results from the addition of some biochar types in particular soils. Van Zwieten et al. (2010a) reported reduced growth in wheat and radish with the addition of a paper mill sludge biochar in a calcarosol. In a pot trial of *R. sativus* in an Alfisol, a 10 t/ha green waste biochar and N fertiliser amendment resulted in a biomass decrease of 30%. This latter study also reported



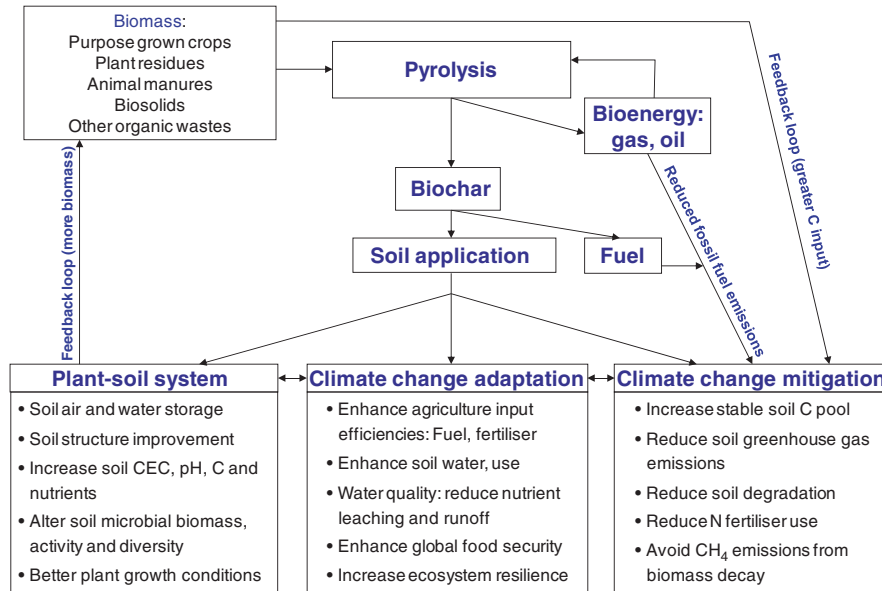
biomass increases at higher biochar rates. Other studies have reported a decline in soil N availability with wood biochar addition, potentially causing reduced yields (Asai et al. 2009). The inconsistency of plant response, ranging from small declines to large increases, would indicate a need for further research to verify the different plant responses to different biochars under varying soil conditions.

## **15.4 Role of Biochar in Climate Change Mitigation and Adaptation**

The previous sections of this chapter have demonstrated the considerable potential for biochar to enhance the fertility and productivity of agricultural systems, as well as provide a stable form of carbon for sequestration in soil. As the sustainability of agriculture becomes increasingly threatened by climate change (Chap. 1), tools such as biochar will be needed to enhance resilience and productivity of these systems, so that world food supply can satisfy demand. Changes to world rainfall patterns may see declines in some of the major food producing areas of the world (Howden et al. 2007); the role of biochar in enhancing moisture retention may prove critical to maintaining production in these locations. Increases in soil health and crop productivity may have a range of resultant environmental, social and greenhouse gas balance implications. For example, higher crop productivity due to improved soil health could result in less use of land for the same yield, thereby reducing the need to produce food on more marginal land, and potentially increasing production per unit of gaseous emission. Enhanced crop productivity from biochar application may also reduce the rate of land clearing and deforestation, or encourage the rejuvenation of degraded land, again with significant positive ecological, social and economic consequences. A schematic of potentially interrelated ecosystem benefits of biochar production/application systems, including enhanced climate change mitigation and adaptation and improved performance of plant–soil systems, is presented in Fig. 15.2, and evidence for some of these benefits is described below.

### ***15.4.1 Mitigation of N<sub>2</sub>O Gas Emissions from Soil***

Soil represents a significant source of the greenhouse gas nitrous oxide (N<sub>2</sub>O). The microbial processes nitrification and denitrification are largely responsible for production of N<sub>2</sub>O in soil (Chen et al. 2008; Dalal et al. 2003; Yanai et al. 2007). As the global warming potential of N<sub>2</sub>O is 298 times greater than the equivalent mass of CO<sub>2</sub> in the atmosphere (Forster et al. 2007), technologies to minimise soil N<sub>2</sub>O emissions need to be implemented to meet demands for climate change mitigation. Some recent studies have provided evidence that emissions of N<sub>2</sub>O



**Fig. 15.2** Potential ecosystem benefits from biochar production/application systems

may be reduced by biochar application to soil (Singh et al. 2010a; Spokas and Reicosky 2009; Van Zwieten et al. 2010b; Yanai et al. 2007). The magnitude of reduction in N<sub>2</sub>O emissions is dependent on soil type, biochar type and application rate, soil moisture content, and biochar ageing (Singh et al. 2010a; Spokas and Reicosky 2009; Van Zwieten et al. 2010b). However, in some cases, emissions of N<sub>2</sub>O from soil can also be increased or not affected by the presence of biochar. For example, Clough et al. (2010) showed short-term increases in N<sub>2</sub>O emissions in a pasture soil following biochar application (at 4.3% w/w) in the presence of ruminant urine; however, no significant differences were observed in cumulative N<sub>2</sub>O emissions over the 53-day laboratory incubation between the biochar plus urine and urine-only treatments. Likewise, Spokas and Reicosky (2009) found that application of a high nitrogen compost-amended biochar (at 10% w/w) resulted in high N<sub>2</sub>O emissions from three different soils and Spokas et al. (2009) found no significant differences in soil N<sub>2</sub>O emissions at biochar application rates of 2–10% (w/w). The exact mechanisms for observed effects of biochar on N<sub>2</sub>O emissions remain largely unexplored (Van Zwieten et al. 2009). Singh et al. (2010a) found that effectiveness of biochars in reducing soil N<sub>2</sub>O emissions can increase over time, and hypothesised that this may be due to increased sorption capacity of biochars through oxidative reactions on biochar surfaces with ageing. Thus, in addition to its potential long-term soil carbon sequestration value, biochar application could provide considerable greenhouse gas mitigation benefit if reductions in N<sub>2</sub>O emissions are found to apply broadly (Van Zwieten et al. 2009).

### ***15.4.2 Reduced N Fertiliser Requirements***

As the demand for food increases through wealth and population pressures, so too does the need for resources such as fertilisers and water. Nitrogen in particular is a resource that is poorly managed (Spiertz 2010), and more effort is needed to ensure that N supply matches N demand (see Chap. 6). As less than 50% of soil nitrogen can be used by the crop (Baligar et al. 2001), technologies that improve N use efficiency will have implications for productivity and emissions. A large portion of N is lost through mechanisms such as leaching (Olareswaju et al. 2009), or loss by denitrification and ammonia ( $\text{NH}_3$ ) volatilization (Khalil et al. 2009). As the manufacture of nitrogen fertiliser releases more than 3 t  $\text{CO}_2\text{e}$  per t N (West and Marland 2002), technologies that can reduce the frequency and quantity of N application will result in lower emissions from the resulting reduction in fertiliser application. The evidence for increases in N fertiliser use efficiency with biochar amendments is reviewed in Sect. 15.3.5.

### ***15.4.3 Biofuel Production***

With mounting evidence for global warming from anthropogenic emissions of greenhouse gases, alternative forms of energy to reduce society's dependence on fossil fuels are required. The production of biofuels, from the chemical or thermal conversion of biomass (Bridgwater 2003), is currently being promoted as an alternative energy source that may help to reduce reliance on fossil fuel and avoid  $\text{CO}_2$  emissions. The chemical and thermal pathways that produce biochar result in the co-production of combustible gas and/or oil which can be used for bioenergy production. It has been estimated that agricultural lands in the USA could provide enough manure through feedlot and intensive dairies to supply 0.7 billion US dollars of energy in terms of barrel of oil equivalents, based on a 20% thermochemical conversion factor of biomass (Ro et al. 2009). The energy output of pyrolysis has been favourably compared to that of the production of ethanol from corn. Even when pyrolysis is optimised for biochar production, energy output is 2–7 MJ, per MJ of fossil energy input (Gaunt and Lehmann 2008) compared with 1–2 MJ for corn to ethanol (Cherubini et al. 2009). The future decline in world fossil fuel reserves may enhance the relative merits of sustainable energy technologies such as pyrolysis with the added benefits of biochar application to soils.

