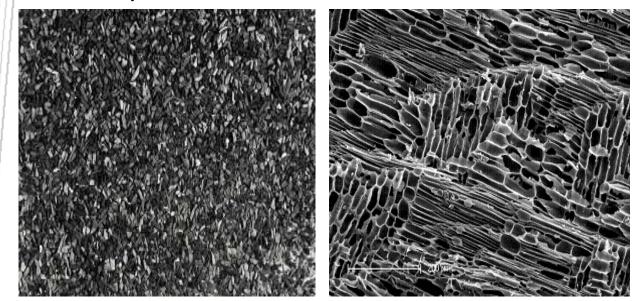


# Biochar, climate change and soil: A review to guide future research

Saran Sohi<sup>1</sup>, Elisa Lopez-Capel<sup>2</sup>, Evelyn Krull<sup>3</sup> and Roland Bol<sup>4</sup> Corresponding author and editor: Evelyn Krull CSIRO Land and Water Science Report 05/09 February 2009







#### Copyright and Disclaimer

© 2008 CSIRO To the extent permitted by law, all rights are reserved and no part of this publication covered by copyright may be reproduced or copied in any form or by any means except with the written permission of CSIRO.

#### Important Disclaimer:

CSIRO advises that the information contained in this publication comprises general statements based on scientific research. The reader is advised and needs to be aware that such information may be incomplete or unable to be used in any specific situation. No reliance or actions must therefore be made on that information without seeking prior expert professional, scientific and technical advice. To the extent permitted by law, CSIRO (including its employees and consultants) excludes all liability to any person for any consequences, including but not limited to all losses, damages, costs, expenses and any other compensation, arising directly or indirectly from using this publication (in part or in whole) and any information or material contained in it.

Citation: Sohi, S<sup>1</sup>.Loez-Capel, E<sup>2</sup>., Krull, E<sup>3</sup>., Bol, R<sup>4</sup>., 2009. Biochar's roles in soil and climate change: A review of research needs. CSIRO Land and Water Science Report 05/09, 64 pp..

<sup>1</sup>Centre for Bioenergy and Climate Change, Rothamsted Research, Harpenden, AL5 2JQ, UK; now at UK Biochar Research Centre, School of Geosciences, University of Edinburgh, UK, Email: saran.sohi@ed.ac.uk

<sup>2</sup>School of Civil Engineering and Geosciences, University of Newcastle, Newcastle uponTyne, NE1 7RU, UK, Email: <u>elisa.lopez-capel@ncl.ac.uk</u>

<sup>3</sup>CSIRO Land and Water, PMB2, Glen Osmond SA 5064, Australia, Email: <u>evelyn.krull@csiro.au</u>

<sup>4</sup>Biogeochemistry of Soils and Water group, North Wyke Research, UK, Okehampton, EX20 2SB, UK, Email: roland.bol@bbsrc.ac.uk

#### Cover Photographs:

Cover photo 1 Fragments of biochar 0.2-0.5mm diameter comprising willow stems carbonised at 600 C. Source: Saran Sohi

Cover photo 2 Scanning electron micrograph of biochar formed from rubber tree stems at 800 C in a 200kW gasification plant in rural Cambodia. Source: Simon Shackley and Erik Middelink

© 2008 CSIRO

# ACKNOWLEDGEMENTS

The preparation of this report was funded by the CSIRO Land and Water Opportunity Development Fund.

Rothamsted Research and North Wyke Research received grant-aided support from the Biotechnology and Biological Sciences Research Council (BBSRC) in the UK. Rothamsted Research is an Institute of the UK Biotechnology and Biological Sciences Research Council.

Newcastle University receives grant-aided support from the Engineering and Physical Sciences Research Council (EPSRC) in the UK.

Keith Goulding (Manager of the Cross-Institute Programme for Sustainable Soil Function Department of Soil Science, Rothamsted Research), Peter Hairsine (Leader, Science Development CSIRO Land and Water) and Mike Grundy (Theme Leader, Managing Australia's Soil & Landscape Assets. CSIRO Land and Water) provided helpful reviews and comments that improved the final version of the report.

# EXECUTIVE SUMMARY

*Biochar* is the charred by-product of biomass pyrolysis, the heating of plant-derived material in the absence of oxygen in order to capture combustible gases. The objective of this report was to review and evaluate published studies with regard to what evidence and arguments currently exist that assess the application of biochar to soil to a) sequester carbon and b) produce secondary agronomic benefits. Current analyses suggest that there is global *potential* for annual sequestration of atmospheric  $CO_2$  at the billion-tonne scale ( $10^9$  t yr<sup>-1</sup>) within 30 years. So far, however, the underlying published evidence arises mainly from small-scale studies that do not currently support generalisation to all locations and all types of biochar.

From the available published and peer-reviewed literature the following general findings can be made for eight key questions. It is noted that for each of these key questions there remains major research questions that require the attention of researchers. This summary provides these outstanding research issues along side the major findings.

#### 1. Is all biochar the same?

Key chemical and physical properties of biochar are greatly affected both by choice of feedstock (crop waste, energy crop, wood chip, municipal waste, manure, etc.) and process conditions (mainly temperature and time). These properties affect the interactions biochar has within the environment of its application as well as its fate. A rapid screening technique that provides the means for biochar products to be compared or matched to a particular use does not currently exist.

#### 2. How stable is it?

Studies of charcoal from natural fire and ancient anthropogenic activity indicate millennial-scale stability. However, it is difficult to establish the half-life of modern biochar products using short experiments due to the presence of small amounts of labile components, partial oxidation and biotic or abiotic surface reactions. At the moment there is no established method to artificially-age biochar and assess likely long-term trajectories.

#### 3. Is it safe to use?

Analysis of a limited number of biochar samples has indicated concentrations of toxic combustion products such as polycyclic aromatic hydrocarbons that are not at environmental risk level. However, a more systematic evaluation for a more complete range of other potentially harmful chemical contaminants associated with combustion, as well as toxic substances within feedstocks, has not been made. An environmental risk assessment that includes the impacts of these on terrestrial or aquatic ecosystems is outstanding. Given the stability of biochar, safe rates of applications need to be determined for individual soil types to avoid possible detrimental effects due to overapplication (e.g. reduction in soil productivity).

#### 4. What are the agronomic benefits?

Currently, a large number of studies have been conducted where biochar application has shown significant agronomic benefits with a minor number of studies showing no significant effects of biochar application on crop productivity and some studies reporting adverse effects. This suggests that the extent of the effect of biochar on crop productivity is variable, due to the different bio-physical interactions and processes that occur when biochar is applied to soil, which are not yet fully understood.. There is a need for models to allow extrapolation of location-specific findings by accounting for mechanistic effects of geographic variations in soil type, climate, cropping and pyrolysis feedstock.

#### 5. Is it economically viable?

The economic value of sequestered carbon will be determined within complex carbon markets that are influenced by energy supplies and demand, the supply and demand for

low emissions technologies, the availability of alternative carbon sequestration technologies and global policy responses to climate change. The growing price of waste disposal is likely to make the production and application of biochar for electricity and waste management economically viable. Carbon offsets will have a greater role once biochar is certified under the Clean Development Mechanism (CDM) of the Kyoto Protocol. Uncertainty over market interventions may risk the investment in energy facilities that are able to produce biochar.

#### 6. What are the environmental and societal benefits?

Models exist for viable agronomic use of biochar (without energy capture) in subsistence agriculture. However, relevant technological innovation is required to deal with environmental issues such as smoke production from traditional char production and associated health risks. Socio-economic constraints are not adequately researched. Higher crop yields resulting from biochar applications would be expected to mitigate pressures on land and would also have relevance to land restoration and remediation. Other environmental benefits of biochar application may lie in its application to rehabilitate contaminated wetlands and as a means to assist in managing (avoiding) algal blooms in aquatic ecosystems through adsorption of nutrients.

#### 7. Are the benefits of biochar in mitigating greenhouse gases widely accepted?

It is generally accepted that biochar is a highly stable form of carbon and as such has the potential to form an effective C sink, therefore sequestering atmospheric CO<sub>2</sub>. Several projects are currently underway assessing/monitoring greenhouse gas emissions in fields Colombia, amended with biochar in USA, Kenva and Australia (<http://www.css.cornell.edu/faculty/lehmann/research/biochar/biocharproject.html>). While biochar surpasses other biological forms of C with regard to its stability, estimates on the mean turnover time of biochar in soil vary from hundreds to thousands to tens of thousands of years. The mitigation potential of biochar with regard to other greenhouse gases, such as  $N_2O$  and  $CH_4$ , through its application to soil is less well established and requires further research.

#### 8. What are the research gaps and future challenges?

#### Biochar performance

Currently, the predictive capacity for biochar 'performance' does not exist and how to best optimise the multiple useful characteristics as a function of feedstock has not been assessed. This is currently inhibiting the realisation and application of this technology.

#### Interaction of biochar with soil microbial communities and plants

The physical, biological and chemical processes that biochar may exert on microbial communities and their symbiotic interaction with plants, and possibly enhanced nutrient use efficiency, are not yet understood. The apparent contradiction between the high stability of biochar, soil organic matter accumulation and apparent enhancement of soil microbial activity needs to be resolved. Research in Japan and in Germany has indicated that biochar can complex the carbon from dead micro-organisms. Further research work is required to determine under what conditions this complexation takes place.

#### Cation exchange capacity (CEC)

While the CEC of fresh char itself is not very high, biochar that has resided in soil for hundreds of years has been shown to have much higher CECs, comparable to those of zeolites. However, several studies have reported an increase in soil CEC after the application of fresh biochar. Thus, the processes that are instrumental in developing CEC over time as well as the effects that lead to an increase in CEC by addition of fresh (low CEC) biochar require detailed understanding.

#### Water holding capacity and aggregate stability

While some studies report positive effects of biochar application on water-holding capacity, the specific mechanism that biochar exerts on water retention, macro-aggregation and soil stability are poorly understood – yet should be of critical importance in climate change adaptation, where mitigating drought, nutrient loss and erosion are critical.

#### Erosion, transport and fate

The loss of biochar through vertical or lateral flow is not quantified, and only recently have studies been initiated to examine movement through soil profiles and into waterways. These processes complicate the task of confining the range of current estimates (from hundreds of years to millennia) of the mean residence time of biochar in soil. Long-term monitoring research stations (analogous to the Waite permanent rotation trial in Australia or the Rothamsted long-term experiments in the UK) are required to adequately assess the long-term stability and dynamics of biochar in soil.

#### Decreased emissions of non-CO<sub>2</sub> greenhouse gases (e.g. N<sub>2</sub>O and CH<sub>4</sub>)

The currently available data on the effect of biochar additions on trace gas emission is very limited, but has a potentially great impact on the net benefit of biochar application. Development of cost effective means of measuring decreased emissions will ensure this potentially large greenhouse saving can be compliant with emissions trading schemes.

#### Soil carbon modelling

Modelling of the linked carbon and nitrogen cycles in soil with and without application of biochar is essential to understanding the fundamental mechanisms referred to above and the impact on soil-based emissions of greenhouse gases.

#### Project specific Life Cycle Assessment (LCA)

The total environmental life-cycle assessment has been conducted for some biochar case studies. Greenhouse balances, for example, are very project specific and hence there is opportunity to assess the benefits over a large range of feedstock, process and biochar application scenarios.

# CONTENTS

1.	Intro	duction .		1			
2.	Bioc	ochar2					
	2.1.	. What is biochar?					
		2.1.1.	Why and how is biochar made?	3			
			Biochar feedstocks				
			Biochar production systems				
			Slow pyrolysis				
			Fast pyrolysis				
			Intermediate pyrolysis				
			Carbonisation				
		2.1.3.5.	Gasification	9			
		2.1.3.6.	Production of ammonia during pyrolysis	.10			
	2.2.	Biogeoch	emical characterisation of biochar	.10			
		•	The purpose of biogeochemical characterisation				
			Physical and chemical characterisation				
			Quantification of biochar and char				
			Background and biochar history: from terra preta to terra nova				
3.	Bioc	har appli	cation in Agriculture	16			
0.	3.1.		Ind climate change				
	5.1.	3.1.1.	Soil organic matter and climate change				
		-	Carbon stabilisation and sequestration using biochar				
			Combined bioenergy and biochar production				
		3.1.4.	Evaluation of biochar systems				
		3.1.4.	Stability of biochar in soil				
			Stability of biochar in natural systems				
		3.1.5.2.	Influence of biochar feedstock on stability				
			Climatic effects on biochar mineralisation				
			Soil biological activity and the stability of biochar				
			Effects of biochar on ease of tillage and mechanical disturbance				
			Indirect impacts of biochar on CO <sub>2</sub> -equivalent emissions				
			Indirect effects of yield benefits and nutrient requirement				
			Impact of biochar on nitrous oxide emission from soil				
			Impact of biochar on methane emission from soil				
			Biological activity and stabilisation of soil organic matter				
		3.1.6.5.	Effects of biochar on tillage and irrigation requirements				
		3.1.7.	Biochar scenarios for agriculture				
		3.1.8.	Notes on the natural cycling of char in soil	.31			
	3.2.	Biochar, o	crop productivity and resource management	.32			
		3.2.1.	Soil fertility	.32			
		3.2.2.	Crop yield				
		3.2.3.	Soil moisture retention				
		3.2.4.	Nutrient retention and use-efficiency				
		3.2.5.	Use of biochar to manage water quality	.37			
		3.2.6.	Potential risks to soil and water from use of biochar				
4.	Polic	cy contex	t and Analysis	38			
	4.1.	-	ork to evaluate applications of biochar				
	4.2.		s for the uptake of biochar for use in soil				
	4.3.		tervention and carbon trading				
			5				
	4.4.		cceptability issues				
	4.5.	Research	1	41			

5.	Rese	earch Priorities and Future Challenges	. 41
	5.1.	Fundamental mechanisms	42
	5.2.	Properties, qualities and environmental risk assessment	43
	5.3.	Carbon cycle modelling	44
	5.4.	Beneficiaries	44
	5.5.	Commentary on likely barriers to the adoption of a large scale enterprises utilisin Biochar	•
Refe	rence	es	.46

# **TABLE OF FIGURES**

- Figure 1. Biochar as a C sequestration tool
- Figure 2. Summary of pyrolysis processes
- Figure 3. Illustrative slow pyrolysis process
- Figure 4. Schematic process diagram for fast pyrolysis
- Figure 5. Simplified flow chart of how biomass releases energy as it captures  $CO_2$  as ammonium carbonate
- Figure 6. Scanning electron microscope image of biochar from pelletised peanut shell
- Figure 7. Components of black carbon assessed by available quantification methods
- Figure 8. Comparison of profiles of terra preta and adjacent soils
- Figure 9. The key physical (purple arrows), natural (orange arrows) and anthropogenic (red arrows) interactions of biochar in the environment
- Figure 10. Scenario for multi-feedstock production of biochar, and multi-application use, emphasising the spatial context

# **TABLE OF TABLES**

- Table 1. Fate of initial feedstock mass between products of pyrolysis processes
- Table 2. Reported elemental composition for a range of bio-oil and biochar products
- Table 3. Properties of biochar from bagasse carbonisation
- Table 4. Physico-chemical properties of terra preta and adjacent soils
- Table 5. Summary of experiments assessing the impact of biochar addition on crop yield

## 1. INTRODUCTION

Periodic fire across Australian landscapes results in a natural process of carbon (C) sequestration from atmosphere to soil by the conversion of biomass to charcoal. The extent of this process has recently been quantified for Australia (Lehmann, 2009). There are increasing calls to mirror and enhance this process by the concerted use of 'biochar', a form of charcoal produced with the simultaneous production and capture of bio-energy which is then applied to the soil. A measure of the need and interest for a concerted effort in this area has been the evolution of an organised consortium, known as the International Biochar Initiative (IBI) (<<u>www.biochar-international.org</u>>).