### ***15.4.4 Soil Structure Improvements***

Well-structured soils are generally characterised by stable aggregation, high saturated hydraulic conductivity, low tensile strength and often high water-holding

capacity. These qualities are all desirable as they assist in maintaining soil and plant productivity. Amendments such as biochar that may assist in the efficient capture, storage and utilisation of water in soils through structural improvement will become increasingly vital with any decline in rainfall as a consequence of a changing climate.

A poorly structured soil can present a substantial challenge for plant root development due to physical constraint associated with higher bulk densities and high soil tensile strength. Soil structure can be improved through the accumulation of soil organic matter (e.g. Perie and Ouimet 2008; Ruehlmann and Korschens 2009), with the more labile forms increasing the stability of macro-aggregates and less labile forms increasing the stability of micro-aggregates (Tisdall and Oades 1982). The evidence for better soil structure and enhanced physical properties (see Sect. 15.3.1) suggests that biochar may be a useful tool to mitigate climate change outcomes such as reduced rainfall, or extreme weather events (e.g. floods). Increased soil water use efficiency can help mitigate the impact of reduced annual rainfall on plant growth, while soil and nutrient losses from erosion during extreme weather events can be greatly reduced by increased soil aggregate stability and decreased surface runoff through enhanced infiltration.

As soil tensile strength and compaction increase, so does the requirement for greater cultivation draught capacity and frequency of tillage (O'Sullivan and Simota 1995). It could thus be anticipated that as biochar amendments can reduce soil tensile strength in a hard setting soil (Alfisol) as reported by Chan et al. (2007), and in a Norfolk loamy sand (Busscher et al. 2010), it would be reasonable to suggest that biochar could, in some soils, also reduce cultivation requirements, and hence reduce fuel usage. However, there is little direct evidence for overall enhancement of soil aggregation by biochar application, and the timeframe required; this aspect needs further research, especially as part of long-term assessment of potential agronomic and environmental benefits of biochar application in field studies.

#### **15.4.5 Ecological Resilience**

Appropriate biological functioning in soil systems can contribute to climate change adaptation through improvements in nutrient availability (Geisseler et al. 2009; Lavelle 1988), disease suppression (Larkin 2008) and aggregate stability (Lee and Foster 1991; Rillig and Mummey 2006). Many studies have reported increased microbial biomass in response to biochar amendments (O'Neill et al. 2009; Steiner et al. 2008a; Warnock et al. 2007; see Sect. 15.3.3). Biochar may enhance the symbiotic associations between MF and terrestrial plants, strengthening the plant's adaptability to climate change. Furthermore, biochar could provide long-term storage of carbon in soils while enhancing soil productivity, thereby enhancing the sustainability of agro-systems.

#### 15.4.6 *Net Mitigation Benefits*

As indicated above, biochar may deliver mitigation benefits to terrestrial systems through several routes: stabilisation of soil organic matter, thus reducing its rate of oxidation while also decreasing soil erosion through improved aggregation; production of bioenergy that can displace fossil energy emissions (see Chap. 16); reduction in  $\text{N}_2\text{O}$  emissions from soil and fertilisers; reduction in fuel requirement for cultivation; increased carbon stock in plants and soil (Woolf et al. 2010). Furthermore, some biomass feedstocks, when used in biochar production, may deliver added benefit through avoided emissions: biomass that would have been deposited in landfill would have released methane ( $\text{CH}_4$ ), while decomposition of manures can release  $\text{CH}_4$  and  $\text{N}_2\text{O}$  gases (Gaunt and Cowie 2009). Therefore, the production and sequestration of biomass C in the form of biochar (with co-production and utilisation of bioenergy to offset fossil fuel emissions) could help slow climate change through the net removal of  $\text{CO}_2$  from the atmosphere and avoiding emissions in the order of 1.0–1.8 Mt  $\text{CO}_2\text{e}/\text{year}$  at current levels of feedstock availability (Woolf et al. 2010). Gaunt and Cowie (2009) estimated net emissions reduction of 130–5,900 kg  $\text{CO}_2\text{e}/\text{t}$  feedstock for biomass residues (straw, manure and greenwaste), with variation arising from differences in feedstock properties, conventional use of feedstock and fossil energy source displaced. Roberts et al. (2010) also calculated an emissions reduction of 800–900 kg  $\text{CO}_2\text{e}/\text{t}$  biomass for similar biomass feedstocks (corn stover and yard waste). However, the mitigation benefit was much reduced for purpose grown biomass: Roberts' estimates ranged from a reduction of 440 kg  $\text{CO}_2\text{e}/\text{t}$  feedstock to an increase of 36 kg  $\text{CO}_2\text{e}/\text{t}$  feedstock, depending on the method used to estimate emissions from land use change (Roberts et al. 2010).

The sequestration benefit coupled with the creation of carbon neutral fuel (emissions from the burnt fuel are balanced by C sequestered in its production) could potentially reduce American emissions of  $\text{CO}_2$  by 10% (Laird 2008). Globally, the potential mitigation benefit from biochar has been estimated at between 0.7 and 2.6 Gt C/year by 2050 (Laird et al. 2009).

### 15.5 Implementing Biochar Globally

The biochar supply chain includes biomass sourcing, conversion technology, product distribution and use. Due to the widely distributed nature of many biomass sources, biochar will need to be converted efficiently and economically from local biomass resources for distribution into regional agricultural soils.

The conversion of biomass to energy on a global scale will require a range of systems that use available resources while recognising regional socio-economic constraints and desired outcomes. For example, while up-scaling of “industrialised” biochar systems will be attractive to investors in developed countries, there is



potential to implement clean, efficient biochar solutions at a small scale in developing nations to improve community welfare and reduce greenhouse gas emissions (Bailis 2009; Ewing and Msangi 2009). Existing thermal conversion technologies may be enhanced through the development of more sustainable sources of biomass (e.g. plantation biomass) and the implementation of modern kilns. Advantages of these more efficient systems may include rapid carbonisation, reduced gaseous emissions and higher yield of biochar from a greater potential range of feedstocks. The production outcomes from these systems will vary according to local resources and needs, ranging from small-scale production of biochar for fuel to larger industrialised production of liquid/gas energy and biochar for soil amendment.

The quantity of wood charcoal traded by the global forestry industry in 2008 was 49.35 million tonnes, of which more than half was produced in Africa and only 0.6% in Europe (FAO 2010). While the sustainability of this biomass source needs to be secured to remove the threat of net deforestation, with technological modernisation, growth in this industry could supply the energy needs of communities while meeting the expanding demand for biochar in agriculture. The relatively small amounts of charcoal produced in industrialised nations, under strict environmental regulatory control, are generally for specialised applications which can afford the more expensive process technology to ensure product meets specification.

The large-scale production of biochar for a low-value agricultural market requires the commercialisation of a new generation of clean and safe thermal conversion technology. The additional costs of the various regional environment and planning regulations can perhaps be offset through the lower cost of feedstock that comes with the efficient conversion of waste residue feedstocks to biochar. Commercial viability may also be assisted if the technology enables the utilisation of co-products such as bio-oils and gas for energy generation. Examples of commercial biochar production systems that have been able to demonstrate that large-scale reliable, economically viable and environmentally sustainable supply of product are largely non-existent at this time.

## 15.6 Future Directions

Biochar research is in its infancy; further investment in research is needed to understand the mechanisms of its impacts, particularly in relation to N<sub>2</sub>O emissions, nutrient retention and interactions with soil constituents such as native organic matter and minerals in a range of soil type, vegetation systems and climatic conditions. As the impacts of biochar on soil processes may change over time, there is a need for long-term studies to assess biochar's potential to provide the projected benefits. Measures to secure sustainable feedstock supply and novel biochar processing technologies are needed to ensure that biochar production delivers net environmental benefits. Measures could include certification against an agreed standard, similar to the sustainability certification undertaken in the

forestry sector and being developed for bioenergy. Government incentives for commercial demonstration are needed to enable the technologies to become an acceptably low-risk proposition in a free market economy. With the possibility of multiple environmental benefits from its use, biochar-amended systems may become a vital tool to mitigate climate change and enhance the sustainability and productive capacity of global terrestrial systems.

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*Appendix H - Biochar effects on nutrient leaching*

## Biochar Effects on Nutrient Leaching

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### Introduction

Leaching is often an important aspect of nutrient cycling in agriculture (Brady and Weil, 2008). It occurs when mobile nutrients in the soil solution are displaced by percolating water to an area outside the rooting zone where plants cannot utilize them. Nutrients adsorbed to small mobile particles or colloids can also be leached to deeper soil horizons through facilitated transport. For nutrients dissolved in the soil solution, a migration of anions must be accompanied by an equivalent migration of cations for the maintenance of electro-neutrality. As such, the loss of highly mobile nitrate molecules after nitrogen (N) fertilization or organic matter mineralization must occur along with the loss of cations such as calcium (Ca), potassium (K), magnesium (Mg), etc. The amounts of plant-essential nutrients lost from the rooting zone by leaching can be considerable: losses up to 80 per cent of applied N (Lehmann et al, 2004), 172 per cent of applied Ca (Omoti et al, 1983) and 136 per cent of applied Mg (Cahn et al, 1993) have been reported in the field. Values greater than 100 per cent indi-

cate that nutrients other than those added were also mobilized (e.g. by the process of desorption). Leaching, like most soil properties and processes, can be spatially and temporally highly variable.

While large proportions of nutrient losses certainly imply economic impacts with fertilizer-use efficiency and soil nutrient stock depletion, the environmental impacts brought about by nutrient leaching can be considerable. Phosphorus (P) and other nutrients cause eutrophication when they leach or run off from agricultural land into water bodies. This is currently one of the most common causes of unacceptable water quality levels in the developed world (Daniel et al, 1998; Sharpley et al, 2001). In 1992, as much as 26 per cent of water wells in intensive agricultural areas of the US were found to have nitrate levels above the maximum contaminant level (MCL) set by the Environmental Protection Agency (EPA) (Mueller et al, 1995). British water supply companies have made costly investments in blending and other technology to reduce

nitrate levels to European Union (EU) limits (through the UK Department for Environment, Food and Rural Affairs, or Defra).

Biochar has been found to decrease nutrient leaching on its own (Downie et al, 2007; Dünisch et al, 2007), as well as after incorporation within soil (Lehmann et al, 2003). In this chapter we review empirical evidence on the magnitude and dynamics of biochar's effect on nutrient leaching, and discuss possible mechanisms and processes by which this effect is observed.

### **General factors that influence nutrient leaching**

Before considering the effect of biochar application on soil nutrient leaching, the contributory factors to the leaching process must be examined. Indeed, factors other than biochar application, such as rainfall patterns, will probably be stronger determinants of leaching losses. Biochar application represents a controllable production factor and has the potential to help manage such losses.

#### ***Management of vegetation and fertilization***

Nutrient leaching is generally greatest under fertilized row crops such as maize or horticultural crops, and targeting these cropping systems may yield the best results for reducing leaching. Roots exert suction on the soil, and the horizontal and vertical distribution of roots that are intercepting and taking up nutrients influences leaching. Deep-rooted plants such as trees can act as 'safety nets' and recycle leached nutrients that have migrated to deeper soil horizons (Rowe et al, 1998; Allen et al, 2004). Nutrient-use efficiency also varies among crop species and varieties, as well as if other stress factors are present, such as drought and pest pressure. Lower efficiencies should lead to greater losses of unutilized nutrients through leaching. The amounts, chemical form, timing and

placement of fertilizers, synthetic and organic, also greatly affect nutrient leaching patterns (Melgar et al, 1992; Cahn et al, 1993; van Es et al, 2002). Ideally, these should match crop requirements in both time and space; but practical considerations often prevent this. With greater nutrient retention by biochar additions to soil, timing of nutrient applications will become less critical with respect to nutrient leaching.

#### ***Soil structure and texture***

Surface soil porosity is critical in determining the rate at which rain can infiltrate into soil and carry nutrients with it away from the rooting zone. There, small pores retain soil solution by capillarity, reducing leaching and crop water stress. Amounts of leached nitrate are greater on coarser-textured soil, or when hydraulic conductivity and infiltration rates are higher (Melgar et al, 1992; van Es et al, 2002, 2006). This suggests that biochar should have the greatest value for reducing nutrient leaching in sandy soils. However, in certain cases, differences between soil textures could be linked to changes in denitrification rates and the loss of N gases, and not to changes in water percolation (van Es et al, 2002). The flow of nutrient-carrying water through soil is also greatly influenced by the soil's macropore structure, which allows water to avoid permeating the soil matrix and can cause rapid flow down the profile (Ghodrati and Jury, 1990; Flury et al, 1994; Renck and Lehmann, 2004), even through paddy rice soil where surface structure is periodically destroyed (Sander and Gerke, 2007). The physical characteristics of biochar (see Chapter 2) suggest that it can change the pore-size distribution of the soil and possibly alter percolation patterns, residence times of soil solution and flow paths.

#### ***Rainfall patterns***

As expected, a linear relation exists between depth of movement of nitrate, which is highly mobile in soil, and cumulative rainfall



(Melgar et al, 1992). Biochar may therefore be most effective in reducing leaching losses in regions of high rainfall. Rainfall patterns, through their effect on N mineralization as well as leaching, influence surface soil N availability, at times more so than soil drainage class (Sogbedji et al, 2001; van Es et al, 2006). Year-to-year variability in weather – most importantly, rainfall patterns – have often been observed as explaining the most variability in leaching patterns at single sites.

#### ***Soil and soil solution chemistry***

The chemistry of clays, soil minerals (e.g. metal oxides and carbonates) and organic matter, as well as the chemistry of elements in the soil solution, affect leaching. For example, whether a nutrient is organic or inorganic, the size of the molecule it is a part of and its charge properties will dictate how it will interact with charges on constituents of the soil matrix. Positively charged ions or molecules can be adsorbed to negatively charged clays and soil organic matter (Brady and Weil, 2008), which is quantified as cation exchange capacity (CEC). Biochar displays a

high CEC, and its application to soil will contribute negative charge (see Chapter 5). In a pot experiment, soil-applied biochar increased soil pH by 0.36 and 0.75 units with and without fertilizer, respectively, in acid soil (Lehmann et al, 2003).

#### ***Soil biology and nutrient cycles***

Leaching of nutrients must be considered in the context of the general cycling of nutrients, where fluxes are partitioned among denitrification and other gaseous losses (in the case of N), fixation, precipitation, immobilization, mineralization and leaching. Biochar has been found to reduce N<sub>2</sub>O gaseous losses by more than half under maize (Rondon et al, 2006; see also Chapter 13). Biochar application to soil alongside labile organic N amendments led to increased net rates of nitrification in laboratory experiments using forest soils (Berglund et al, 2004; Gundale et al, 2007), most likely due to the sorption of nitrification-inhibiting phenolic compounds by biochar (see Chapter 14). However, the implications of these processes for N leaching are unclear.

## **Evidence for relevant characteristics of biochar**

Biochar produced from different feedstocks and under different conditions exhibits a range of physical and chemical properties (Treusch et al, 2004; Mermoud et al, 2006; Krzesinska and Zachariasz, 2007) (see Chapters 2 to 5), which will have impacts upon nutrient leaching, once it is applied to soil.