The inspiration for the supplementation of soil with charcoal stems from observations made in the ancient agricultural management practices that created *terra preta*, deep black soils. These soils, found throughout the Brazilian Amazon, are characterised by high levels of soil fertility compared with soils where no organic C addition occurred (Harder, 2006; Marris, 2006; Lehmann, 2007a; Renner, 2007). The evident value of the *terra preta* led to the suggestion that investment into biochar and application to agricultural soil may be both economically viable and beneficial. Rising fossil fuel prices, the need to raise yields in light of the global food crisis, and the emergence of a significant global market for trading carbon appear to promise added economic incentives in the future.

At the same time the need to protect soils under an increasingly uncertain climate makes the apparent ability of biochar to increase the capacity for soil to absorb and store water vitally important. It also appears that adding biochar to soil may be one of the only ways by which the fundamental capacity of soils to store and sequester organic matter could be increased.

There are a number of detailed reviews describing charcoal formation (Knicker, 2007) and associated C dynamics (Preston et al., 2006; Czimczik et al., 2007), including its role in the global carbon cycle (Schmidt et al., 2000). Forthcoming is a compendium of review articles ("Biochar for Environmental Management: Science and Technology"), which will place existing studies in the context of pyrolysis bioenergy (Lehmann and Joseph, 2009b).

A number of studies have now highlighted the net benefit of using biochar in terms of mitigating global warming and as an active strategy to manage soil health and productivity (Figure 1) (Lehmann, 2007a; Lehmann, 2007b; Lehman et al., 2005; Ogawa et al., 2006; Laird, 2008; Mathews, 2008; Woolf, 2008). However, relatively few studies exist that make a quantitative assessment of biochar-based soil management scenarios with regard to greenhouse gas, energy, and economic perspectives (Fowles, 2007; Gaunt et al., 2008). Nonetheless, the concept and value of biochar production and application is gradually incorporated by policy makers and governments (Winsley, 2007).

Current studies are in many cases conceptually or geographically limited, and are often constrained by limited experimental data. In particular, mechanistic descriptions of the characteristics of biochar and its function in the soil and experimentation relevant to widescale applications of biochar are currently limited. In this report we examine existing published research within a framework constrained by a policy context. Thereby, we aim to identify gaps where new research should be focused in a way that will enable biochar to engage with climate change mitigation and to maintain soil productivity.

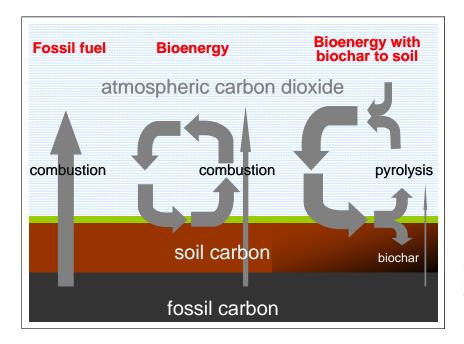


Figure 1. Biochar can result in a net removal of carbon from the atmosphere, especially with enhanced net primary productivity

## 2. BIOCHAR

## 2.1. What is biochar?

Biochar is a fine-grained and porous substance, similar in its appearance to charcoal produced by natural burning. Biochar is produced by the combustion of biomass under oxygen-limited conditions. The definition adopted by the International Biochar Initiative (IBI) furthermore specifies the need for purposeful application of the material to soil for agricultural and environmental gain.

The term biochar was originally associated with a specific type of production, known as 'slow pyrolysis'. In this type of pyrolysis, oxygen is absent, heating rates are relatively slow, and peak temperatures relatively low (Section 2.1.3.1). However, the term biochar has since been extended to products of short duration pyrolysis at higher temperatures known as 'fast pyrolysis' (Section 2.1.3.2) and novel techniques such as microwave conversion.

It is important to note that there is a wide variety of char products produced industrially. For applications such as activated carbon, char may be produced at high temperature, under long heating times and with controlled supply of oxygen. In contrast, basic techniques for manufacture of charcoal (such as clay kilns) tend to function at a lower temperature, and reaction does not proceed under tightly controlled conditions. Traditional charcoal production should be more accurately described as 'carbonisation' (Section 2.1.3.4), which involves smothering of biomass with soil prior to ignition or combustion of biomass whilst wet. Drying and roasting biomass at even lower temperatures is known as 'torrefaction' (Arias et al., 2008).

A charred material is also formed during 'gasification' of biomass, which involves thermal conversion at very high temperature (800°C) and in the partial presence of oxygen (Section 2.1.3.5). This process is designed to maximise the production of synthesis gas ('syngas'). Materials produced by torrefaction and gasification differ from biochar in physico-chemical properties, such as particle pore size and heating value (Prins et al., 2006) and have industrial applications, such as production of chemicals (methanol, ammonia, urea) rather than agricultural applications.

In order to differentiate biochar from charcoal formed in natural fire, activated carbon, and other black carbon materials, the following list of terms aims to better define the different products. The differences, however, are relatively subtle since all products are obtained from the heating of carbon-rich material.

- Char: the solid product arising from thermal decomposition of any natural or synthetic organic material. Examples are char from forest fire and soot resulting from the incomplete combustion of fossil hydrocarbon.
- Charcoal: produced from the thermal decomposition of wood and related organic materials, mainly for use as an urban fuel for heating and cooking, but also traditional uses as soil amendment or control of odour (Okimori et al., 2003). Temperatures in traditional kilns approach 450-500°C, which is similar to that of industrial pyrolysis but with lower yields: conversion of feedstock dry mass may be as low as 10 % compared to 35% using more formal production technology. Also, all heat as well as gaseous and liquid co-products are lost during the combustion process.
- Activated carbon: manufactured by heating carbonaceous material at a high temperature (above 500°C) and over long (>10 hours) periods of time. The resulting material is characterised by a very high adsorptive capacity. It is not used as a soil amendment but has been applied for cleansing processes, such as water filtration and adsorption of gas, liquid or solid contaminants (Tomaszewski et al., 2007).
- Black carbon: a general term that encompasses diverse and ubiquitous forms of refractory organic matter that originate from incomplete combustion (Baldock et al., 2002). The diversity of burning conditions results in black carbon occupying a continuum of material. The review by Schmidt (1999) provides a thorough account of the 'black carbon' continuum, its constituents and definitions.

Biochar from pyrolysis and conventional charcoal and char share key characteristics which are related to carbon sequestration (long residence time) and soil fertility (soil conditioning effect). This is important since there is currently a much greater amount of research for char (Glaser et al., 2002) than for biochar. Biochar produced in association with bioenergy generation may be more applicable in some countries than others, depending on economic circumstance, political priorities, technology and infrastructure.

The central quality of biochar and char that makes it attractive as a soil amendment is its highly porous structure, potentially responsible for improved water retention and increased soil surface area. Addition of biochar to soil has also been associated with increased nutrient use efficiency, either through nutrients contained in biochar or through physico-chemical processes that allow better utilisation of soil-inherent or fertiliser-derived nutrients. Importantly, it is the apparent biological and chemical stability that allows biochar to both act as a carbon sink, as well as provide benefits to soil that are long-lived.

Using pyrolysis to turn sustainably produced biomass into a recalcitrant substance that is decomposed at a much slower rate, constitutes both a tool for carbon sequestration and avoided emission. It is argued that sequestration of carbon in biochar allows for a much longer storage time compared with other terrestrial sequestration strategies, such as afforestation (Schulze et al., 2000). The stability and carbon sequestration potential of biochar in soil is examined in Section 3.1.2.

## 2.1.1. Why and how is biochar made?

Modern industrial bioenergy systems involve pyrolysis and gasification, the heating of a biomass feedstock under controlled conditions to produce combustible synthesis gas ('syngas'), and oil ('bio-oil') that can be burnt to produce heat, power, or combined heat and power. Biochar, the third combustible product produced in pyrolysis, is the solid charred and carbon-rich residue.

The balance in energy release and biochar formation can be optimised. Effectively, it is a 'combustion' process that may be curtailed at a point where any desired ratio in these products has been achieved. This ratio can then be adjusted and re-optimised to satisfy changing objectives. Whereas simple combustion of a feedstock maximises energy yield per unit mass, combusting syngas from pyrolysis gives – where optimised for biochar – a much greater energy yield per unit of carbon release.

If incorporating biochar into soil can reliably deliver the environmental benefits outlined in 3.1.2, the carbon-equivalent saving resulting from conversion of biomass using pyrolysis can be increased further, relative to the production of energy only (i.e. combustion).

Globally, there is an estimated  $15 \times 10^9$  ha of cropland (Ramankutty et al., 2008). On the basis of calculations by Gaunt (2008), the application of biochar once every ten years to this land area would result in a CO<sub>2</sub> -equivalent gain of 0.65 GtC yr<sup>-1</sup>.

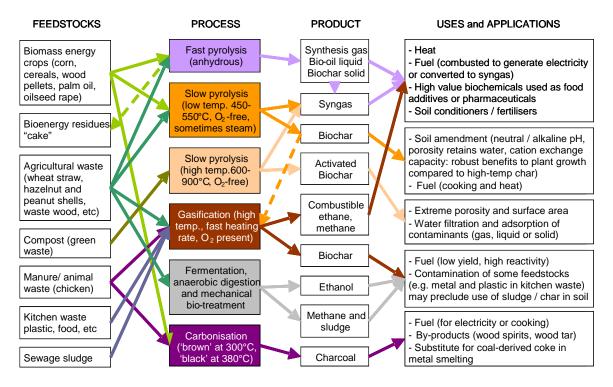


Figure 2. Summary of pyrolysis processes in relation to their common feedstocks, typical products, and the applications and uses of these products

Pyrolysis has a requirement for initial energy, in the same way as in straight combustion some heat in the flame is used to initiate combustion of new feedstock. But the relative requirements must be carefully compared, together with any difference between pyrolysis and alternative bioenergy technologies in the energy requirement of feedstock transportation and drying.

The potential advantage of pyrolysis-derived bioenergy over other bioenergy strategies in terms of greenhouse gas emissions results not only solely from the retention of up to 50% of the feedstock carbon in stable biochar, but from indirect savings that may result from the use of biochar in agriculture, specifically the soil (Gaunt et al., 2008).

Biomass pyrolysis and gasification are well established technologies for the production of biofuels and syngas. However, commercial exploitation of biochar by-products as a soil amendments is still in its infancy. In Japan, which has the largest market for such products, approximately 15 000 t yr<sup>-1</sup> is traded annually for soil use (Okimori et al., 2003). More usually biochar products are gasified for extraction of residual energy, or used in production of high value products such as activated carbon (Demirbas et al., 2006b).

The pyrolysis process greatly affects the qualities of biochar and its potential value to agriculture in terms of agronomic performance or in carbon sequestration. The process and process parameters, principally temperature and furnace residence time, are particularly important; however, the process and process conditions also interact with feedstock type in determining the nature of the product.

These variables together are key influences on the chemical, biological and physical properties, which limit the potential use for biochar products. A summary of feedstock, production processes and products is illustrated in Figure 2. The assignment of feedstock to process in Figure 2 is based on examples from the literature and does not indicate that they should be an exclusive classification.

Each category of pyrolysis process is characterised by a contrasting balance between biochar, bio-oil and syngas (Table 1). The precise ratio in these products may vary between plants, and may be optimised at a particular installation; however, it is critical that maximising the production of biochar relative to mass of initial feedstock (Demirbas, 2006), is always at the expense of usable energy in the liquid or gaseous form. Although a greenhouse gas mitigation strategy may favour maximising the biochar product (Gaunt et al., 2008), the balance that is realised is a function of market and engineering constraints.

In a generalised analysis, the economic cost of maximising the retention of carbon in biochar using slow pyrolysis has been assessed against the possible net gain in  $CO_2$ -equivalent emissions from using the product in soil, after accounting for the additional fossil-carbon offset that could be obtained through complete combustion of the feedstock (Gaunt et al., 2008). The net carbon gain over fossil fuel scenarios was 2–19 t  $CO_2$  ha<sup>-1</sup> y<sup>-1</sup>, encompassing figures 2–5 times higher than those for strategies based on biomass combustion. The eligible portion of this added saving would have to attract  $CO_2$ -offset at a value sufficient to cover the USD 47 t<sup>-1</sup> value of residual energy in biochar. A more detailed description of this analysis and discussion of the competing processes associated with energy and char production is discussed in detail in Chapter 3.

Process	Liquid (bio-oil)	Solid (biochar)	Gas (syngas)	
FAST PYROLYSIS Moderate temperature (~500 °C) Short hot vapour residence time (<2s)	75% (25% water)	12%	13%	
INTERMEDIATE PYROLYSIS Low-moderate temperature, Moderate hot vapour residence time	50% (50% water)	25%	25%	
SLOW PYROLYSIS Low-moderate temperature, Long residence time	30% (70% water)	35%	35%	
GASIFICATION high temperature (>800 °C) Long vapour residence time	5% tar 5% water	10%	85%	

Table 1. Fate of initial feedstock mass between products of pyrolysis processes (IEA, 2007)

## 2.1.2. Biochar feedstocks

Although current results suggest that the type of feedstock used for pyrolysis is more important where biochar is to be applied as a soil conditioner (Section 3.2.) there is little consensus as to what constitutes optimal feedstock for energy production.

This is mainly due to the fact that the number of existing commercial plants is small, and that these plants are dedicated to specific waste streams, giving little incentive to experiment with this parameter. However, some research-scale pyrolysis plants have conducted experiments with a wider range of feedstocks (Day et al., 2005; Das et al., 2008; Gaunt et al., 2008).

Feedstocks currently used at a commercial-scale or in research facilities include wood chip and wood pellets, tree bark, crop residues (including straw, nut shells and rice hulls), switch grass, organic wastes including distillers grain, bagasse from the sugarcane industry and olive waste (Yaman, 2004), chicken litter (Das et al., 2008), dairy manure, sewage sludge (Shinogi et al., 2002) and paper sludge.

The elemental ratios of carbon, oxygen and hydrogen are key feedstock parameters in commercial use and the quality of fuel products (Friedl et al., 2005). The feedstocks which are favoured for bio-oil and fuel-gas are those that have low mineral and N content. These include wood and biomass from energy crops, including short-rotation woody plants (such as willow), high productivity grasses (such as *Miscanthus* spp.), and a range of other herbaceous plants. They may also include abundant, available and low-cost agricultural by-products, including cereal straw.

The proportions of hemi-cellulose, cellulose and lignin content determine the ratios of volatile carbon (in bio-oil and gas) and stabilised carbon (biochar) in pyrolysis products. Feedstocks with high lignin content produce the highest biochar yields when pyrolysed at moderate temperatures (approx. 500 °C) (Fushimi et al., 2003; Demirbas, 2006). In the future, selection of feedstock may be dictated by the desired balance between pyrolysis products (gas, oil and biochar), and whether the production process is slow pyrolysis, or a related process.

Charring of agricultural waste products such as nut shells and rice hulls for energy production may be advantageous compared to disposal as waste by some other means (Demirbas, 2006; Demirbas et al., 2006a). Alternative use for such materials includes composting and mulching. However, it is important to recognise that continuous removal of crop residues from the same land compromises soil cover and diminishes soil nutrient supply. This is further discussed in Chapter 3.

#### 2.1.3. Biochar production systems

Biochar is a multi-process product whose qualities are dependent on each process and also the material to which the process is applied. Since the technology is still in a period of development and not yet optimised to producing a product for use in soil, it is useful to review the various technologies currently in use. The processes of slow- and fast-pyrolysis are exemplified in Figure 3 and 4 and discussed in the subsequent sections.

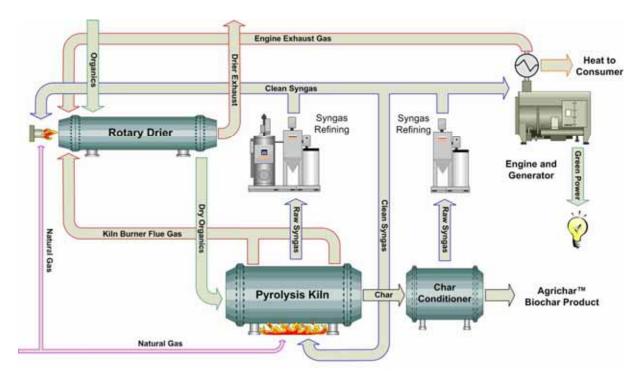


Figure 3. Illustrative slow pyrolysis process (Source: BEST Energies)

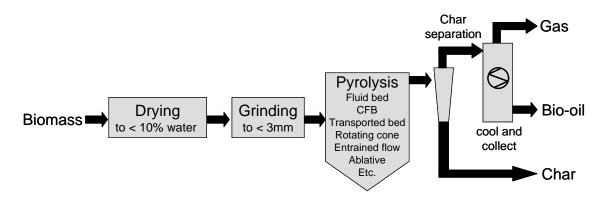


Figure 4. Schematic process diagram for fast pyrolysis (modified from Bridgewater (2006))

## 2.1.3.1. Slow pyrolysis

Slow pyrolysis is the thermal conversion of biomass by slow heating at low to medium temperatures (450 to 650°C) in the absence of oxygen, with the simultaneous capture of syngas. Feedstocks in the form of dried biomass pellets or chips of various particle sizes are fed into a heated furnace and exposed to uniform heating, generally through the use of internal or external heating as retort furnace or kilns, respectively. Conventional production conditions have been summarised by Peacocke and Joseph in <<u>http://www.biochar-international.org/images/Terminology.doc</u>> :

- residence times: >5 seconds for the production of syngas; minutes, hours or days for biochar production
- relatively low reactor temperatures (450-650°C)
- reactor operating at atmospheric pressure
- very low heating rates, ranging from 0.01–2.0°C s<sup>-1</sup>
- very short thermal quenching rate for pyrolysis products: minutes to hours.

Several commercial facilities generate syngas and biochar using a continuous flow system in which feedstock passes slowly through a kiln in an auger feed, with combustible syngas continuously drawn away.

Biochar, bio-oil and syngas are formed in approximately equal proportions due to the slow speed of the combustion process, which promotes extensive secondary reactions within biochar particles and in the gas and vapour phases, leading to condensation.

The pyrolysis reaction itself is mildly endothermic, with the bulk of energy capture being in the form of the syngas and bio-oil condensates. The biochar has a residual energy content of about 30–35MJ kg<sup>-1</sup> (Ryu, 2007), and conventionally this is extracted within the plant by burning or gasification, providing heat to drive the primary pyrolysis (Demirbas, 2006), or to dry incoming feedstocks. The syngas product may be combusted on site to generate heat or electricity (via gas or steam turbine), or both.

A variant of slow pyrolysis includes a steam gasification step, a technology developed by Eprida in collaboration with the University of Georgia (<<u>http://www.eprida.com/hydro/></u>). Adding steam to the pyrolysis reaction liberates additional syngas from the biochar product, mainly in the form of hydrogen. The biochar that remains after this 'secondary' pyrolysis displays rather different properties from the primary product, differing in pore size and carbon to oxygen ratio (Demirbas, 2004).

Syngas can be purified through a sequence of operations to yield pure streams of the constituent gases: hydrogen (50% of gas yield), carbon dioxide (30%), nitrogen (15%), methane (5%), and lower molecular weight hydrocarbons, as well as some carbon monoxide (Day et al., 2005). There is a small energy penalty associated with these steps.

Slow pyrolysis research plants currently process feedstock at a rate of 28–300 kg hr<sup>-1</sup> on a dry mass basis, and commercial plants operate at 48–96 t d<sup>-1</sup>. Comparing the efficiency of pyrolysis plants is complex since the mix and use of products vary, and the composition and heat value of syngas differs. Feedstock quality and moisture content is also variable, and there is a conversion loss in the generation of electrical power through steam or gas turbines.

## 2.1.3.2. Fast pyrolysis

Very rapid feedstock heating leads to a much greater proportion of bio-oil and less biochar (Table 1). It was with the objective of achieving this high yield of liquid fuel that fast pyrolysis technology was developed.

The time taken to reach peak temperature of the endothermic process (the 'resistance time') is approximately one or two seconds, rather than minutes or hours as is the case with slow pyrolysis. The lower operating temperature also enhances the overall conversion efficiency of the process relative to slow pyrolysis.

Maintaining a low feedstock moisture content of around 10% and using a fine particle size of <2mm permits rapid transference of energy despite relatively moderate peak temperatures of around 450°C (and in the range 350 to 500°C). In many systems the transfer is further increased by mechanically enhancing feedstock contact with the heat source or maximising heat source surface area. Various technologies have been used and proposed or tested including: fixed beds, augers, ablative methods, rotating cones, fluidized beds and circulating fluidized beds. Surface charring must be continuously removed during reaction to prevent pyrolysis of particle interiors being inhibited by its insulating effect.

Bio-oil is condensed from the syngas stream under rapid cooling, with the combustion of syngas providing the pyrolysis process heat. The bio-oil is a low grade product with a calorific value, on a volume basis, approximately 55% that of regular diesel fuel. It is unsuitable as a mainstream liquid transport fuel even after refining, and is most suitable as a fuel-oil substitute. It is considered to have an advantage over typical fuel oils in zero  $SO_x$  and low  $NO_x$  emission on combustion (Bridgewater, 2004). In addition to combustion for electricity generation, bio-oil may be converted to syngas for production of clean fuels (gasification).

Bio-oil also contains high value bio-chemicals of relevance to food and pharmaceutical industries.

The biochar product of fast pyrolysis is granular and displays a lower calorific value  $(23-32 \text{ MJ kg}^{-1})$  than that of slow pyrolysis (Demirbas, 2001). However, there are currently no published studies to assess the effects of biochar from fast pyrolysis when it is applied to soil. It is highly likely that condensed volatiles will be present in the product and that this will affect its performance and desirability.

## 2.1.3.3. Intermediate pyrolysis

This term describes a hybrid technology under evaluation at Aston University, UK, designed to produce bio-oil with very low tar content, with perceived potential for use as a motor fuel. The process has been tested with woody and non-woody feedstocks, and produces biochar in greater quantity and of contrasting quality as compared to fast pyrolysis.

## 2.1.3.4. Carbonisation

Carbonisation describes a number of pyrolysis processes that most closely resemble traditional, basic methods of charcoal manufacture, and which produce biochar of the highest carbon content. The auto-thermal carbonisation process is the small-scale method widely used in rural communities around the world (FAO, 1987). The second requires fossil fuel to provide an external heat source, and is associated with industrial, mass production of charcoal (FAO, 1985). The process is optimised for the solid products of pyrolysis, but condensed gases provide an industrial product known as 'wood vinegar', which as well as providing the basis for food flavouring ingredients, is considered to have a fertiliser value to plants.

The auto-thermal process as the most realistic option has been proposed for the participation of local communities in using biochar to build soil fertility, especially in developing countries. It is lower cost, and easier and simpler than pyrolysis systems where ratios of solid, liquid and syngas products have to be optimised. A comparison of three alternative options has recently been investigated for the carbonisation of biomass wastes from tree plantations: a drum kiln, a Hume pipe kiln, and a brick kiln (Okimori et al., 2003; Ogawa et al., 2006). For wood, 24% of wood mass was converted to biochar of 76% carbon content at 400 to 500°C, but carbonisation at 600°C gave 28% biochar with a higher carbon content of 89%. The 50% of feedstock carbon stabilised in each case was similar to the maximum yield obtained in slow pyrolysis.

Brazil has the largest concentration of industrial charcoal manufacture. This is associated with the pig-iron (smelting) industry, where substitution of charcoal for fossil-derived coke has been achieved in a number of very large projects under the Clean Development Mechanism, and associated with large-scale plantations of eucalypt.

#### 2.1.3.5. Gasification

Gasification is the process by which any carbonaceous material (coal and petroleum as well as biomass) is substantially converted into a stream of carbon monoxide and hydrogen in a high temperature reaction and controlled-oxygen environment, sometimes at high pressures of 15–50 bars (Bridgewater, 2006). The gas mixture is the key energy output and the gasification process has an application as a clean waste disposal technique (Bapat et al., 1998). In slow pyrolysis facilities, gasification is often used to generate further syngas from biochar 'waste'.

Syngas may be used for electricity generation via gas or steam turbines (or both), used to manufacture chemicals and fertilisers, or further cleaned for use as liquid fuel. Since conversion of feedstock to syngas is often the main objective, the process is maximised for gas production and so the biochar yield from gasification tends to be very low (Table 1). However, this also carries the risk of higher levels of metals and minerals that may be

concentrated in biochar, with potential safety implications with regard to application to soil (Fernandes et al., 2003a). Although biochar from gasification has a high calorific value (Demirbas, 2006; Demirbas et al., 2006a), it has high value use as the basis for activated carbon production. Its potential to act as the carrier in a slow nutrient release fertiliser product has also been noted (Ueno, 2007).

Worldwide, gasification has been used on a commercial scale worldwide for more than 50 years, mainly in the refining, fertiliser, and chemical industries, and for more than 35 years in the electric power industry. There are more than 140 gasification plants currently in operation, with worldwide gasification capacity projected to grow 70% by 2015, with 80% of this growth occurring in Asia (Anon, 2008). The majority of gasification plants produce chemicals, mainly methanol or ammonia and urea, and use coal or refuse-derived feedstocks (Kedco, 2008). However, biomass feedstocks are also used, for example wood pellets, wood chips or paper and sugar cane bagasse (Ueno et al., 2007), and rural gasification projects are expanding.

#### 2.1.3.6. Production of ammonia during pyrolysis

In the Haber-Bosch process, a fossil hydrogen source (usually methane) is used to fix atmospheric nitrogen and create ammonia for manufacture of fertiliser. Hydrogen in syngas streams from pyrolysis (7-8% of slow pyrolysis syngas) can substitute methane and be used, potentially not only to create ammonia but, if conducted on the same site as the pyrolysis, fix ammonia to a biochar co-product. This offers the prospect of a crop fertiliser that simultaneously adds stabilised carbon to soil, possibly with slow release characteristics. This could offer greater net benefit in terms of  $CO_2$  -equivalents than using syngas to, for example, generate electricity. The process of fixing ammonia from the hydrogen syngas stream at atmospheric pressure and ambient temperature has been demonstrated (Day et al., 2005) and is illustrated diagrammatically in Figure 5. However, agronomic evaluation of the product has not been published and the concept has not yet been commercialised.

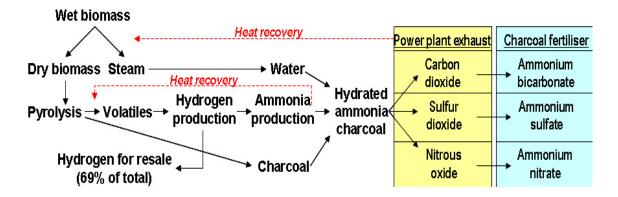


Figure 5. Simplified flow chart of how biomass releases energy as it captures  $CO_2$  as ammonium carbonate (modified from Day et al., 2005)

## 2.2. Biogeochemical characterisation of biochar

## 2.2.1. The purpose of biogeochemical characterisation

Although commercial biochar products are being developed for use in soil, credit for carbon storage will require predictable levels of stability and the ability to verify actual rates of degradation through quantitative soil analysis (Ogawa et al., 2006; Matthews, 2008). Identifying the characteristics that determine the stability of biochar will enable its properties to be optimised and standardised in production. Techniques to unambiguously detect and

measure its abundance in soil are necessary to verify its application and to trace the fate of particular biochar products.

Biogeochemical characterisation techniques may also help understand the function of biochar products in soil at the process level. With specific knowledge of the nature of biochar-driven processes in the soil, predictive capacity for the longevity and reactions of biochar in soil that will determine its value as a soil carbon sink and soil conditioner are possible.

From a practical point of view it is important that the methods devised enable biochar characteristics to be determined sufficiently rapidly and inexpensively to permit widespread application and use.

#### 2.2.2. Physical and chemical characterisation

Kuwagaki (1990) proposed that seven properties should be measured for a quality assessment for agronomically-used biochar: pH, volatile compound content, ash content, water holding capacity, bulk density, pore volume, and specific surface area.

Feedstock is a primary factor governing the chemical and physical properties of biochar. The elemental composition reported for a range of bio-oil and biochar products from various feedstocks are compared in Table 2.

	Elem	HHV*			
Product	С	н	N	0	(MJ/kg)
Beech-trunk bark biochar	87.9	2.9	0.6	10.6	33.2
Beech-trunk bark bio-oil	68.8	8.9	0.8	21.5	34.6
Rapeseed cake biochar	66.6	2.5	6.1	24.3	30.7
Rapeseed cake bio-oil	73.9	10.8	4.7	10.6	36.5
Wood bark biochar	85.0	2.8	_	12.2	30.8
Wood bark bio-oil	64.0	7.6	_	28.4	31.0
Cotton stalk biochar	72.2	1.2	_	26.6	21.4
Cotton stalk bio-oil	59.7	7.8	1.8	30.6	26.0
Bio-char from hazelnut shell	95.6	1.3	-	3.1	32.0
Sunflower bio-oil	72.1	9.8	5.2	12.9	36.2

Table 2. Reported elemental composition for a range of bio-oil and biochar products (% dry ash-free mass)

\*HHV= higher heating value (enthalpy of complete combustion of a fuel including the condensation enthalpy of former water); Demirbas et al.,(2004)

In general, the carbon content of biochar is inversely related to biochar yield. Increasing pyrolysis temperature from 300 to 800°C decreased the yield of biochar from 67 to 26% and increased the carbon content from 56 to 93% (Tanaka, 1963). Beyond a certain threshold, the mass of biochar may decrease without any affect on the amount of carbon retained within it; but as mass is lost, the ash content of biochar increases. In one study, the proportion of biochar comprised of ash increased from 0.67 to 1.26% between 300°C and 800°C (Kuwagaki and Tamura, 1990).

For a particular feedstock, the elemental composition of the pyrolysis products can still be greatly affected by the processing temperature and pyrolysis residence time. The effect of temperature on the composition of biochar from sugarcane bagasse is listed in Table 3.

There was a corresponding impact on the pH of the biochar from 7.6 at 310°C to 9.7 at 850°C (Kuwagaki and Tamura, 1990).

Parameter or property		Feedstock			
Preset temperature (°C)	500	600	700	800	
Average temperature (°C)	490	690	740	830	
Specific surface area (m²/g)	Nd	270	322	273	Nd
EC (mS m <sup>-1</sup> )	7.78	7.15	6.95	7.83	Nd
рН	7.46	7.59	7.68	7.89	Nd
TN (%)	0.58	0.45	0.32	0.44	0.19
TC (%)	70.5	71.0	65.2	73.9	46.1
Minerals (mg 100g <sup>-1</sup> )	3361	4601	5359	4363	841

Table 3. Properties of biochar from bagasse carbonisation (Ueno et al., 2007)

nd=not determined

There are inevitable accompanying differences in the physical and other chemical properties of biochar. Scanning electron microscopy (SEM) is often used to describe the physical structure of biochar, and the architecture of cellulosic plant material is clearly retained (Figure 6). It has been suggested that the porous structure of biochar can explain its impact on soil water holding and adsorption capacity (Day et al., 2005; Ogawa et al., 2006; Yu et al., 2006).