### **Physical properties**

Water-holding capacity in soils is partly determined by organic matter contents, and organic matter amendments generally increase the water-holding capacity of soil. Humic substances derived from coal have

been found to increase the water-holding capacity, as well as the aggregate stability of degraded soil (Piccolo et al, 1996). Empirical evidence suggests that sandy soils amended with biochar will experience an increase in water content, while the effect could be opposite in clay soil (Tryon, 1948). Lysimeter work using a biochar-amended clay soil from the Amazon showed that water percolation was related to crop growth: less water percolated from soil/biochar mixtures than pure soil, in accordance with increased crop growth when biochar had been added (Lehmann et al, 2003). This indicates that in clay soils, biochar can indirectly reduce water mobility through increased plant biomass

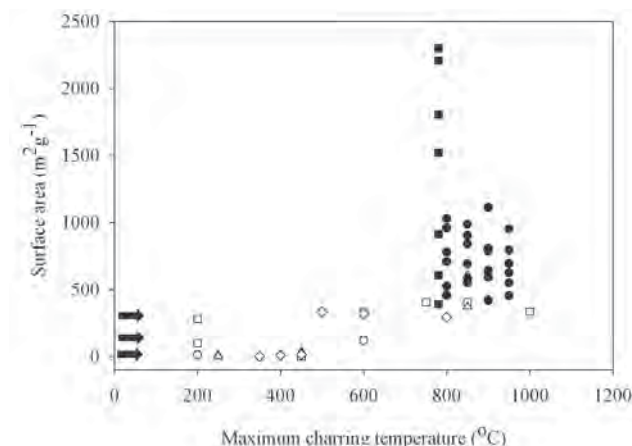
and evaporative surfaces, while in sandy soils this mechanism can be complemented by the direct retention of water by biochar.

The bulk density of biochar is lower than that of mineral soils (see Chapter 2). This suggests that its application to soil will modify soil hydrology in line with application rates because of changes in porosity and, in the long term, aggregation. While fresh biochar alone may not influence the aggregation of 2:1 clays (Watts et al, 2005), it is possible that aggregation will be favoured by interactions with soil organic matter and microorganisms (Warnock et al, 2007) or by additions of biochar and labile organic matter in combination since organic molecules sorb to appropriate biochar domains (Pietikäinen et al, 2000; Smernik, 2005; Tseng and Tseng, 2006; Yu et al, 2006; see Chapter 16). Biochar effects on soil aggregation will, among others, be linked to its surface charge characteristics, which develop gradually by weathering and are affected by overall soil pH (Cheng et al, 2006). Improved soil aggregation promotes water infiltration; thus, the amount of water moving through the soil as opposed to running off could be increased. This may result in increased leaching for soluble and mobile ions such as nitrate.

The total porosity of biochar is high and varies with production method and feedstock (see Chapter 2). For soil, no universal pore-size categorization system is widely accepted (Hayashi et al, 2006); however, proposed classifications are expressed in the micrometre range (Luxmoore, 1981; Soil Science Society of America, 1997; Lal and Shukla, 2004). Water is usually considered mobile when present in pores of sizes in the order of a few tens of micrometres (e.g. 30  $\mu\text{m}$ ) (Brady and Weil, 2008). According to the definition of the Soil Science Society of America (1997), macropores ( $>80\mu\text{m}$ ) can contribute to the rapid flow of water through soil by gravity, and after heavy rainfall can lead to pronounced leaching events (Flury et al, 1994; Renck and Lehmann, 2004). Meso-

pores (30  $\mu\text{m}$  to 80  $\mu\text{m}$ ) will allow water to move in response to matric potential differences (i.e. from 'wetter' to 'drier' areas), while micropores ( $<30\mu\text{m}$ ) hold water in place. Pore sizes for biochar are usually reported according to standard IUPAC value ranges (i.e. micropores are  $<2 \times 10^{-3}\mu\text{m}$  diameter, mesopores  $2\text{--}50 \times 10^{-3}\mu\text{m}$ , and macropores  $>50 \times 10^{-3}\mu\text{m}$ ) (see Bornemann et al, 2007; Chapter 2). Pore-size classification systems make comparisons between biochar and soil difficult, and pore sizes within biochar depend upon the parent material and the charring conditions. However, activated biochar has been found to contain a large proportion (over 95 per cent) of micropores ( $<2 \times 10^{-3}\mu\text{m}$ ) (Tseng and Tseng, 2006), and biochar porosity probably contributes to nutrient adsorption by the trapping of nutrient-containing water held by capillary forces as in soil micropores. If 95 per cent of biochar pores are  $<2 \times 10^{-3}\mu\text{m}$  in diameter, the mobility of soil water through the matrix after biochar application will be reduced. In sandy soil where the volumetric amount of water held decreases sharply as matric potential increases (i.e. as the soil dries), biochar particles may act similarly to clay and hold large volumes of immobile water even at elevated matric potentials. Nutrients dissolved in this water would thus be retained near the soil surface if water is immobile or moves slowly. Plants can access part of the nutrients in this retained soil solution as they transpire and elevate soil matric potential.

Evidence suggests that biochar porosity contributes to nutrient adsorption directly through charge or covalent interaction on a large surface area. The high porosity of biochar is accompanied by high surface areas (see Figure 15.1), to which both hydrophobic and hydrophilic molecules can sorb depending upon the functional groups displayed by the biochar (see Chapters 5 and 16). Surface area generally increases with charring temperature, and activation processes can drastically increase surface area further (see



**Figure 15.1** Surface area of activated and non-activated biochar produced at varying temperatures

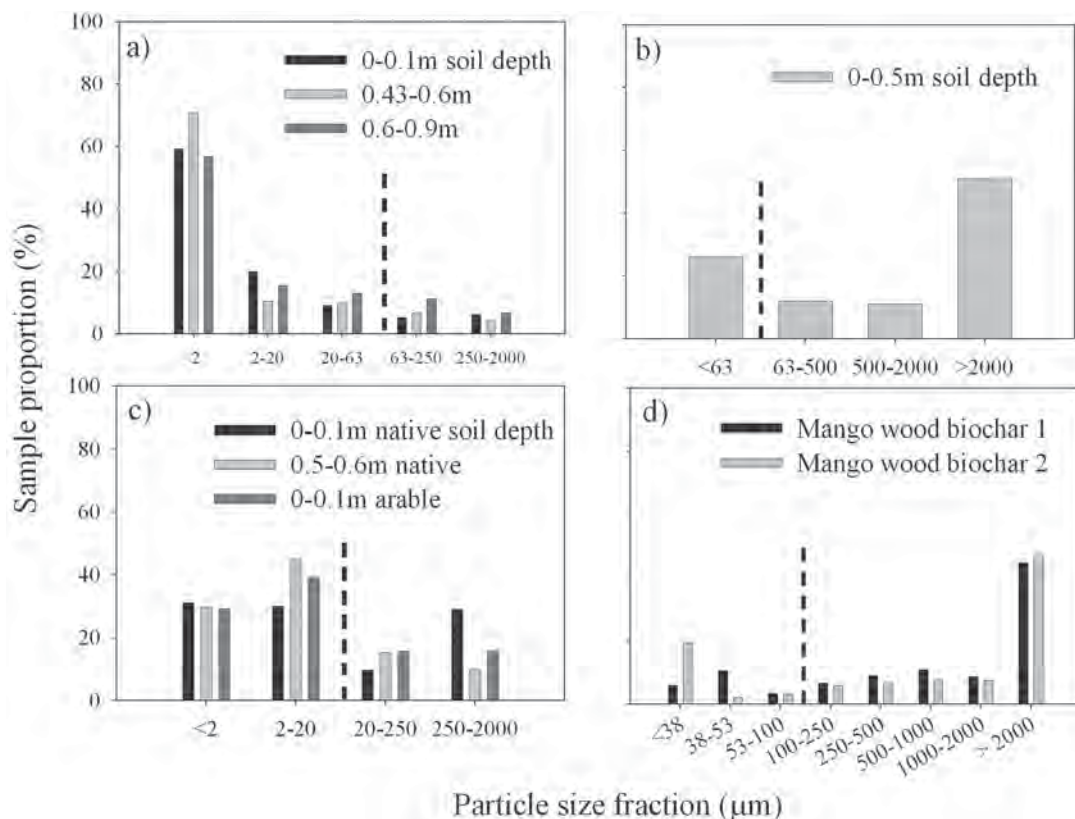
Source: chapter authors, from data specified in notes below

Notes: Non-activated hardwood biochar (open symbols): TRIANGLE Bornemann et al (2007); DIAMOND Lehmann (2007); SQUARE Nguyen et al (2004); CIRCLE Macias-Garcia et al (2004). Activated (filled symbols): CIRCLE hardwood, Macias-Garcia et al (2004); SQUARE sugar cane pith, Tseng and Tseng (2006). Points above  $1500\text{ m}^2\text{ g}^{-1}$  were obtained by activation using KOH/biochar weight ratios  $>3:1$  at  $780^\circ\text{C}$ . Arrows indicate, for comparison, the surface area of a 72 per cent clay (top), 90 per cent sand (bottom) soil, which were textural extremes and the average (middle) for 33 US soils studied by Cihacek and Bremner (1979). Surface area for all biochars was measured by  $\text{N}_2$  absorption and the Brunauer, Emmett and Teller (BET) equation. Since the surface area of soils increases with increasing moisture content and the  $\text{N}_2$ -BET method uses dry soil, surface area data for soils were obtained using the ethylene glycol monoethylene ether (EGME) method on moist samples.

Chapter 2). It is clear from Figure 15.1 that biochar must be produced at temperatures at or above  $500^\circ\text{C}$  or be activated if its application to soil is to immediately result in increased surface area for the direct sorption of nutrients.

Apart from impacts upon the movement of the soil solution and direct interactions with nutrients dissolved in it, the size of biochar particles may also influence leaching potential. Leaching of organic and inorganic nutrients sorbed to larger biochar particles may be either reduced or facilitated by colloidal transport with small particles as they themselves travel through the soil profile. Negatively charged colloids were shown to facilitate the downward migration of metals and organic pollutants through soil (Karathanasis, 1999; Sen and Khilar, 2006). Particle sizes of biochar produced for soil application can be controlled to some extent. Very small particles (e.g.  $<2\mu\text{m}$ : the size of clay particles) will most likely be present in

the material after pyrolysis or created during transportation and application (see Figure 15.2). After soil application, rain impact, chemical weathering and physical disturbance from biota will also result in fine biochar particles. Soil porosity varies widely among soils, and particles of up to  $10\mu\text{m}$  were found to move through a structured sandy loam in the laboratory (Jacobsen et al, 1997), particles with a median size of  $2\mu\text{m}$  to  $5\mu\text{m}$  moved from topsoil through a sandy loam in the field (Laubel et al, 1999), and natural colloids of up to  $200\mu\text{m}$  were mobilized through a coarse disturbed soil (Totsche et al, 2007), also in the field. The data compiled in Figure 15.2 show that fine biochar particles smaller than values mentioned above can represent a large proportion, and these particles are subject to movement through the soil profile and can act as agents of facilitated transport of nutrients.



**Figure 15.2** Particle-size distribution of naturally occurring chars (a) in fertilized intensive crop soil, Germany; (b) in burned savannah soil, Zimbabwe; (c) in a Russian steppe Mollisol; and (d) hardwood biochar produced traditionally in mounds for soil application, hand ground to pass through a 0.9mm sieve

Note: Bars to the left of vertical dashed lines (<200μm) represent the proportion of sample particles which may be translocated through soil profiles.

Source: Brodowski et al (2007): fertilized intensive crop soil, Germany; Bird et al (1999): burned savannah soil, Zimbabwe; Rodionov et al (2006): Russian steppe Mollisol; Major et al (unpublished): hardwood biochar

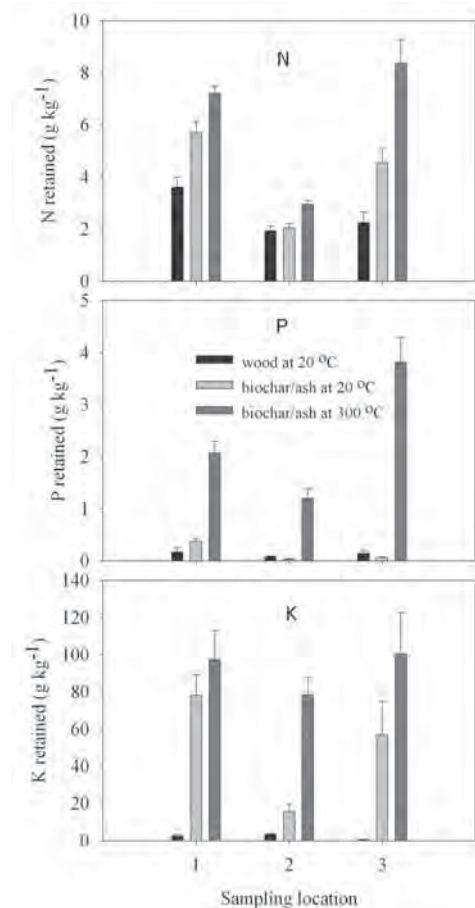
## Chemical properties

Aged biochar has a high CEC, as shown by high concentrations of negative charges on biochar surfaces, as well as the adsorption of charged organic matter to biochar surfaces (Liang et al, 2006). As is the case with clays, this high CEC may promote soil aggregation where organic matter and minerals bind to each other and to biochar. Abiotic processes are more significant in driving the oxidation of fresh biochar surfaces than are biotic

processes in the short term (i.e. months), with higher temperatures leading to the oxidation and creation of negative charge on deeper layers of biochar particles (Cheng et al, 2006); thus, variation occurs between different climate regimes (Cheng et al, 2008). Fresh biochar may also sorb anions, and the CEC and anion exchange capacity (AEC) vary with overall soil pH, and age and weathering environment of biochar (Cheng et al, 2008). The intrinsic pH of biochar materials can be acidic or basic (see Chapter 5).

Fresh biochar, with low surface oxidation, is hydrophobic and sorbs hydrophobic molecules, such as organic contaminants (Lebo et al, 2003; Bornemann et al, 2007) (see Chapter 16). Organic hydrophobic forms of nutrients (e.g. N, P and S) could also become sorbed to biochar particles; in fact, this might effectively reduce their surface area at the molecular scale by steric hindrance, and block the subsequent direct adsorption of organic and inorganic nutrients directly to biochar particles. This effect will depend upon the size and composition of the macro-molecules and the temperature (Kwon and Pignatello, 2005; Pignatello et al, 2006). Since molecules of various sizes and chemical characteristics could sorb onto biochar particles, adsorption is likely whereby inorganic molecules sorb directly to biochar surfaces, to minerals or organic matter attached to biochar, or precipitate on biochar surfaces (e.g. Ca-phosphates). As mentioned above, soil aggregation could be modified in this way; but it is not clear to what extent and how rapidly this process occurs.