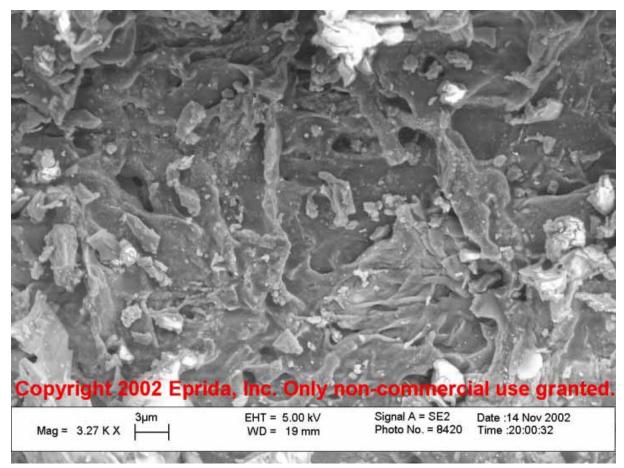


Figure 6. Scanning electron microscope (SEM) image of biochar produced at 400°C from pelletised peanut shell (Jason Nadler, Eprida, Day et al., 2005)

Process temperature greatly affects the surface area of pyrolysis products. In one study, surface area was shown to increase from  $120 \text{ m}^2\text{g}^{-1}$  at  $400^\circ\text{C}$  to  $460 \text{ m}^2\text{g}^{-1}$  at  $900^\circ\text{C}$  (Day et al., 2005). This effect of temperature has led to suggestions that biochar created at low temperature may be suitable for controlling the release of fertiliser nutrients (Day et al., 2005), whilst high temperature biochars would be more suitable for use as activated carbon (Ogawa et al., 2006). The surfaces of low temperature biochar are, however, hydrophobic and this may limit the capacity to store water in soil.

The form and size of the feedstock and pyrolysis product may affect the quality and potential uses for the biochar product. Initially, the ratio of exposed to total-surface-area of biochar is affected by its particle size. However, although low temperature biochar is stronger than high temperature products, it is brittle and prone to abrade into fine fractions once incorporated. Thus, over the long term, surface area, i.e. of weathered biochar, may not be greatly affected by this parameter.

Biochar comprises part of a continuum of materials described as 'black carbon' (Schmidt et al., 2001), which are difficult to quantify. Techniques that have been used to characterise this wider class of materials – which includes soot, charcoal, and char from vegetation fire – may be applied to detect the presence of biochar in soil, sediments and air.

These methods include extractive techniques analogous to those applied to soil organic matter, solid state <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy (with cross-polarization, CP, or Bloch decay, combined with magic angle spinning, MAS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy (Baldock et al., 2002; Fernandes et al., 2003b; Lehmann et al., 2005b).

Biochar occurs naturally in soil as a consequence of wildfire (see Section 3.1.5.1.) and is considered to be a distinct soil carbon pool (Krull et al., 2003). Research to quantify and characterise this material has highlighted the limitations of various analytical techniques when applied to soil and separation procedures to physically separate char from other soil organic matter. A key problem is the interference that the mineral matrix poses, particularly with its associations with highly stabilised soil organic matter, which chemically resembles char. This has been successfully addressed through the use of high energy ultraviolet photo-oxidation, which oxidises most non-char carbon (Smernik and Oades, 2000; Smernik et al., 2000). Thermal oxidation to remove lignin (De la Rosa et al., 2008) and chemical oxidation using hydrofluoric acid to remove mineral interferences (Simpson and Hatcher, 2004a) have also been used.

## 2.2.3. Quantification of biochar and char

The categorisation of organic carbon in soil is in general a major challenge. Quantifying different components of black carbon is particularly difficult, on account of its chemical complexity and its inherently un-reactive nature. To compare the efficacy of candidate methods depicted in Figure 7, a ring trial was recently undertaken using a selection of 12 materials of contrasting origin and source (Hammes et al., 2007).

Methods included in the trial included approaches based on biomarkers, particularly benzene polycarboxylic acids (BPCA). Chemical oxidative treatments using acid dichromate or sodium chlorite were represented; other oxidative approaches used ultra-violet treatment (photo-oxidation) with correction for non-black aromatic carbon through <sup>13</sup>C NMR analysis of oxidised residues. A chemo-thermal oxidation method used a temperature threshold of 375°C, also with <sup>13</sup>C NMR and elemental analysis of residues. A purely thermal (gravimetric) analysis was represented using a helium gas flow containing 20% oxygen. Purely spectroscopic methods included thermal or optical laser transmittance and reflectance, and mid-infrared. Additional methods assessed were matrix assisted laser desorption ionisation (MALDI –TOF) and hydrogen pyrolysis.

The most promising reference techniques for determination of biochar in soils were UV or chemical oxidation with elemental analysis and <sup>13</sup>C NMR analysis of residues (Skjemstad et

al., 1999; Smernik et al., 2002), thermal analysis (De la Rosa et al., 2008; Hammes et al., 2007) and hydrogen pyrolysis (Ascough et al., 2008).

Mid-infrared spectroscopy shows promise as a means to rapidly estimate black carbon (Janik et al., 2007) and has been applied to large sample sets (Lehmann et al., 2008). This is a correlative technique calibrated against a reference method.

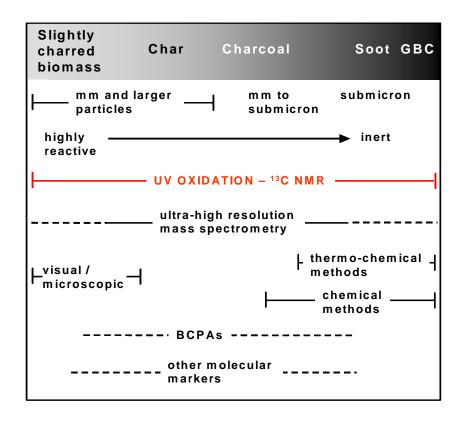


Figure 7. Components of black carbon assessed by available quantification methods across a continuum of recalcitrance increasing from left to right (Hammes et al., 2007)

#### 2.2.4. Background and biochar history: from terra preta to terra nova

The *terra preta* of the Brazilian Amazon are anthropogenic dark earths, characterised by enhanced levels of soil fertility and popular locally for growing cash crops such as papaya and mango. These crops are said to grow three times faster than on surrounding land, a landscape characterised by soils of generally low fertility. Although the *terra preta* occur in small patches averaging 20 ha, sites as large as 350 ha have been reported (Smith, 1999). Similar soils have not only been identified elsewhere within the region, namely Ecuador and Peru, but also beyond, in West Africa (Benin, Liberia), and the savanna of South Africa (Lehmann et al., 2003).

The *terra preta* display high levels of soil organic matter (SOM) and nutrients such as nitrogen, phosphorus, potassium and calcium (Table 4). These characteristics and their high fertility is attributed in part to a high char content (Glaser et al., 2001), which is the main reason why the *terra preta* tend to be much darker in colour than adjacent soils (Figure 8). The source of the large amounts of char is considered to have been incompletely combusted biomass carbon, such as wood from kitchen fires or in-field burning, conducted by relatively large and settled communities in the distant past.

The *terra preta* phenomenon has widespread public appeal and has attracted extensive coverage in popular science publications, TV and film, and a plethora of websites. The potential relevance of the *terra preta* as a model for modern day variants using by-products of bioenergy is now well established and recognised in popular science (Lehmann, 2007b; Baskin, 2006) as well as high impact scientific journals (Marris, 2006; Lehmann, 2007a). From this, the idea of *terra nova* has emerged: soils whose properties would be enhanced by modern variants of the management practices that created *terra preta*,

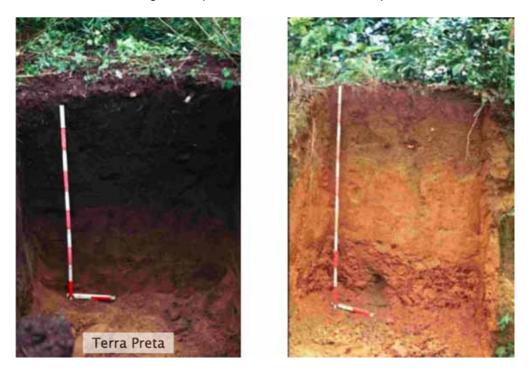


Figure 8. Comparison of profiles of *terra preta* and adjacent soils (Source: IBI website)

Table 4. Physico-chemical properties of <i>terra preta</i> and adjacent soils (data from Solomon et
al., 2007; Liang et al., 2006)

Site	Soil type	Depth range (cm)	Age (yr)	Clay content (% soil)	рН	Organic carbon (mg g <sup>-1</sup> soil)	Total soil nitrogen (mg g <sup>-1</sup> soil)	C:N ratio
Listahara	terra preta	43-69	600-1000	27.0	6.4	22.0	1.0	23
Hatahara	Adjacent soil	0-10	600-1000	35.9	4.6	21.8	1.6	14
Lago	terra preta	0-16	900-1100	22.6	5.9	31.5	1.8	18
Grande	Adjacent soil	0-8	900-1100	26.7	4.2	17.5	1.3	14
Acutuba	terra preta	48-83	2000-3000	10.4	5.6	15.7	1.0	16
Aculuba	Adjacent soil	0-30	2000-3000	8.5	4.7	15.4	0.8	20
Dona	terra preta	190-210	6700-8700	0.3	5.0	16.5	1.1	15
Stella	Adjacent soil	0-12	6700-8701	0.3	3.9	10.2	0.4	27

# 3. BIOCHAR APPLICATION IN AGRICULTURE

In the context of this report, carbon sequestration is the primary driver for considering the application of biochar to soil. Policy makers charged with meeting greenhouse gas emission targets and addressing public concern over increasingly evident climate change may recognise the potential for biochar-based strategies. The land-owner or farmer is likely to have a more practical or financial perspective.

A particular combination of feedstock, pyrolysis technology, energy conversion and byproduct usage can comprise a biochar-based system. Alternative systems have different greenhouse gas balances. In Section 3.1.4, economically and politically conceivable systems for different regions of the world are considered. The future price of carbon and the inclusion of biochar in carbon-trading schemes is a key factor. The likely additional benefits of biochar to agricultural production are reviewed in Section 3.2. These factors are critical since they dictate whether relevant practices are adopted on a large scale through their effect on the decision making of individual farmers.

From a global and policy perspective the potentially negative impacts of biomass use on climate forcing must be considered. These include the effects of soot and trace gases that are emitted into the atmosphere during combustion. Airborne transport and deposition of soot has been implicated in the acceleration of polar ice melt, but conversely in facilitating cloud formation and 'global dimming' (McConnell et al., 2007; Ramanathan et al., 2008).

Currently biomass burning accounts for 10% of global  $CH_4$  emissions and 1% of  $N_2O$  (Crutzen et al., 1990). Although current charcoal production activity could account for a component of these emissions (Woolf, 2008), a general shift to pyrolysis-based systems would decrease, if not eliminate, them. However, the net result with great expansion of alternative bioenergy systems has not been assessed.

As is apparent in the *terra preta*, the addition of biochar can dramatically darken the colour of soil, especially in soils that are low in organic matter. A relationship between soil colour and low temperature fire occurrence has been demonstrated (Ketterings et al., 2000). Oguntunde (2008) found soil at charcoal manufacturing sites to have 8% greater hue, and 20% higher value and chroma. Since dark soils absorb more solar energy they may, depending on water content and plant cover, display higher soil temperatures (Krull et al., 2004). This will affect rate processes, enhancing the cycling of nutrients and potentially extending the growing season in seasonal climates. In Japan it is a traditional farming practice to apply charcoal to accelerate snow melt. Anecdotal evidence suggests more rapid crop establishment in temperate soils enriched in char, but to date no quantitative relationships between biochar application rate and these parameters have been reported. The study of Oguntunde (2008) showed a one-third reduction in soil albedo in soils enriched in char. On a large spatial scale, the application of biochar could affect the albedo of the Earth's surface. Increasing surface albedo has been proposed as a possible mitigation measure for climate forcing (Crutzen, 2006).

The frequency with which potentially toxic compounds materialise in biochar and their concentration is inadequately researched. Two classes of compounds are of generic concern, since they can potentially from in the pyrolysis of any feedstock: polycyclic aromatic hydrocarbons (PAH) and dioxins. These compounds and available evidence for their presence in biochar is examined in Section 3.2.6.

## 3.1. Biochar and climate change

The natural carbon cycle includes natural char production from wildfires, the ensuing transport of char from the soil to watercourses and the ultimate burial in marine or estuarine sediments. Since routine and universally acceptable methods for black carbon and specifically charcoal are still outstanding, the precise magnitude of the rates and processes, and the relative size and stability of char in the soil and sediment pools are still uncertain

(Schmidt, 2004; Simpson and Hatcher, 2004b). However, the potential to enhance the contribution that char makes to the natural carbon cycle through the addition of biochar in soil is a topic of much public discussion and a rising profile in influential policy circles, for example, in Australia (Garnaut, 2008). The contribution that such strategies can have on climate change mitigation depends on attaining a much more extensive research base and detailed economic analyses.

It is useful to consider a biochar-based strategy against more established approaches to increase the organic carbon stored in soil, such as the use of manures and composts. The longevity of biochar in the soil is an important element when comparing pyrolysis bioenergy and biochar production with conventional bioenergy strategies, in mitigating climate change. However, it is also vital to assess any indirect reduction in net greenhouse gas emissions from agriculture through the use of biochar. There may be additional benefits arising from the contribution of biochar to facilitating agricultural development and improving the socio-economic circumstances of farmers in developing countries. Figure 9 captures the complexity of potentially beneficial interactions of biochar in the context of natural cycles and anthropogenic interventions.

## 3.1.1. Soil organic matter and climate change

In order to understand the potential significance of carbon in soil in the form of biochar, its characteristics and dynamics should be compared to those of the remaining soil organic matter, which accounts for most of the carbon that exists in soil (the exception being calcareous soils which contain stocks of inorganic carbon in carbonate minerals). Depending on land-use and climate, most soils contain up to approximately 100 t ha<sup>-1</sup> carbon as organic matter. Peat soils, though, comprise mainly organic matter and contain much more carbon on a per unit area basis. It is increasingly recognised, however, that a greater proportion of the total carbon may comprise an accumulated store of the products of burning or fire (Skjemstad et al., 2004a), and that this has implications for the response of the wider soil carbon pool to climate change (Skjemstad et al., 1999; Lehmann et al., 2008).

Modelling indicates that about 90% of the organic matter present in soils turns over on decadal to centennial timescales (Coleman et al., 1996; McGill, 1996). Most organic matter in soil is derived from plant roots, plant debris and microbially re-worked substances. The presence of soil organic matter is important for a range of useful soil properties, which has been comprehensively reviewed by Krull (2004). The process of microbial energy acquisition (and concomitant  $CO_2$  release) from substrate is accompanied by a release of various nutrient elements, which may be conserved in the soil in microbial biomass or the particulate residues of substrate decomposition. A portion of certain nutrients may also be released in soluble form, and a fraction may be lost from the soil through leaching or run-off; which is essential to crop nutrition. This is particularly the case where external nutrient provision (from fertiliser or manure) is limited or absent.

Overall, a balance slowly develops between the rate of carbon addition and the emission of  $CO_2$ , which are specific to the land-use and environmental conditions. The amount of organic matter maintained once this balance is reached, depends on its average rate of turnover. To date there have been few means proposed that permit manipulation of this rate, so that soil carbon can be permanently increased. Beyond simply increasing the amount of external organic matter inputs (Smith et al., 2000), the main strategies are to disturb the soil less by using less intensive tillage or zero tillage (Lal, 1997; Smith et al., 1998), or by selecting particularly recalcitrant, lignin-rich amendments (Palm et al., 2001).

Although conversion to no-till soil management has been widely promoted as an approach to enhance soil organic matter as well as to control erosion and conserve water, the main effect appears to be a vertical re-distribution of organic matter, and an increase toward the surface more or less matched by a corresponding depletion at depth (Bhogal et al., 2007; Blanco-Canqui et al., 2008). Nonetheless, the Chicago Climate Exchange includes a specification for 'conservation tillage' amongst its Carbon Financial Instruments for carbon sequestration and thus a precedent for the active engagement of farming in the carbon market (<http://www.chicagoclimatex.com/>). Managing decomposition in soil by manipulating the quality of inputs has been explored extensively in tropical environments where decay is rapid (Palm, 2001). But simply altering the composition of soil inputs has only a relatively minor impact on the composition and long-term fate of the small portion that is stabilised, with incorporation and repeated decomposition inside the dominant, slow turnover pool.

Thus the main emphasis in the sequestration debate has been focused on increasing soil carbon by increasing organic matter additions in the form of straw or other crop residues, and from external sources such as manures and a range of organic wastes: sewage sludge, municipal compost, paper waste, and so on. Although there is a large amount of such material available, the quantity is relatively small compared with the total flux through soil, particularly the size of the global soil carbon pool. When a soil is at an equilibrium, only about 10% of the carbon added to soil is stabilised for more than one year. During a transition, progress to new equilibrium is slow, with the annual increase being small relative to the carbon invested. As equilibrium is approached the annual rate of accumulation decreases, and once reached, the new level of input has to be sustained simply to maintain it. Furthermore, the capacity to store organic matter is ultimately limited (with the capacity varying with soil type, water regime and climatic factors); thus the improvement in carbon storage that is possible for each incremental increase in input (Stewart et al., 2007; Gulde et al., 2008). As well as added carbon being rapidly re-emitted into the atmosphere, carbon is lost in the formation of soil organic matter through digestion in the animal gut or oxidation in conversion to compost. The level of carbon sequestration or offset that could be realised through an alternative use of these materials, including fossil fuel substitution, must be considered when assessing the efficacy of these strategies from the perspective of climate mitigation alone (Schlesinger, 2000). For example, the carbon cost of producing N fertiliser is relevant when proposing to increase soil carbon storage indirectly through enhanced plant growth (Schlesinger, 2000).

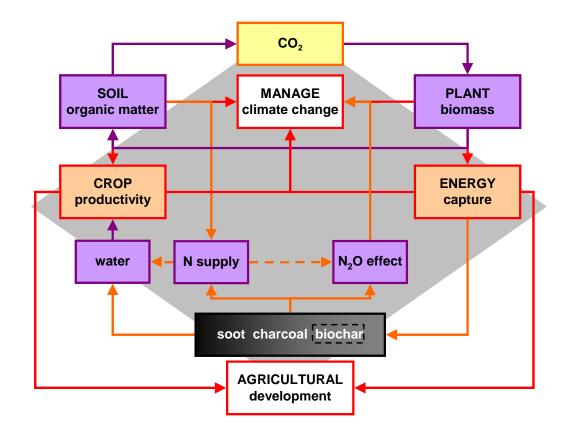


Figure 9. The key physical (purple arrows), natural (orange arrows) and anthropogenic (red arrows) interactions of biochar in the environment

In the context of the interventions generically referred to as 'management options', important soil physical benefits may be gained by accumulating soil organic matter (Janzen, 2006). However, these must be balanced against the opportunity costs, the forgone benefits that might arise from its breakdown and turnover, most importantly the release of crop nutrients (Janzen, 2006). In general, however, any form of organic matter added to the soil degrades resulting relatively quickly in  $CO_2$  emission. Thus adding degradable organic matter into the soil is inefficient in terms of climate change mitigation, with the energy contained being captured and dissipated by soil microbes rather than in power plants where it can offset fossil fuel use (Woolf, 2008).

## 3.1.2. Carbon stabilisation and sequestration using biochar

Turning biologically-derived organic matter into a highly stabilised form can decrease  $CO_2$  emission from soil by considerably lowering its rate of decomposition. Whether stabilisation by conversion to biochar represents a net carbon saving depends on the time horizon for the comparison. However, the immediate  $CO_2$  emission from syngas released by pyrolysis would, within a few months, be exceeded by the  $CO_2$  emitted in decomposition if the same material had been added to soil directly (Lehmann et al., 2005a). Also, although there is a  $CO_2$  emission associated with provision of heat for the pyrolysis process, the calculations of Gaunt (2008) indicate that it is relatively small; in an example where pyrolysis consumed 40% of the carbon in the feedstock (in producing syngas), the  $CO_2$  resulting from provision of process heat for that process would equate to only a further 10%. Even in temperate environments where decomposition in soil is relatively slow, it is calculated that within two to five years, the effective emission in the pyrolysis scenario is already less than that which would have accrued from the soil (Gaunt et al., 2008). Over a period of the one to five decades relevant to mitigation of climate change, the net saving is therefore considerable.

Even within the first few years, however, the higher initial loss of  $CO_2$  may be offset by the effects of biochar on other soil processes, in particular prevention of  $N_2O$  and  $CH_4$  release from soil. Natural emissions of  $N_2O$  from soil are a function of soil moisture status and possibly tillage (Pekrun et al., 2003). Because biochar in soil may modify the moisture regime and physical location of water within the soil matrix, it may mitigate the enhanced emission of  $N_2O$  that may occur in no-till systems. Methane emissions produced from agricultural soils, mainly under paddy rice agriculture, account for 12% of the global methane emission from all sources. Some studies have suggested that addition of biochar may partially suppress methane emissions. The evidence for these effects is examined in Section 3.1.6.2.

There may be additional, potentially important offsets of other indirect emissions. These could include avoided emission of  $CO_2$  if the fertiliser required to produce a tonne of product is decreased via a positive effect of biochar on crop use efficiency. This extends to avoided emissions of  $N_2O$  during the manufacture of the fertiliser as well as from the soil upon application – it is estimated that a carbon-equivalent emission of 1.8 tC is associated with production and use of 1000 kg of fertiliser nitrogen (Mortimer, 2003). Any effect of biochar on increased crop yield could significantly ease pressure on natural lands if implemented on a large scale. Since the conversion of forest or savannah to agriculture can result in an emission as high as 100 tC ha<sup>-1</sup> (from above- and below-ground carbon stocks) this could be important (Searchinger et al., 2008).

It has been suggested from visual observation of the *terra preta* that biochar could also lead to a net stabilisation of other organic matter (Sohi et al., 2006; Lehmann and Sohi, 2008). If this is the case, this could be another factor benefiting the overall net carbon gain from biochar-based soil management strategies. This is a particularly intriguing prospect since the capacity for soils to store biochar, not relying on protective capacity of a limited clay surface area, is not finite in the way that it appears to be for other soil organic matter. Thus in addition to representing a carbon store of its own, it is possible that biochar can enhance the intrinsic soil organic carbon storage capacity of soil by affecting the turnover of indigenous carbon. However, apparently contradictory data have been published, which seems to suggest an accelerated decomposition of leaf litter in soil amended with biochar (Wardle et

al., 2008). The mechanisms and predictive description are, however, still to be determined and defined.

A carbon balance for a pyrolysis scenario that appears positive with respect to the atmosphere in the short term (i.e. a net emission) may be rendered negative if the feedstock for biochar production comprises a new, additional and sustainably supplied resource. This resource could derive from a managed increase in the above-ground productivity of existing crops, or by maintaining vegetation in a state of high net primary productivity through growth continuous cropping. Maintaining high net primary productivity above ground also promotes higher productivity below ground, with an associated increase in root exudation and root turnover. Plant and root productivity can also be enhanced by the use of fertiliser; noting, however, the overall carbon balance of a strategy based on increasing soil carbon through increased use of fertiliser. In assessing the carbon balance of a biochar strategy, it is important to include the carbon cost of transporting feedstock and biochar between field and pyrolysis facility and vice versa. In the scenario where there is no energy capture from pyrolysis of organic matter, gains will depend on positive impacts on crop yield and soil health.

## 3.1.3. Combined bioenergy and biochar production

Greatest overall impact on greenhouse gas emissions are likely to be realised where gases produced during pyrolysis are captured and utilised in a manner that offsets fossil fuel energy. In comparing a strategy that involves biochar production and its use in soil, it can be argued that the reference scenario should be the use of the same feedstock in some other form of bioenergy capture, such as simple combustion or, alternatively, pyrolysis with gasification or combustion of the biochar by-product.

Bioenergy in general is often described as carbon neutral, since the carbon emitted in the use of the energy approximates to the amount removed from the atmosphere to create the feedstock in photosynthesis. For a biochar-based strategy to be carbon-negative, the avoided carbon emission – or rather  $CO_2$  -equivalent emissions (since other greenhouse gases have to be considered) – from use of 1t carbon in feedstock must exceed 1tC (Renner, 2007). If it is assumed that the feedstock would otherwise decompose and return to the atmosphere as  $CO_2$ , as is the case for organic material added to soil, the carbon emission from producing biochar and adding the stabilised residue to soil may alone, over a few years, be close to one unit. Thus, with any net energy capture through use of gases (or oils) produced during pyrolysis, the technology may be considered carbon negative (Lehmann, 2007). The indirect effects on carbon emissions resulting from a positive impact on agricultural productivity, plus an effect of biochar or the emission of non- $CO_2$  greenhouse gases from soil, may enhance this.

However, the carbon-negative status of the technology has been questioned by Bruun (2008), who considered the additional fossil fuel offset that could be obtained if biochar was used for non-energy purposes. Furthermore, biomass pyrolysis itself did not extract more energy from a feedstock when compared to another bioenergy use. Bruun (2008) also pointed out that over longer timescales, an increasing proportion of the carbon initially sequestered in biochar would be slowly returned to the atmosphere through its slow degradation back to  $CO_2$ .

In terms of energy captured per unit of  $CO_2$  released it may be correct that biochar production is not associated with less carbon emission than other forms of bioenergy. However, when expressed in terms of energy captured per unit of carbon in the feedstock, this is not the case. During pyrolysis the majority of energy embodied in feedstock (about 70%) is converted into combustible syngas, but with the liberation of only half of the feedstock carbon (Lehmann et al., 2005a). This is because energy rich but less carbonaceous functional groups are liberated first.

In the pyrolysis of organic wastes and crop residues, the emission avoided in preventing its natural decomposition in soil, composting or landfill (for example) is an important part of the overall  $CO_2$  -equivalent savings. In the utilisation of non-waste feedstocks, such as biomass

crops, there is no such avoided emission. Indirect  $CO_2$ -equivalent savings resulting from use of biochar in soil must then exceed the energy embodied in the biochar and allowance made for the implications of land use.

## 3.1.4. Evaluation of biochar systems

Since pyrolysis is a more carbon-efficient way to capture bioenergy compared with other bioenergy systems (in terms of  $CO_2 MJ^{-1}$ ), manufacture and storage of biochar would add significant benefits for climate change mitigation alone. From this perspective, storage of biochar does not need to be in the soil, and it had been proposed that entire valleys could be used as storage facilities for biochar (Seifritz, 1993). However, applying biochar to agricultural soils is currently the most widely proposed path, since it is more likely to overcome the opportunity cost in energy production (the recoverable energy forgone in the biochar). If biochar can provide reliable agronomic benefit it may command a value in crop production in addition to a potential carbon credit.

However, whilst the potential for management of the terrestrial carbon cycle is the reason for the current interest in biochar, to be workable a biochar-based scenario must: (1) assess the monetary value of direct and indirect emission savings arising from the use of biochar against the opportunity cost of biochar combustion or alternative use, (2) provide certainty, verification and possibly evidence for carbon-equivalent savings and (3) consider the indirect costs and benefits to land users and upstream food processors from the use of biochar in soil. The latter might include the cost of biochar application, weighed against the marketing benefits gained through carbon-neutral food products.

In short, a full life-cycle analysis of alternative scenarios is required. However, greater certainty is required on the following in order to fully assess biochar-based soil management for specific applications: (a) the stability of biochar carbon in soil, (b) the indirect impacts of biochar on carbon-equivalent emissions and (c) the security, reliability and constancy of price for pyrolysis feedstocks. These are reviewed in more detail in the next sections.

The potential for technological developments in pyrolysis to enhance flexibility and overall efficiency is a separate topic, and will be facilitated by its expansion and forums such as IBI, and national networks such as the Network of Australian and New Zealand Biochar Researchers, and the UK Biochar Research Centre. It should be highlighted, however, that from the perspective of the economics of energy capture, the value of biochar and the overall outcome of the analysis is sensitive to the price of heat and power generated from other fuels. It is also affected by any subsidy for renewable energy, which may have the effect of inflating the monetary value of the energy in biochar (Woolf, 2008).

#### 3.1.5. Stability of biochar in soil

Its extraordinary stability means that charcoal particles in soil have been used as a tool for dating and paleo-environmental reconstruction as well as evaluation of cropping practices over centennial and millennial timescales (Ferrio et al., 2006, Scott et al 2000). Studies of the age of the carbon in *terra preta* of Brazil, as well as similar black carbon accumulations in the soils of other natural ecosystems that have resulted from natural fire events, provide considerable reassurance for the general long-term stability of at least some significant component of biochar. However, laboratory-based studies using freshly-made char tend to show some mass loss – sometimes large – in a period of days to years.

The paradox of apparent long-term stability against measurable short-term decomposition suggests that biochar comprises both stable and degradable components. At the moment there is insufficient data in the literature to compare the responses between short- and long-term stability under different climates and in different soils, which could enable the relative size of these fractions to be assessed.

Combustion conditions during pyrolysis as well as the type of feedstock are probably influential in determining the proportion of relatively labile components in biochar products. Measuring the influence is essential for the optimisation of pyrolysis for maximum net carbon

stability. In optimising biochar production against energy capture to address climate change most effectively, a consistent level of stability in biochar is the aim. Maximising retention of carbon into biochar is counter-productive however, in both carbon and economic terms, if the additional material is in fact associated with short- or medium-term loss to the atmosphere.

The chemical composition of biochar provides the principal explanation for its generally high level of stability and is reflected in broad terms by its elemental composition: highly aromatic and with a very high carbon content. It is likely that its stability is strongly modified by its physical properties and structure, however. If the biotic and abiotic processes determining the fate of biochar are the same as those for other soil organic matter, higher soil temperature, moisture availability, lower clay content and intensive tillage will accelerate decomposition rate.

The soil system has a remarkable propensity to degrade organic substrates introduced into it. As a substrate generally very low in the concentration of key crop nutrients, the rate at which biochar degrades in situ may also be influenced by the exudation of labile, nutrient rich substances in the rhizosphere. This, in turn, is affected by cropping pattern.

## 3.1.5.1. Stability of biochar in natural systems

Soils that contain large amounts of char are those that have experienced relatively frequent natural fires over a period of millennia (Lehmann et al., 2008). Converting a fraction of standing plant biomass to black carbon in soil constitutes net removal of  $CO_2$  from the atmosphere (Forbes et al., 2006). A relatively minor under-estimation in our estimates for the percentage converted could explain up to one-fifth of the so-called missing carbon sink, that is the imbalance between carbon eliminated from forest and fossil fuels, against observed atmospheric  $CO_2$  (Kuhlbusch, 1998).

In natural systems it is not possible to determine the exact amount of biochar added to a soil over the long-term history and the biochar in these soils will be of disparate age. However, a loss rate constant can be derived mathematically by assuming that current and historic levels of standing biomass are representative (Graetz et al., 2003; Mouillot et al., 2005; Forbes et al., 2006), and a simple factor applied to capture the rate of conversion of biomass to charcoal in burning episodes. This approach has yielded the best estimates for long-term mean residence times, which are in excess of 1000 years (Lehmann et al., 2009). Direct monitoring of archived soils from medium-term experiments seems to support such stability (Skjemstad et al., 2001).

A portion of black carbon in soils globally also comprises condensed aromatic carbon in the form of soot particles. This, in turn, can be confused with soot similarly formed in fossil fuel combustion. Such black carbon is considered to lie at the most stable end of a black carbon continuum (Masiello, 2004). Over extended timescales the physical transport of this material through the soil and into water and sediment is inevitable and is seen in its accumulation in marine sediment (Masiello et al., 1998). This observation highlights the potential to confuse physical transport of biochar from a trial site for oxidative loss. It also indicates the importance of such processes to the sequestration of carbon in the natural carbon cycle (Smittenberg et al., 2006).

Although char from wildfire offers opportunities to study the long-term dynamics of pyrolysed biomass, the fire and low rate of biomass conversion to char suggests probable differences in composition and function. Simple charcoal manufacture probably began with the discovery of fire; therefore, it is not surprising that sites of ancient habitation are associated with soils enriched in char. Whilst the *terra preta* provide a neat and convincing example for the deliberate use of biochar in agriculture, there is circumstantial evidence for its informal use in other regions, not only in the distant past but in recent centuries (Young, 1804) and in the current day (Lehmann and Joseph, 2009a).