Dünisch et al (2007) noticed a larger mass of N, P and K sorbed to wood biochar/ash samples after these materials were dipped in a commercial inorganic fertilizer solution compared to 'fresh' wood feedstock (see Figure 15.3). However, the amount of water absorbed by these materials was not taken into account and, thus, the greater nutrient sorption might result partly from greater amounts of solution and dissolved nutrients held in the porous biochar before drying and analysis. Still, given different proportional increases for each nutrient, it seems that water absorption alone did not explain observed differences. Smaller-sized particles generally sorbed more nutrients than larger ones, suggesting an effect of surface area. In addition, up to 52 per cent of the P in dairy farm effluent was removed by chicken litter biochar (made at 500°C, activated) in a 100:1 effluent/biochar mixture at 50°C (Downie et al, 2007). Phosphorus



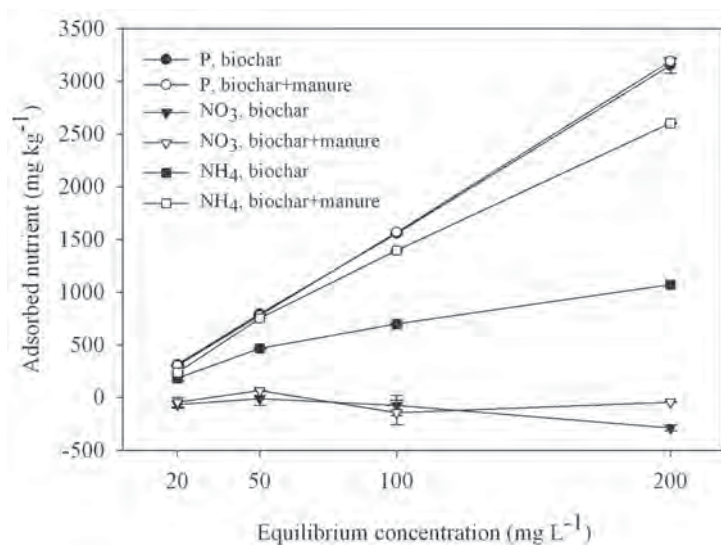
**Figure 15.3** Compilation of results obtained by Dünisch et al (2007) for wood feedstocks and biochar–ash mixtures obtained after pyrolysis: a given weight of substrates at 20°C or 300°C in mesh bags was submerged in a nutrient solution for 30 minutes

Note: Data are for particles <5mm, the smallest size class in the report.

Source: adapted from Dünisch et al (2007)

probably precipitated, along with Ca, on the alkaline biochar matrix. Importantly, 70 per cent of this removed P could subsequently be extracted from the biochar using  $\text{CaCl}_2$ , suggesting that it would, nevertheless, remain available to plants (Neri et al, 2005). While reducing nutrient leaching losses is valuable,





**Figure 15.4** Adsorption isotherms for biochar from the tree *Robinia pseudoacacia* L., with and without manure

Notes: Adsorption isotherms were obtained by equilibrating 3g soil in a 20mL centrifuge tube with 10mL solution containing 0, 20, 50, 100 or 200mg L<sup>-1</sup> of KH<sub>2</sub>PO<sub>4</sub>, KNO<sub>3</sub> or NH<sub>4</sub>Cl. A 10 per cent azide solution was added to each tube to suppress microbial activity. The tubes were agitated on a horizontal shaker at room temperature (about 20°C) for one day. Samples were centrifuged at 5000rpm (relative centrifugal force of 2988g) for ten minutes and the supernatant was analysed for phosphate using the molybdate ascorbic acid method, and for nitrate and ammonium by segmented flow analysis.

Source: Lehmann et al (2002)

retained nutrients should equally remain available for plant growth. This is not the case when P in bulk soil is irreversibly adsorbed by amorphous metal oxides in acid soils (Brady and Weil, 2008). In this experiment, the sorption of NH<sub>4</sub>-N to biochar was not found to be significant or to follow any trends.

Lehmann et al (2002) produced adsorption isotherms for P, NH<sub>4</sub> and NO<sub>3</sub> on fresh laboratory-produced biochar and biochar/manure mixtures (see Figure 15.4). This work clearly shows that phosphate was adsorbed readily by both the biochar and biochar/manure mixture, while nitrate was not adsorbed at all. Ammonium had an intermediate behaviour, with the biochar/manure mixture adsorbing more than pure biochar. Phosphorus was also shown to adsorb vigorously to biochar made from pine and surface litter at 561°C to 700°C (Beaton et al, 1960).

### Biochar interactions with soil biota

Soil-applied biochar particles harbour microorganisms (see Chapter 6), including

bacteria (Pietikäinen et al, 2000) and mycorrhizal fungi (Ezawa et al, 2002; Saito and Marumoto, 2002). Such organisms often have a great impact on plant nutrition – for example, through the mineralization of organic N into forms available to plants or susceptible to volatilization, and through improved P and Mg nutrition via extensive fungal hyphal systems. Current data (reviewed by Warnock et al, 2007) indicate that biochar application is often followed by an enhancement of mycorrhizal communities in the rhizosphere, coinciding with improved nutrient uptake by associated plants, thereby potentially reducing leaching. While reductions in gaseous N emissions have been observed in biochar-amended soil (Rondon et al, 2006), it is possible that N leaching and gaseous losses could also be favoured in certain cases where mineralization by bacteria occurs beyond the plants' N requirements, and if anaerobic conditions prevail around microorganisms because of changes in water retention. Nitrogen immobilization is not likely to be directly increased by biochar application since the bulk of biochar carbon

(C) is recalcitrant and not expected to immediately enter the C cycle – hence, the C sequestration properties of biochar (see Chapter 11). Still, if present, easily mineraliz-

able labile biochar domains could cause N immobilization in the short term (Gundale and DeLuca, 2007; see Chapters 5 and 14).

### Magnitude and temporal dynamics of biochar effects on nutrient leaching

Currently, experimental work that assesses the impact of biochar on nutrient leaching is scarce. Some work has been carried out using biochar alone under laboratory conditions and biochar/soil mixtures in the greenhouse, as well as in the field. However, results on nutrient leaching *per se* have not yet been reported for field experiments.

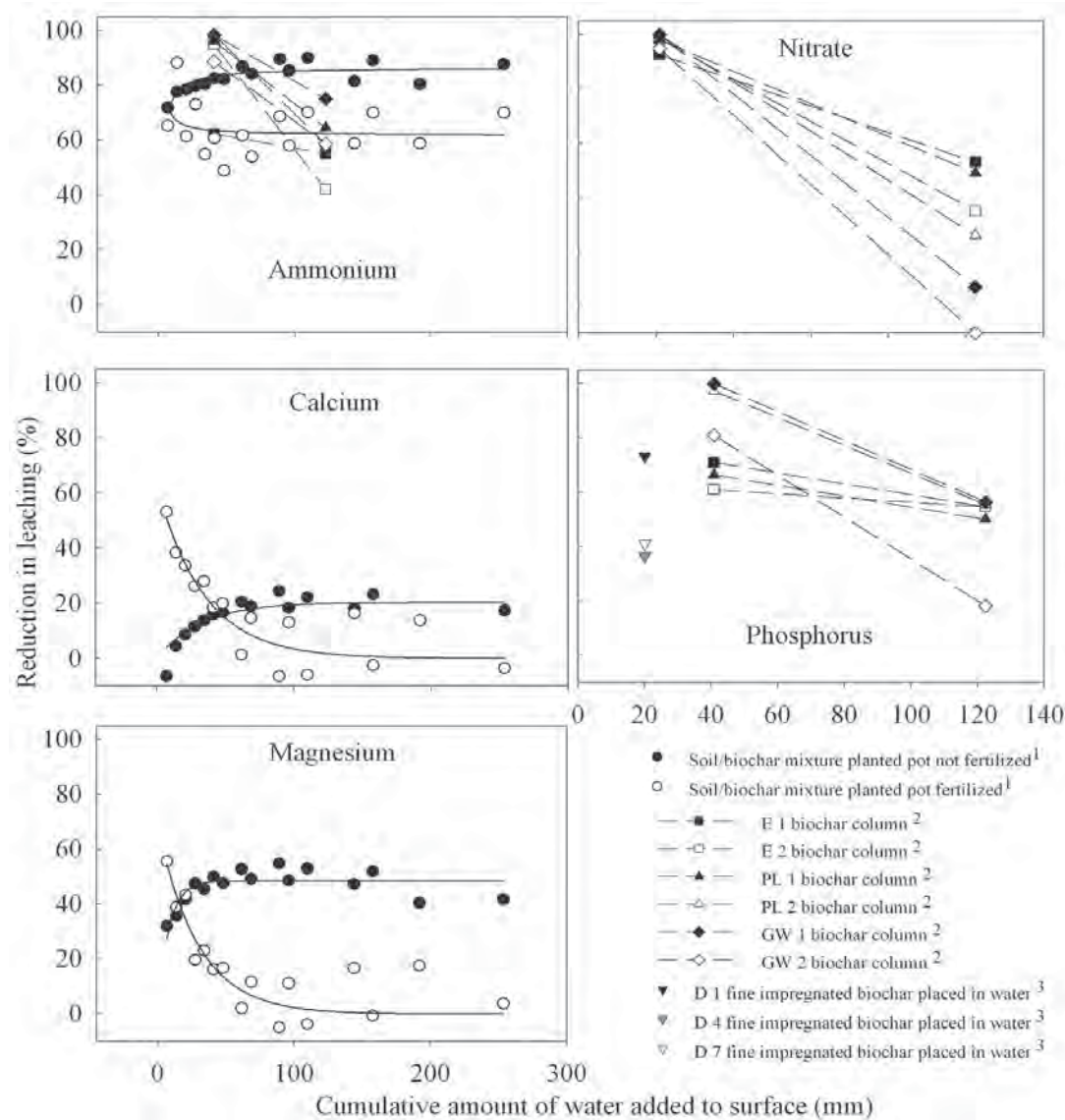
Direct nutrient leaching measurement in biochar/soil mixtures were undertaken only by Lehmann et al (2003), using pot lysimeters in the greenhouse (see Figure 15.5). Biochar made locally near Manaus in the central Brazilian Amazon was mixed with a typic Hapludox, rice was seeded and fertilizer applied. Leaching of applied ammonium was generally reduced by more than 60 per cent over 40 days of cropping rice, compared to treatments not receiving biochar (Lehmann et al, 2003). Fertilization reduced the efficiency of biochar for nutrient retention, perhaps due to high amounts of nutrients being present. Leaching of Ca and Mg was also reduced during the first week, although absolute amounts were low. Leaching of K was not reduced since fresh biochar typically contains large amounts of K. Aged biochar with much greater CEC (Cheng et al, 2008) may have much greater retention capacity. Lehmann et al (2003) showed that in Amazonian Dark Earths (ADE) that contain large proportions of aged biochar, leaching of Ca was approximately 20 per cent lower than in Oxisols with low biochar contents. At the same time, Ca availability on the exchange sites of ADE was more than double. It appears that aged ADE biochar resulted in greater nutrient availability, while simultane-