## 3.1.5.2. Influence of biochar feedstock on stability

In soils where charcoal has been known to be abundant, it is associated mainly with the very fine, sub-50 µm soil fraction (Brodowski et al., 2006). This suggests that through some abrasive physical process or the destructive physical impacts of freeze-thaw and shrink-swell, the initial size of brittle biochar particles may be relatively unimportant to its long term interactions in soil. Ponomarenko (2001) found biochar evenly distributed across particle size and biochar particles to become increasingly rounded over time at a rate dependent upon the abrasiveness of the soil. Ponomarenko (2001) also found the concentration of clay-sized mineral particles embedded in biochar pores to increase with time and noted that this would inhibit their isolation using density-based techniques.

Brodowski (2006) found a small proportion of biochar particles in soil to be associated with micro-aggregates, but for this biochar to account for a rather large proportion of the carbon that is present in such structures i.e. compared to other particulate organic matter. The authors used this as evidence for physical protection of biochar against degradation and also noted that biochar might act as a binding agent for organic matter in aggregate formation. Although they did not specify whether the latter would be a purely physical interaction or a consequence of biological activity, Watts (2005) previously found no effect of charcoal on aggregation at low temperatures designed to preclude biological activity. In an earlier publication Glaser (2000) found a large proportion of biochar in *terra preta* to be present in unprotected fractions. Obtaining similar results, Murage (2007) noted that the misleading impression might be gained that active soil fractions turn over more slowly in soils that are enriched in biochar.

Currently there is no published information to demonstrate whether the physical diminution of biochar in soil is accompanied by oxidative loss of carbon. However, X-ray photoelectron spectroscopy showed abiotic oxidation (with proliferation of carboxyl groups) to occur in the porous interior of biochar, whilst biotic oxidation affected external surfaces only (Cheng et al., 2006). Biotic oxidation might therefore be enhanced as particle size decreases, although in the study of Cheng (2006) it was also quantitatively less important. These findings have been further validated (Lehmann et al., 2005b) using synchrotron-based techniques (near-edge X-ray absorption fine structure spectroscopy).

At the macro-scale biochar products range from powdery to brittle, depending upon the physical microstructure of the material from which they are derived. Those produced from woody feedstock display a predominantly xylemic structure that is coarse and strong. These also display the highest carbon contents, in excess of 70% C and up to 90% C, and are low in trace elements. Those produced from rye grass, maize and digested feedstocks i.e. manures are powdery, lower in C (over 60%), and enriched in minerals and nutrients. Thus the latter are not only less physically recalcitrant, they are also a more attractive microbial substrate.

#### 3.1.5.3. Climatic effects on biochar mineralisation

Climate determines soil temperature, which affects the rate at which both biotic process and abiotic reactions occur in the soil. However, in the absence of water the effect of temperature is irrelevant, as water is essential for biological cell function, and solution phase reactions proceed by definition only where water is present. Thus synchrony in a conducive environment of rainfall and temperature and rainfall conditions is required in order to maximise overall soil activity.

Biochar should modify not only the soil water holding capacity of the bulk soil, but also the physical location of water within the soil matrix, since the smallest pores become water-filled first and remain moist the longest (Gaskin et al 2007). The size of these pores makes them relevant to microbial populations as a physical niche. There is also evidence that mean soil temperature and diurnal temperature fluctuations are impacted by the effect of biochar on soil colour (Krull et al., 2004; Oguntunde et al., 2008).

The effect of climate on biochar oxidation has been evaluated in a transect study spanning several climatic zones. Sites along the transect had each received inputs of biochar during a brief and defined period in industrial history 130 ybp, but received greatly contrasting mean annual temperatures (Cheng et al., 2008). The accumulation of cation exchange capacity was correlated to mean temperature and the extent of oxidation was seven times higher on the external surfaces of biochar particles than in the interior.

The potential consequence of a warmer global climate releasing  $CO_2$  through accelerated mineralisation of black carbon was first scoped by Druffel (2004) who indicated potential emission rates of 2 to 7 GtC y<sup>-1</sup> by 2100. However, if a larger proportion of the global soil carbon stock comprises recalcitrant black carbon than is assumed in current models, the more active pools must be smaller and the overall response to warming significantly slowed (Lehmann et al., 2008). General arguments concerning the relative response of recalcitrant carbon and more active carbon pools to changing temperature has not been resolved (Fang et al., 2006).

## 3.1.5.4. Soil biological activity and the stability of biochar

A number of relatively short-term laboratory incubation experiments have been conducted using soil mixed with biochar, with or without added substrate, to assess the biological and chemical degradation of biochar to CO<sub>2</sub>. Early studies found that even graphitic carbon could significantly be mineralised biologically (Schneur, 1966).

Laboratory studies where loss routes can be controlled have generally found some measurable initial loss of carbon from biochar (Cheng et al., 2006); however, a few studies have found a much larger loss (Hamer et al., 2004). In the Hamer (2004) study, not only was charcoal substantially degraded within 60 days, but the mineralisation of simultaneously added glucose solution was also enhanced, suggesting a priming effect. Combined products comprising labile nitrogen and stable carbon have been proposed (Day et al., 2005). However, the evidence (Hamer et al., 2004) suggests that the addition of nitrogen could impact on the stability of biochar and its value in carbon sequestration. This has not, however, been experimentally assessed to date.

Further studies seem to indicate that biochar may prime the decomposition of native soil organic matter. After nine years in the field, Wardle et al. (2008) measured mass loss greater in a charcoal-litter mixture, than for the sum loss in a charcoal-only plus litter-only. However, the mesh bags in which the samples were contained had been buried in a forest litter layer, and thus separated from mineral soil. Although the loss could have been from the priming of litter decomposition, it was also possible that the loss could result from priming of charcoal loss (Lehmann and Sohi, 2008).

If the level of organic matter input to the soil by plants is steady for a particular ecosystem, enhanced microbial activity over the long term is not consistent with a net accumulation of non-black organic matter (as well as charcoal) that is observed in *terra preta*, compared to their adjacent soils. But in fact these observations need not be contradictory if carbon that is mobilised in the litter layer is, once transported to the mineral soil, rapidly stabilised. The latter effect could directly involve biochar surfaces or minerals in subsoil, as well as mineral material in the surface horizon (Lehmann and Sohi, 2008).

## 3.1.5.5. Effects of biochar on ease of tillage and mechanical disturbance

If, as proposed, natural soil movement influences the breakdown of biochar through its reduction in size, then the rate of breakdown would be expected to be further accelerated by tillage. This is important to consider since tillage is perhaps envisaged as the primary means to incorporate biochar into soil.

Quénéa (2006) reported a 60% decrease in both the soot and charcoal content of sandy soil under temperate forest during 22 years after conversion to intensive agriculture with annual tillage. The loss of total soil carbon over the same period was 30%, suggesting that biochar and charcoal were relatively less resistant to degradation than bulk soil organic matter after

disturbance. However, the analysis of the charcoal data was based on larger hand-picked fragments and it seems likely that particles broken down into very fine fractions might have led to an overestimate of the loss. The initial soot content was very low. In contrast, 50 years of cropping and cultivation had no measurable change in the aromatic aryl carbon, taken to reflect charcoal, whilst other fractions declined rather rapidly (Skjemstad et al., 2001).

More research may enable likely rates of breakdown to be predicted. If, for example, tillage was a key factor, maximum longevity of biochar targeted by application on land where minimum tillage is practised. In no-till systems, biochar could be sequestered into soil through a one-time addition at the time of conversion from a tilled system.

## 3.1.6. Indirect impacts of biochar on CO<sub>2</sub>-equivalent emissions

The net carbon gain resulting from stabilisation of carbon into biochar, and its storage in soil, needs to be refined. There is even less information available for the impact of biochar in soil on the emission of greenhouse gases other than  $CO_2$ . The contribution of nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>) are major contributors to climate forcing and have significant agricultural sources, including soils. There is evidence that biochar may suppress the emission of these gases from soil.

There may be additional indirect benefits in terms of greenhouse gas emissions, resulting from improved crop production through use of biochar. Although the global possibilities are currently hypothetical, in an era of falling global grain stocks, the value of biochar could extend beyond a purely financial consideration for land users and become increasingly relevant politically and economically. Growing concerns around both energy and food security may accelerate the development and application of biochar technology and associated Governmental or inter-Governmental market interventions to support it.

## 3.1.6.1. Indirect effects of yield benefits and nutrient requirement

The direct impacts of biochar on crop yield are reviewed in Section 3.2.2.

Where economically optimal fertiliser rates are currently applied, biochar has the potential to deliver the same crop yield with a lower application rate – with potentially significant greenhouse benefits. In more detailed assessments for the overall carbon balance of a biochar strategy (Gaunt et al., 2008), an assumed 10% reduction in the fertiliser required to maintain current crop yield was found to be a particularly important component of the net carbon benefit. This reflected the energy intensive nature of nitrogen fertiliser production and the  $N_2O$  emissions that result from fertiliser application and use.

The purpose of biochar application might not simply be to attain a greater yield, however, but possibly to achieve predictability in yield through a lower susceptibility to climatic events such as floods and drought.

Also, the economic optimum after biochar application could be gained through a gain in crop yield at the same current or possibly higher rate of application, in which case the net result would be higher per hectare yields.

Furthermore, biochar could increase, maintain or at least limit gradual decreases in crop yield on land where soil fertility and productivity is currently in decline. Under changing climate the benefit of biochar in response to increasingly erratic or intense rainfall events could be more acute, and/or enable plants to better exploit higher  $CO_2$  concentrations. This suggests a potential role for biochar to assist in adaptation to climate and environmental change.

These factors would benefit global carbon balance in several very important ways. Firstly it could reduce the degradation of existing agricultural land, and thus alleviate pressure on natural systems, which usually represent a significant store of carbon as well as biodiversity. Maintaining or enhancing productivity of existing land may also make relatively more land available for bioenergy or other alternative crop production systems.

Modelling of these possibilities, at this stage, may not be possible due to too many uncertainties (economic as well scientific). However, if we view biochar as a technology with the potential to be practised on a very large scale, they have to be assessed in the long term. Importantly, they highlight the complexity of the biochar topic and the need to think carefully about the system boundaries drawn in assessing benefits and impacts.

#### 3.1.6.2. Impact of biochar on nitrous oxide emission from soil

The global warming potential (GWP) of a gas reflects two aspects: the efficiency of the molecule in absorbing incoming solar radiation and its rate of chemical breakdown in the atmosphere. By definition the global warming potential (GWP) of  $CO_2$  is 1.0; by comparison the GWP of nitrous oxide is 310. Under anaerobic conditions N<sub>2</sub>O is emitted from soil through denitrification, a process in which specialised microbes that obtain energy from the reduction of nitrate (NO<sub>3</sub><sup>-</sup>), or intermediate gases, to dinitrogen (N<sub>2</sub>). However, it appears that nitrifying bacteria generally involved in conversion of N<sub>2</sub> to ammonium (NH<sub>4</sub><sup>+</sup>), i.e. nitrification, may simultaneously denitrify (Bateman, 2005).

The availability of  $NH_4^+$  is generally controlled by organic matter mineralisation, which is climate driven, but its concentration is greatly enhanced by the application of nitrogen fertiliser or, in livestock and gazed grassland systems, from dung or slurry application. Regardless of the setting or source, the majority of soil nitrogen is in organic form and N<sub>2</sub>O emanates from the utilisation of a relatively small and dynamic nitrogen pool.

Life cycle assessments quantifying the benefits of biochar-based strategies for energy depend quite heavily on a decrease in the emission of  $N_2O$  that frequently follows the addition of mineral nitrogen fertiliser. Accounting for this effect makes a great difference to the overall analysis of how a biochar to soil strategy impacts on net greenhouse gas balance (Gaunt et al., 2008). The expectation for this effect relates to the general impact of biochar on retention of N in the soil in a way that also enhances crop nutrition (see Section 3.1.6.1.). If the latter effect is surface-mediated, it seems unlikely that biochar confines N to a physical location – such as very small pores – where it is inaccessible to denitrifying bacteria. It may be that, instead, biochar inhibits the process by sequestering dissolved mineral N.

Published data demonstrating the effect of biochar on suppression of  $N_2O$  remains very limited. In the most widely cited study to date (Yanai et al., 2007) 'bio-waste' charcoal was applied during a re-wetting of a former grassland soil, high in organic matter, in laboratory incubation (25°). Nine-tenths of  $N_2O$  was suppressed in five-day emission episodes after wetting of soils to 73% and 78% water filled pore space. At a slightly higher water filled pore space (83%), charcoal had the opposite effect, increasing  $N_2O$  emission. The rate of biochar addition used in the study equated to a relatively high application rate of 180 t ha<sup>-1</sup> in topsoil. However, the authors were able to exclude the possibility that the alkalinity of their charcoal, or its nutrient content, were significant factors in their observations.

In an arable soil with much lower C content (2.2 %C), Sohi (2008) has studied the effect of willow charcoal at a much lower rate of 10 t C ha<sup>-1</sup> which were assessed during 20°C incubation of wet (70% water holding capacity) and re-wetted (from 20% water holding capacity) soils, with and without simultaneous addition of small amounts of inorganic N (equivalent 75 kg N ha<sup>-1</sup>). A more modest suppression of 15% was proportionally similar for all treatments where there was any response at all (the already-wet soil did not emit significant N<sub>2</sub>O). After six months, available soil N would have been largely consumed and the soils thoroughly equilibrated. A second inorganic N addition (without new charcoal) at this time showed no difference in N<sub>2</sub>O emissions between amended and control soils.

If any correspondence exists between the two studies it appears that not only is effect of biochar on  $N_2O$  likely to be non-linear with respect to rate of application (and significant but not large at realistic rates) but – as authors of both papers conclude – the effects are likely to reflect the impacts of biochar on soil physical properties, particularly modification of pore-size distribution (of which water holding capacity is not a sensitive measure). In particular the effect may only be seen during re-wetting, and not when soils are maintained wet. Whether the benefit upon re-wetting is repeatable remains to be established.

Measurements of  $N_2O$  emission in the field environment are difficult due to the transient and spatially variable nature of denitrification. Like the studies described in Chapter 3, the availability of sample biochar in the quantities required to assess its many effects in true randomised plot designs presents a major challenge. Biochar field experiments with periodic measurement of  $N_2O$  in cover boxes is currently in a third year in upstate New York (<a href="http://www.css.cornell.edu/faculty/lehmann/research/biochar/biocharproject.html">http://www.css.cornell.edu/faculty/lehmann/research/biochar/biocharproject.html</a>).

In tropical environments field experiments have been established in Columbia and in Kenya. Results from the Columbian trials indicate 80% suppression of N<sub>2</sub>O emissions (Renner, 2007).

#### 3.1.6.3. Impact of biochar on methane emission from soil

Methane has a relatively low GWP of 21, but is six times more abundant in the atmosphere than  $N_2O$  (1.8 ppm compared to 0.3 ppm for methane), and has an annual flux approximately 50 times higher. Aside from industrial emissions, including natural gas exploitation and distribution (accounting for about 20%), methane emanates primarily from the soil of natural habitats and thus, uniquely for the main greenhouse gases, increasing rates of emission have begun to stabilise. Within agriculture, paddy cultivation of rice and the guts of the growing ruminant population (primarily grazing domestic animals) are key methane sources (IPCC-2001,

<a href="http://www.grida.no/publications/other/ipcc%5Ftar/?src=/climate/ipcc\_tar/wg1/index.htm">http://www.grida.no/publications/other/ipcc%5Ftar/?src=/climate/ipcc\_tar/wg1/index.htm</a>)

Specialised methanotrophic bacteria make most aerobic soils a net sink for methane, however, and the relatively rapid consumption of methane explains to a large extent its relatively low GWP. The link between methane consumption and aerobicity is important in the context of reduced tillage, however. These practices have been widely promoted for their sequestration of carbon. Whilst higher topsoil organic matter is liable to improve both water infiltration and holding capacity, increased moisture status is likely to result in a relative increase of methane emissions (e.g. Castro et al., 1995).

Field experimentation with biochar in Columbia showed the elimination of  $CH_4$  emission (Renner, 2007). A number of studies are currently assessing the impact of biochar on the emission of methane from paddy soils. At this time there are no results published in the scientific literature.

#### 3.1.6.4. Biological activity and stabilisation of soil organic matter

The stability of biochar and the biological activity that results from its application are intrinsically linked, as are soil properties such as clay content, pH and cation exchange capacity (CEC) and climatic variables.

The ancient *terra preta* are higher in organic matter compared with adjacent soils that do not contain black carbon (Lehmann et al., 2003). This has lead to the hypothesis that black carbon in soil leads to increased stabilisation and hence accumulation of other carbon. This may provide one of the few mechanisms by which the intrinsic capacity of a soil to store organic matter can be modified from a management perspective, and if correct, increases the net carbon gain from the use of biochar.

However, some studies have reported increased microbial activity in soils enriched in biochar (Steiner et al., 2003; Steiner et al., 2008). Upon addition of biochar to soil for the first time, mineralisation may be stimulated by the presence of an active fraction and associated soluble nutrients or labile carbon fractions. It has also been noted that the physical structure of typical biochar products provides a secure environment for microbial colonies (Ogawa, 1994). However, it should be noted that experiments must be designed such that the system is correctly monitored, e.g. all soil layers, gaseous losses and plant growth. Currently, findings to date should be viewed as provisional.

Microbial biomass is not a measure of microbial activity but the abundance of microbial cells. Thus whilst an increased microbial population associated with increased soil organic matter without any obvious increase in substrate supply may seem paradoxical, it might suggest a decrease in microbial efficiency, possibly associated with a change in the balance between different groups of microbes. A simultaneous increase in CO<sub>2</sub> emission, however, would indicate enhanced plant growth and higher inputs of labile carbon via the plant roots.

In soils where char is present naturally in higher concentrations as a result of natural forest fire or prescribed burning, the microbial community may include specialised species with a capacity to degrade a relatively scarce and challenging substrate. This may explain the distinct communities observed in *terra preta*, but is not clear whether these species are truly ubiquitous to other soils (if scarce), or whether the capacity for soils to degrade such materials is acquired over relatively long periods.

## 3.1.6.5. Effects of biochar on tillage and irrigation requirements

Lower bulk density and/or higher organic matter reduce the fuel requirement for mechanical tillage, which can be managed in few other ways. It may also facilitate the process of reducing the tillage used in agricultural systems. Soils with higher organic matter content also tend to display higher water-holding capacity. Thus a further saving in energy costs can come from reduced irrigation frequency or intensity. Surprisingly little information has been collected on the impact of biochar on such parameters. However, in Ghana, kiln sites showed topsoil bulk density approximately 10% lower than in adjacent soils (Oguntunde, 2008).

## 3.1.7. Biochar scenarios for agriculture

In addition to the price of biochar, land-users will incur the direct costs of applying biochar to the soil. There are also potential non-monetary costs associated with the collection of straw from their land as a pyrolysis feedstock, which affects the readiness of land owners to engage in the market. In 'closed' systems where biochar is returned to the same land that the feedstock originated, there may be opportunity costs. Currently, no socio-economic studies exist that would address questions on these matters. However, one key advantage of a biochar strategy is that, assuming that the provision of key functions is limited only by the longevity of the biochar, its stability would dictate that annual or even regular applications would be unnecessary to obtain benefits.

Widespread use of non-waste feedstocks for energy and biochar (or only biochar) could impact not only commodity prices but, in a manner analogous to that seen with large-scale bio-ethanol production in the USA, impact on the economics of continued energy production through feedbacks on land and input prices. This raises complex socio-economic issues that must be considered (The Royal Society, 2008) and modelled (Rokityanskiy et al., 2007). Also, as for any assessment of bioenergy systems, it is essential to define boundaries that spatially allow all possible land-use effects to be assessed, in the context of the overall net greenhouse gas benefit (Searchinger et al., 2008).

The proximity of a pyrolysis facility to an adequate catchment for feedstock must be economically and logistically viable, and can potentially affect the  $CO_2$  -equivalent savings. This is the case for biomass and bioenergy facilities generally. However, for biochar the proximity of suitable locations for biochar application to soil is important as well. If the gathering of feedstock and distribution of biochar occur over the same area, the logistical and cost impacts may not be greatly affected. However, it is important to think about biochar scenarios in a spatial context (Figure 10).

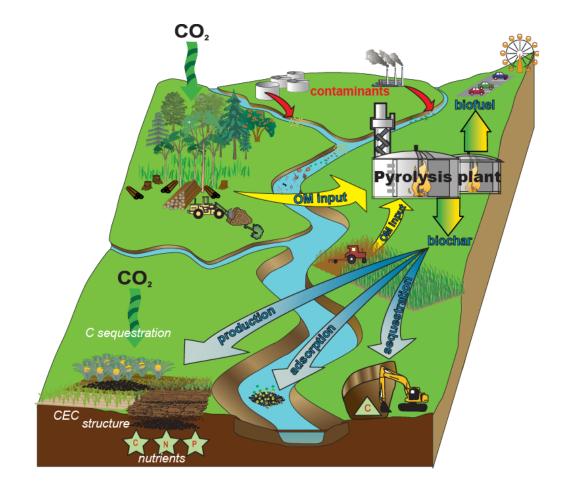


Figure 10. Scenario for multi-feedstock production of biochar, and multi-application use, emphasising the spatial context

Possible off-farm resources include municipal green waste from gardens and parks, composted or compostable urban waste, digested sewage sludge and mixed municipal waste. In addition, in the future, by-products of other bioenergy or bio-fuel systems may be available.

Utilisation of off-farm wastes for biochar production holds the attraction of potential cost savings from avoiding landfill or other disposal charges. In addition, compared to typical or existing disposal methods, there may be a lower emission of  $CH_4$  and  $N_2O$  greenhouse gases than that emanating from direct placement in soil, enhancing the net gain in carbon equivalents through avoided emissions of high GWP gases. However, many such wastes have a high water content which will incur increased emissions (and cost) associated with higher requirement for process energy in pyrolysis.

In a 'closed loop' scenario, biochar is incorporated into the same land, or at least the same enterprise or groups of enterprises, from which the pyrolysis feedstock originates. A typical scenario would involve utilisation of cereal crop straw that in intensive arable areas is often, effectively, a waste product. Although there is no published laboratory work to support the use of biochar produced from wheat straw, there is limited existing information on the relative stability of biochar from rice husk, sugarcane bagasse and straw from maize. In industrial agriculture crop straw may constitute 2 t C ha<sup>-1</sup>. Putting this scenario in the context of the UK

example, with approximately 4 M ha of cereal crops grown, annual total fossil fuel CO<sub>2</sub> emissions amount to 170 M t.

Theoretical comparisons have been made for the carbon-equivalent gain offered by the pyrolysis of maize straw versus use of a dedicated biomass crop (Gaunt et al., 2008). Utilising biomass crops for energy on a large scale has a potential impact on the land available for food production and may exert new pressure on non-agricultural land use.

Biochar produced from the pyrolysis of biomass crops might be incorporated into different agricultural land from where the biomass feedstock was grown. This could be for greater agronomic gain, to apply the product in rotation over a wider area to maximise benefits, or to deal with the cumulative quantity of product. In the combined energy and bio-oil co-production case study considered by Ogawa (2006), the biochar by-product was also returned to adjacent arable land.

Most scenarios considered to date have focused on conventionally managed arable land, where biochar could be added to soil as part of an existing tillage regime. Biochar could be incorporated during conversion of land to no-till, but a strategy of integration into no-till and grazed grassland systems has not yet been considered.

### 3.1.7.4 Forestry

Ogawa (2006) outlined a scheme for carbon sequestration by forestation and carbonisation. This scheme revolved around fast growing plantation tree species fixing atmospheric  $CO_2$ , with the products comprising not only conventional timber, wood chip, and pulp, but diversion of wastes and residues to a carbonisation procedure and re-application of this stabilised carbon back to the plantation soil. This approach has been formally proposed under the Clean Development Mechanism for a scheme in Sumatra, Indonesia.

In the state of Minas Gervais, Brazil, an existing commercial project claims, under CDM, a carbon credit for substitution of coal-derived coke for smelting of iron by pyrolysed plantation eucalypt. The project produces 300,000 t y<sup>-1</sup> charcoal. The charcoal 'fines' that account for about 5% of the product are utilised for briquette manufacture rather than application into soils. In Australia, the potential for integration of oil production from oil mallee trees with processing of wood waste for production of biochar for use in crop production has been examined (McHenry, 2009).

Seifritz (1993) evaluated the size and cost of the carbon gain that could be realised by straight conversion of plantation forest biomass to stockpiled biochar. The scenario included no capture of energy in the conversion, highlighting instead the net primary productivity that is maintained by cropping, and the long lifetime of charcoal compared to the nature and fate of traditional timber products.

In the tropical context, 'slash and char' scenarios have been discussed, where one-off inputs of biochar are made during conversion of land from forest to agriculture (Steiner, 2006), or perhaps 'crop and char', with cycle of positive feedback between one-off, occasional or rotational inputs of biochar and increasing biomass productivity and feedstock resource. In both cases, pyrolysis would be performed using the most basic (and perhaps relatively inefficient) technology such as simple pits of clay kilns. However, as examples of viable, village-scale bioenergy based on gasification technology in developing countries increase, it is conceivable that technological development in tandem with increased income from 'crop and char' practices might ultimately realise combined biochar production and energy capture at the same scale.

In the absence of adequate technological development, charring and manufacture of charcoal may not offer the same benefits to human health as, for example, the substitution of existing biomass burning practices for basic but cleaner and more efficient combustion technology (Wang et al., 1999). Conventional charcoal production may also release methane and other trace greenhouse gases (Edwards et al., 2003). Sub-micron soot particles produced by condensation reactions in gas streams from combustion comprise the most recalcitrant forms (Figure 7) of black carbon but, despite the relatively small quantities of

carbon involved, may be having an important impact on the albedo of both the global atmosphere and ice caps, altering the radiative balance and exacerbating climate change (Ramanathan et al., 2008). Currently the global emission of soot is predicted to decline as rural users of biomass in developing countries switch to clean burning fossil sources (Streets et al., 2004). Charcoal manufacture produces less soot than open burning, but despite the possible scale of future biochar production, its future contributions to the global soot inventory has not been formally examined.

## 3.1.8. Notes on the natural cycling of char in soil

Observation shows that wildfires are a routine natural and indeed often essential feature of many natural grassland, forest and woodland ecosystems, and fire is gradually being incorporated into global ecosystem models (Thonicke et al., 2001). Fire frequency does not appear to decrease soil C by affecting plant productivity (Ansley et al., 2006) and may increase it (Czimczik et al., 2005; Ansley et al., 2006); fire does not destabilize black carbon already present (Ansley et al., 2006) or only partially in organic boreal soils (Czimczik et al., 2005). Studies using remote sensing have attempted to quantify the pattern and frequency of burnings (Seiler et al., 1980) and most estimates suggest approximately 1-5% of standing biomass is converted to black C (Schmidt et al., 2000; Forbes et al., 2006). This figure is much lower than the figure previously proposed by Kuhlbusch (1996), who suggested sequestration into black C during the relatively recent era of forest clearance could explain up to 20% of the so-called missing carbon sink. A detailed analysis in Australia has suggested that natural fire might provide a sink equivalent to 8.3 MtC yr<sup>-1</sup> (Graetz et al., 2003).

In fired-affected systems standing biomass remains in equilibrium, viewed over the long term. However, a modest rate of stable charcoal formation during burning means that the net result of natural fire is that the carbon content of the wider system, including the soil, should gradually increase. However, this is a slow process and difficult to measure in the field with repeated experimental burning (Dai et al., 2005). Given that the net primary productivity of biomass (60 GtC yr<sup>-1</sup>) is quite large relative to the soil C pool (1500 Gt) the black C pool should become dominant in the soil over geological time if this fraction did not degrade at all, even with occasional fire and a low charcoal conversion rate (Graetz and Skjemstad, 2003).

Thus the fact that soil carbon dynamics can be modelled by postulating a relatively small inert- or very slow-turnover pool (Falloon and Smith, 2000; Smith et al., 2000) is an indication that biochar must degrade, at some slow rate, even once transport into water and estuarine sediments is considered (Schmidt, 2004; Simpson and Hatcher, 2004b; Smittenberg et al., 2006) and accounted for (Masiello et al., 1998).

The *Roth-C* soil carbon model explicitly incorporates char as one of its pools (Falloon and Smith, 2000). The inert pool in the *Roth-C* soil carbon model represents more than simply char, but also exceptionally degraded, highly stabilised organic matter (Falloon and Smith, 2000). Radiocarbon dating can be used to experimentally refine the site-specific size of the inert pool to model total soil carbon. However, estimates for a range of sites where such data are available has suggested only a general relationship with soil texture (Falloon et al., 1998). It is likely, however, that long-term field experiments of duration useful in parameterisation of soil C models will provide the data needed to improve on the char pool in the model.

It may be significant that one experimental site where the model does not simulate field measurements well is the site of the Waite plots in Australia, where there is a documented history of burning (Coleman et al., 1997). Also in Australia, Skjemstad (2004b) demonstrated that by re-allocating carbon between soil pools according to a direct measurement of char, the *Roth-C* model may simulate the trajectory of carbon for a range of soils with similar burning history.

In addition, new techniques for quantifying char experimentally (see Section 2.2.3.) reveal that, when applied to a wider variety of sites, observed levels of char were considerably higher than accommodated by the modelled inert pool (Schmidt et al., 1999; Preston et al.,

2006). The implications of this finding for our prediction of climate change feedbacks from enhanced decomposition will become important, as soil models are increasingly linked into global climate modelling (Lehmann and Joseph, 2009b).

Unfortunately the most reliable and direct techniques for quantifying char are currently not sufficiently practical for application at the scale useful to assessing the carbon stock that it represents, at the relevant (global) scales. However, the development of new spectral analysis techniques using mid-infrared wavelengths (Section 2.2.3) may lead to an approach that is both rapid and low cost (Janik et al., 2007).

# 3.2. Biochar, crop productivity and resource management

Conceptually three main mechanisms have been proposed (described in detail below) to explain how biochar might benefit crop production: (i.) direct modification of soil chemistry through its intrinsic elemental and compositional make up, (ii.) providing chemically active surfaces that modify the dynamics of soil nutrients or otherwise catalyse useful soil reactions, (iii.) modifying physical character of the soil in a way that benefits root growth and/or nutrient and water retention and acquisition.

The first mechanism may result in a temporary change in crop productivity, the size and duration of which will be dictated by the natural process of biochar weathering and the effects of crop off-take. This could occur where the biochar has significant mineral nutrient content, or conversely increase in CEC over time as the biochar weathers. If biochar releases these elements, then establishing the fate of biochar carbon during this release is extremely important in the context of the underlying rationale for biochar production and application in soil.

Benefits provided through the second and third mechanisms depend on the long-term physical persistence of biochar and may thus also be finite, although over a much longer timeframe. This would include the impact of porous biochar on water retention or lowering soil bulk density. The magnitude and the relative importance of the three mechanisms in a particular setting will evolve over time as the slow process of chemical and physical modification results in a gradually increasing concentration of smaller, partially-oxidised particles. Evidence for the general resistance of biochar to chemical and biological oxidation is addressed in an earlier section (3.1.5.).

Quantitative evidence for the stability of biochar does not equate to constancy in functional characteristics, since the chemical properties of biochar itself have been shown to develop over time, with implications for functional interactions in the soil environment. In a key multi-parameter study Cheng (2008) showed that properties that become enhanced over time are CEC and pH, as a result of gradual surface oxidation (Section 3.1.5.). The size of biochar particles is relatively rapidly decreased, concentrating in size fractions <5µm diameter (Sections 3.1.5.1. and 3.1.5.5.).