ously exhibiting significantly reduced leaching losses.

Dünisch et al (2007) found that biochar/ash mixtures impregnated with fertilizer in the laboratory ‘leached’ proportionally lower amounts of nutrients back into de-ionized water when compared to equal weights of wood feedstock (see Figures 15.5 and 15.6). Since amounts of nutrients retained by the biochar mixtures during impregnation were greater than for wood (see Figure 15.3), actual amounts leached were similar for both material types. While smaller particles (<5mm) retained greater amounts of nutrients, they also released proportionally more nutrients than large particles. The kinetics of sorption on outer surfaces versus internal pores might explain this, where smaller particles with greater outer surface areas released more nutrients than larger particles where more nutrients were retained inside pores.

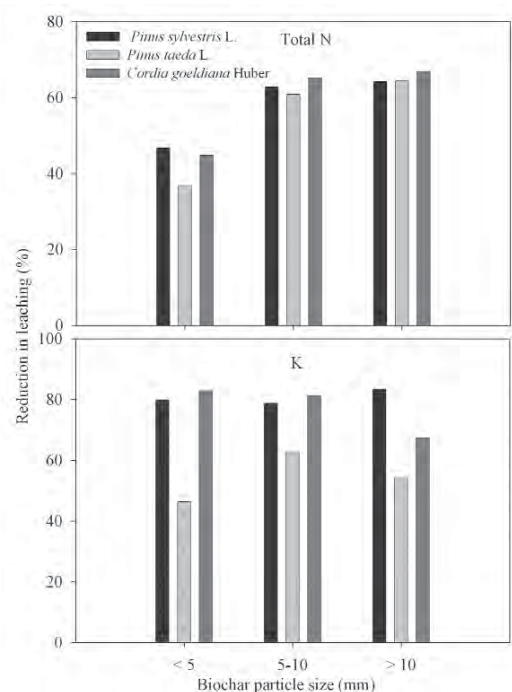
Comparable data were obtained in preliminary laboratory work carried out by Downie et al (2007) on nutrient leaching through columns of fresh biochar without soil (see Figure 15.5). However, biochars in this experiment did not retain any nutrients beyond 20 pore volumes (816mm water applied), which suggests that weak surface processes or water trapping in small pores were probably responsible for the nutrient retention. This mechanism alone would therefore not lead to long-term effects of biochar on nutrient leaching. In addition, bases such as Ca, K and Mg were more abundant in leachate from biochar than acid-washed sand. This is expected since biochar

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**Figure 15.5** Leaching reduction data compiled from the literature:

Notes: 1: Rice grown in lysimeters filled with Oxisol alone or a mixture of soil and wood biochar, with and without fertilization with NPK (Lehmann et al, 2003); 2: reduction is for NPK fertilizer granules placed on top of columns packed with biochar, compared to a control column packed with acid-washed sand; E 1: garden waste (GW) biochar made at 550°C, activated, enriched with N; E2: GW biochar; same as previous with additional minerals; PL 1: poultry litter (PL) biochar made at 550°C, activated; PL 2: PL biochar made at 450°C, non-activated; GW 1: GW biochar made at 550°C, activated; GW 2: GW biochar made at 450°C, non-activated (Downie et al, 2007); 3: reduction is for biochar-ash mixtures compared to original wood feedstock  
D 1: *Pinus sylvestris* L. charred in a flash-pyrolysis plant for bio-oil production, Germany; D 4: *Pinus taeda* L. combusted to heat kiln dryers, Brazil; D 7: *Cordia goeldiana* Huber (same as previous), for particles <5mm. Substrates in mesh bags were impregnated in an NPK solution, dried and placed in de-ionized water for 120 minutes to assess nutrient desorption (Dünisch et al, 2007). Points on P graph for Dünisch et al (2007) were placed at an approximate value on the X-axis since calculating actual volume was not possible.  
Source: Lehmann et al (2003); Downie et al (2007); Dünisch et al (2007)



**Figure 15.6** Reduction in leaching for nutrient-impregnated biochar particles of different sizes

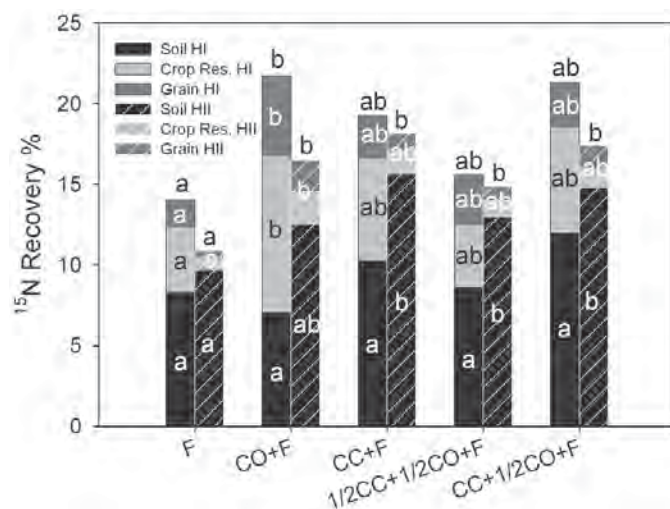
Note: See notes on methodology in Figure 15.5.

Source: Dünisch et al (2007)

contains large amounts of these elements compared to sand, which were probably displaced due to their solubility and to maintain the electro-neutrality of the leachate. For these freshly made biochars, oxidation is most likely not sufficiently advanced to create the negative surface charge observed in incubated or aged biochars (Cheng et al, 2006, 2008). Despite this, short-term retention of nutrients even by fresh biochars could still prove to be highly beneficial – for example, during annual crop establishment, when fertilizer application is facilitated in the field but seedlings are still exclusively using nutrients available in the seed.

In the field, the recovery of fertilizer N in soil (0 to 0.1m depth), harvested material and crop residue was enhanced by the application of both biochar and compost. However, the enhanced N retention in compost-amended plots was mainly a result of higher crop production (retention in plant biomass), whereas on the biochar plots more N remained in the soil especially after the second growing season (see Figure 15.7). These data only provide an assessment of total N losses since the 80 to 90 per cent of fertilizer-N that was not recovered could have left the system through both gaseous losses and leaching below 0.1m, which was not directly measured. Still, deep N leaching in this specific soil was found to be highly significant (Renck and Lehmann, 2004), suggesting that biochar has the potential to reduce leaching in the longer term through more complex mechanisms involving interactions with the soil matrix.

Based on the data presented here, biochar is effective in reducing the leaching of all nutrients tested, at least in the short term. Several studies show that leaching of P, ammonium- and nitrate-N, which are usually most limiting to crop growth, was reduced by over 50 per cent initially, and in one case after 250mm of water were applied to the surface (Lehmann et al, 2003). Ca and Mg were also retained after biochar addition without fertilizer (20 and 40 per cent leaching reduction after 250mm water applied, respectively). When NPK fertilizer was applied, biochar addition significantly reduced Ca and Mg leaching during the first week only. Potassium retention was also high with impregnated biochar reported by Dünisch et al (2007). However, Lehmann et al (2003) found that K in leachate increased after the addition of biochar to soil, and attributed this to the high K content of the biochar itself.



**Figure 15.7** Recovery of  $^{15}\text{N}$ -labelled fertilizer applied to an Oxisol in the Brazilian Amazon during two growing seasons (HI, HII)

Notes: Crop was Sorghum sp; F: synthetic fertilizer; CO: compost; CC: biochar. Organic amendments were applied and soil was sampled to 0.1 m depth. Rate of biochar application was  $1 \text{ t ha}^{-1}$ , and compost was applied at the same C-based rate. The last treatment received 1.5 times the C applied to others. Different letters represent significant differences ( $p < 0.05$ ;  $n = 5$ ) between treatments. In HII, letters for crop residue and grain recovery were the same and are only shown once.

Source: data from Steiner et al (2008)

## Conclusions and research needs

We reviewed data which suggest that biochar application to soil will affect nutrient leaching through several mechanisms – for example, by increasing the retention of water in the rooting zone, by directly binding or sorbing nutrients or by interacting with other soil constituents, and by facilitating the movement of attached nutrients when fine biochar particles are transported in percolating water. These mechanisms may either increase or decrease leaching. However, data available, to date, suggest that biochar does sorb organic and inorganic molecules and, in the case of inorganic nutrients, retains them against leaching losses. Table 15.1 summarizes biochar characteristics relevant to nutrient leaching and associated leaching reduction mechanisms, and indicates the extent to which each has been demonstrated. Figure 15.8 illustrates these mechanisms schematically. Long-term leaching reduction has not been shown directly, and some experiments presented here focused on pure biochar systems and inorganic nutrients, where microbes were excluded or not a study factor.

Research on biochar effects on leaching in agronomic settings must be carried out in

soil–biochar and soil–biochar–plant systems, in the laboratory as well as in the field and, ultimately, on a watershed scale using an ecosystem approach. Clearly, biochar interacts with other soil constituents, and biochar–soil mixtures will behave differently than pure biochar, especially over long periods of time. Increased plant productivity also needs to be part of leaching assessments because this alone can translate into reduced nutrient leaching through increased uptake. Both fresh and aged biochar should be tested, since the oxidation of these materials varies. The effect of various application methods for biochar as well as for nutrients should also be tested.

The mechanisms that explain nutrient retention by biochar require investigation since this information will probably allow the production of specific biochar for particular uses (e.g. for nutrient management in acid or degraded soil). As mentioned, interactions between biochar and soil are probably significant, complex and can drastically modify the chemical and physical characteristics of biochar surfaces and, thus, its interaction with nutrients. These interactions require



**Table 15.1** *Proposed biochar characteristics affecting nutrient leaching, related mechanisms and degree of certainty associated with each process*

<i>Mechanism</i>	<i>Impact upon leaching</i>	<i>Biochar characteristic<sup>1</sup></i>	<i>Leaching impact mechanism<sup>2</sup></i>	<i>Source(s)</i>
Biochar's negative surface charge directly retains positively charged nutrients	Decrease for positively charged ions and domains of nutrient-containing organic matter	Proven	Strong evidence	Liang et al (2006); Downie et al (2007)
Biochar increases the soil's water-holding capacity	Decrease (extent will vary with soil texture)	Strong evidence	Not proven	Tryon (1948)
Biochar leads to increased soil aggregation	Increase or decrease	Not proven	Not proven	NA
Biochar increases microbial biomass and nutrient cycling	Increase or decrease	Proven	Strong evidence	Reviewed by Warnock et al (2007); Steiner et al (2008)
Sorbed nutrients are preferentially transported by biochar particles	Increase	Not proven	Not proven	NA
Fresh biochar sorbs nutrients in hydrophobic organic matter	Decrease	Strong evidence	Not proven	Lebo et al (2003); Smernik (2005); Bornemann et al (2007)

Note: 1 Degree of certainty for this characteristic of biochar when applied to soil.

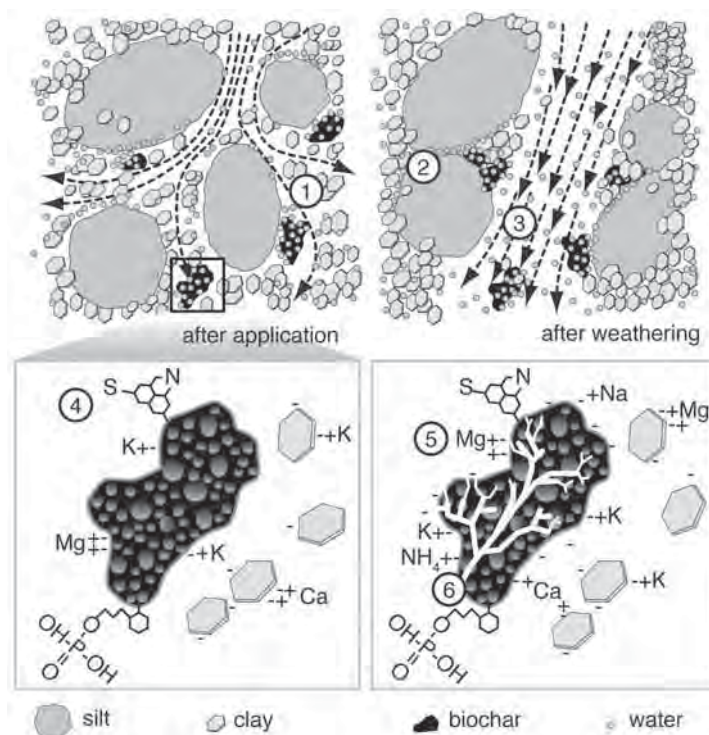
2 Degree of certainty in attributing this mechanism to changes in leaching by biochar.

NA = not available.

further study. The beneficial effect of biochar on leaching should also be related to other factors that impact upon leaching in the field, such as rainfall or crop management.

We consider that biochar could become a useful tool for the complex task of managing crop nutrition and its environmental impacts. Managing soils with biochar to reduce nutrient leaching would bring a dual benefit of

decreasing applied fertilizer requirements, as well as mitigating the environmental effects of nutrient loss. Reduced fertilizer applications not only decrease environmental concerns of non-point source pollution by agriculture, but also translate into reduced C emissions from the production and transport of synthetic fertilizers (see Chapter 18).



**Figure 15.8** Schematic representation of proposed biochar effects on nutrient leaching: (1) Upon biochar application to soil, water retention increases because porous biochar particles retain water and reduce its mobility; (2) after weathering, soil aggregation is improved as biochar binds to other soil constituents, and preferential flow of water occurs as well as the facilitated transport of biochar particles (3); (4) at a smaller scale, newly applied biochar sorbs hydrophobic organic forms of nutrients; (5) after weathering, the surface charge of biochar increases, thus improving cation exchange capacity, and soil biota is enhanced (6)

Note: This illustration is not strictly to scale, and water is not shown in the bottom panels.

Source: chapter authors

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