In assessing the agronomic performance of biochar, comparisons should be made against the properties of both the same feedstock un-pyrolysed and alternative biochar produced from other feedstocks. If the feedstock is produced from the same land to which the material is returned (e.g. cereal straw), biochar would not normally substitute all deliberate returns of organic matter to a soil, but rather a one-time or occasional amendment. This is important since as previously noted (Section 3.1.1.) soil fertility depends on degradation of organic matter, and the recycling of plant nutrients. Biochar should be viewed as a mechanism to enhance that process through its moderation, and not its termination. In any case, the material potentially used in pyrolysis, is roughly matched by the amount of labile organic matter exuded into the soil by the plant roots.

## 3.2.1. Soil fertility

Expectation of increased soil fertility benefits arise from studies of the *terra preta* that contains high proportions of black carbon (Haumaier et al., 1995; Glaser et al., 2002; Lehmann et al., 2003; Lehmann and Rondon, 2006). The evident fertility of the *terra preta* is generally attributed to high soil organic matter content – organic matter assists in the retention of water, soil solution and cations – and the retentive capacity of aged biochar itself for nutrients and water (Section 3.2.3 and 3.2.4),

The black carbon present in *terra preta* is thought to originate from partially-combusted biomass residues derived from a range of anthropogenic activities, including kitchen fires and field burning. A particularly striking characteristic is a stronger relationship between soil carbon content and soil CEC in these soils relative to adjacent land, indicating that biochar comprises a greater proportion of soil carbon (Liang et al., 2006). Since CEC is indicative of the capacity to retain key nutrient cations in the soil in plant-available form and minimise leaching losses (Section 3.2.4), this is cited as a key factor where differences in crop productivity are observed.

High rates of biochar addition in the tropical environment have been associated with increased plant uptake of P, K, Ca, Zn and Cu (Lehmann and Rondon., 2006). In contrast to mainstream chemical fertilizer, biochar also contains bioavailable elements such as selenium that have potential to assist in enhancing crop growth.

There has been much speculation concerning the potential effects of biochar on microbial activity in soil, which in the context of *terra preta* has been reviewed in detail by Steiner (Steiner et al., 2003). Assuming that plant inputs and hence microbial substrate remain unchanged, enhanced microbial activity alone would diminish soil organic matter. However, this is contrary to the observation in *terra preta*, where soil organic matter is generally higher than in similar surrounding soil (Liang,2006). However, a change in the balance of microbial activity between different functional groups could benefit crop nutrition, specifically enhancement of mycorrhizal fungi (Ishii et al., 1994), and this could feed back into higher net primary productivity and carbon input.

There is relatively extensive literature documenting stimulation of indigenous arbuscular mycorrhizal fungi by biochar, and this has been reflected in plant growth e.g. Rondon (2007), Nishio (1996). This literature has been reviewed in some detail by Warnock (2007), who proposed four mechanistic explanations, of which a combined nutrient, water and CEC effect was considered most probable.

## 3.2.2. Crop yield

The majority of currently published studies assessing the effect of biochar on crop yield are generally small scale, almost all short term, and sometimes conducted in pots where environmental fluctuation is removed. These limitations are compounded by a lack of methodological consistency in nutrient management and pH control, biochar type and origin. Studies in a wide range of climates, soils and crops have been conducted. It is not therefore possible at this stage to draw any quantitative conclusion, certainly not to project or compare the impact of a particular one-time addition of biochar on long-term crop yield. Nonetheless, evidence suggests that at least for some crop and soil combinations, moderate additions of biochar are usually beneficial, and in very few cases negative.

Glaser (2001) reviewed a number of early studies conducted during the 1980s and 1990s. These tended to show marked impacts of low charcoal additions (0.5 t ha<sup>-1</sup>) on various plant species. Higher rates seemed to inhibit plant growth. In later experiments, combination of higher biochar application rates alongside NPK fertiliser increased crop yield on tropical Amazonian soils (Steiner et al., 2007) and semi-arid soils in Australia (Ogawa, 2006). Due to the year to year variation in climate and its impact on short-term dynamics, results from a number of field experiments recently set up are, whilst generating data, not yet published.

The nature and mechanistic basis for interactions between crop, soil type, biochar feedstock, production method and application rate will have to be understood to gain predictive capacity for the performance of biochar in soil, and open the possibility for large scale deployment.

Authors	Study outline	Results summary	
Iswaran et al (1980)*	Pea, India	0.5 Mgha-1 char increased biomass 160%	
Iswaran et al (1980) *	Mung bean, India	0.5 Mgha-1 char increased biomass 122%	
Kishimoto & Sugiura (1985) *	Soybean on volcanic ash Ioam, Japan	<ul> <li>0.5 Mgha-1 char increased yield</li> <li>151%</li> <li>5 Mgha-1 char decreased yield to</li> <li>63%</li> <li>15 Mgha-1 char decreased yield to</li> <li>29%</li> </ul>	
Kishimoto & Sugiura (1985) *	Sugi trees on clay loam, Japan	<ul> <li>0.5 Mgha-1 wood charcoal increased biomass 249%</li> <li>0.5 Mgha-1 bark charcoal increased biomass 324%</li> <li>0.5 Mgha-1 activated charcoal increased biomass 244%</li> </ul>	
Chidumayo, (1994}*	Bauhinia trees on alfisol/ultisol	Charcoal increased biomass by 13% and height by 24%	
Glaser (2002)	Cowpea on xanthic ferralsol	67 Mgha-1 char increased biomass 150% 135 Mgha-1 char increased biomass 200%	
Lehmann (2003)	Soil fertility and nutrient retention. Cowpea was planted in pots and rice crops in lysimeters at the Embrapa Amazonia Ocidental, Manaus, Brazil	Bio-char additions significantly increased biomass production by 38 to 45% (no yield reported)	
Oguntunde (2004)	Comparison of maize yields between disused charcoal production sites and adjacent fields. Kotokosu watershed, Ghana	Grain yield 91% higher and biomass yield 44% higher on charcoal site than control.	
Yamato (2006)	Maize, cowpea and peanut trial in area of low soil fertility	Acacia bark charcoal plus fertiliser increased maize and peanut yields (but not cowpea)	
Chan (2007)	Pot trial on radish yield in heavy soil using commercial greenwaste biochar (three rates) with and without N	100 t ha <sup>-1</sup> increased yield x3; linear increase 10 to 50 t ha <sup>-1</sup> - but no effect without added N	
Rondon (2007)	Enhanced biological N-2 fixation (BNF) by common beans through bio- char additions. Colombia	Bean yield increased by 46% and biomass production by 39% over the control at 90 and 60 g kg(-1) bio- char, respectively.	
Steiner (2007)	Four cropping cycles with rice (Oryza sativa L.) and sorghum (Sorghum bicolor L.)	Charcoal amended with chicken manure amendments resulted in the highest cumulative crop yield (12.4 Mgha <sup>-1</sup> )	
Kimetu et al. (2008)	Mitigation of soil degradation with biochar. Comparison of maize yields in degradation gradient cultivated soils in Kenya.	doubling of crop yield in the highly degraded soils from about 3 to about 6 tons/ha maize grain yield	

Table 5. Sum	mary of experime	ents assessing the	impact of biochar	addition on crop yield

\*source of selected references (Woolf 2008)

#### 3.2.3. Soil moisture retention

In soil science the following principles are widely accepted and published (summarised in Krull et al. 2004): The mineral and organic components of soil both contribute to soil water holding capacity, but only the latter can be actively managed. Water is held more tightly in small pores, so clayey soils retain more water. The lower soil bulk density generally associated with higher soil organic matter is a partial indication of how organic matter modifies soil structure and pore size distribution.

Many studies where the effect of biochar on crop yield has been assessed have cited moisture retention as a key factor in the results. Given that the pore size of biochar is relatively fixed, whereas that of the mineral soil is determined primarily by texture, it may be expected that charcoal increases available moisture in sandy soil, has a neutral effect in medium textured soils, and decreases available moisture in clayey soil. Any effect of biochar particle size may be short-lived, as it appears to physically break down into fine fractions relatively quickly (Section 3.1.5)

Experimentally, the usual technique for assessing pore size characteristics is the moisture release curve, which indicates how quickly soil moisture is drawn from a soil under increasing tension. The method is well suited to discriminating differences between soils of contrasting texture, but its sensitivity may be less satisfactory for discriminating the effect of contrasting management at one specific location: high levels of replication may be necessary to show a significant impact of a management intervention of realistic magnitude.

In a more recent study (Gaskin, 2007), moisture release curves were determined using samples of loamy sand soil from a field experiment where biochar had been added at rates up to 88 t ha<sup>-1</sup>. For soils where biochar was added at rates up to 22 t ha<sup>-1</sup> there was no difference compared to non-amended soil, but at the highest rate the difference was significant at water potentials in the range 0.01–0.20 MPa. At the highest potential the mean volumetric water content impact was doubled by the biochar addition.

Soil temperature, soil cover, evaporation and evapotranspiration affect available water in soil. Comparison of actual volumetric water content between biochar-amended and control soils in field experiments may therefore be confounded by any indirect effect of biochar on plant growth and soil thermal properties.

Soil organic matter increases soil water holding capacity and in the biochar-enriched *terra preta* with their associated higher levels of soil organic matter, Glaser (2002) reported a water retention capacity that was 18% higher than in adjacent soils in which charcoal was low or absent. This was likely a combined effect of the char itself and the higher levels of organic matter that this promotes (Section 3.1.6.4).

#### 3.2.4. Nutrient retention and use-efficiency

There are several reasons to expect that biochar might decrease the possibility of nutrient leaching in soils, and enhanced nutrient cycling has been cited in various field studies for positive impacts on yield. However, very few studies have demonstrated the effect or attempted quantitative description of the mechanism.

In general, the mineral and organic fractions of soil can both contribute to overall CEC, which affects the ability for soils to buffer periodic flushes of ammonium that result from application of chemical fertilisers or manures, or bursts of organic matter mineralisation during favourable, seasonal conditions. The adsorption of ammonium ions is a relatively loose association that does not necessarily prevent plant acquisition, yet greatly mitigates the potential for leaching loss and the diffuse pollution issues of drinking water quality and eutrophication of riverine and estuarine water bodies. Since considerable fossil energy is

required to fix nitrogen into fertiliser (Section 2.1.3.6), a low ratio of fertiliser nitrogen application to crop nitrogen uptake can impact the overall carbon balance of agricultural activities (see Section 3.1.6.1). Higher fertiliser use efficiency should lead to a lower fertiliser requirement per unit yield and usually lower nitrous oxide emission (Section 3.1.6.2).

Only certain mineral constituents of soil contribute to CEC on account of abundance, and hence surface area, and mineralogy, with certain types of clay being most important. On a mass basis the exchange capacity of soil organic matter may be greater than for any clay (and up to 50 times greater), but it is a relatively small proportion of soil mass in most agricultural situations, particularly under tropical conditions. Given these factors, heavy textured soils under climates that favour higher levels of organic matter show the highest contributions of organic matter – about one-third – to total soil CEC (Stevenson, 1982). Since mineralisation of organic matter is a major source of ammonium release in soil, attempts to raise soil organic matter by increasing rates of input may not decrease – and can potentially increase – leaching losses. In addition to the chemical stabilisation of nutrients, the physical structure of soil determines its capacity to hold water, and hence soil nutrients in solution (Section 3.2.3 above).

There are several reasons to expect that biochar might modify leaching potential in soils. Available evidence suggests that on a mass basis, the intrinsic CEC of biochar is consistently higher than that of whole soil, clays or soil organic matter. An analogy may be drawn to the extreme CEC of activated carbon, which is relevant to its function as a sorption medium for decolourisation and decontamination. Since secondary thermal treatment of charcoal is one means of carbon activation, it is not surprising that the process parameters impact the CEC of primary biochar products with temperature increasing this property (Gaskin, 2007). This is a function of both enhanced specific surface area and the abundance of carboxyl carbon groups that they display. The indirect affect of biochar that may result from its modification of soil pH has not yet been included in most studies by, for example, applying lime to the control soil.

Whilst determination of CEC and water release curves in homogeneous materials such as biochar should be straightforward, it is more complex to quantitatively determine the contribution of biochar once added to soil. Furthermore, the observation that CEC of biochar may develop over time through both abiotic and biotic modification of its surfaces (Cheng et al., 2006) implies that in order to develop a predictive, quantitative understanding, methods to recover aged biochar from soil is required.

Information on the CEC of pyrolysis products is limited mainly by the availability of materials produced from a sufficiently diverse range of feedstock under different production conditions. Information on the CEC of char naturally present in soils is limited by isolation methods, so available studies tend to rely on a comparison of whole soils amended and non-amended with biochar (Lehmann, 2003; Liang, 2006).

The second mechanism for mitigation of leaching relates to the physical retention of soil water, which may be enhanced by biochar in coarse-textured soils and any indirect effect of biochar on the accumulation of soil organic matter (see previous, Section 3.2.3).

The inherent stability of biochar confers a distinction between the CEC benefits that are possible compared to other soil organic matter; importantly there is no immediate constraint to the level that can be attained by repeated addition, so in principal this capacity could be incrementally enhanced. Provided that biochar is biologically stable (Section 3.1.5), the benefit of higher CEC may be obtained without the risk of contributing to seasonal flushes of nitrate.

The possible contribution of modified soil water dynamics and CEC to the apparent effects of biochar on nitrous oxide emission were discussed in Section 3.1.6.2. In addition to mitigating greenhouse gas emissions, limiting gaseous nitrogen loss can be relevant to crop fertiliser requirement.

A beneficial impact of biochar on the plant-available phosphorus has been observed in soils enriched with biochar, which in contrast to ammonium, is not a characteristic generally associated with soil organic matter (Lehmann, 2007b; Steiner et al., 2007). In the context of nutrient availability, the impact of biochar addition on pH may be important.

#### 3.2.5. Use of biochar to manage water quality

Biochar may offer benefits in reducing diffuse pollution originating from agriculture through deployment in soils from which polluting elements arise. It may also be possible to utilise its sorptive capacity to remove contamination in the water treatment process. Studies that demonstrate the capacity for biochar to remove nitrate (Mizuta, 2004) and phosphate (Beaton, 1960) in this context have been cited, and in by-passing the complexity of the soil system, controllability is achieved. However, whilst biochar may loosely hold nutrient elements in a plant-available form, the by-product of water treatment could also be contamination by toxic organic compounds in wastewater; biochar also has an affinity for organic compounds (Kookana, 2006). This could confound use of the post-treatment biochar product on land; the economic and overall carbon and environmental gain to be achieved from centralised versus diffuse deployment for management of water quality have yet to be assessed. The precedent for a centralised approach is the current use of activated carbon for the removal of chlorine and organic chemicals such as phenols, polychlorinated biphenyls, trihalomethanes, pesticides and halogenated hydrocarbons, heavy metals, and organic contaminants (Boateng 2007). It is not clear whether the higher surface area and sorptive capacity resulting from activation of biochar from agricultural crop wastes (Zanzi, 2001) results in significant differences compared to biochar.

### 3.2.6. Potential risks to soil and water from use of biochar

Charcoal production and use appears engrained in many cultures and the apparent success and longevity of the civilisation that created the *terra preta* provides some reassurance as to the long-term safety of biochar incorporation to soil. Currently in Japan, a strong tradition in the use of charcoal as an authorised soil improver for horticultural and agricultural applications means that 15,000 t of carbonized material is annually applied to soil (Okimori et al., 2003).

Nonetheless, a critical and non-prescriptive experimental analysis of risks that might arise from the deployment of biochar has not been undertaken according to modern criteria, taking into account all risks associated with production, distribution and physical application of biochar, as well as its impacts in the soil. The analysis must also be based around products of slow and fast pyrolysis, rather than simply biomass carbonisation.

This assessment is critical for three reasons: the irretrievability of biochar once added to soil, the apparent general permanency of biochar once in the soil and the scale and speed at which the strategy needs to be implemented to contribute to climate change mitigation. In addition, the issue of responsibility and liability with respect to large scale application to land is an impediment for companies seeking to invest in the production of biochar or the sale of food products from treated land, as well as being a moral and political issue for Government and regulatory bodies.

To date, available information is focused on the two classes of toxic compounds that are associated most often with combustion processes, namely PAHs and dioxins. Dioxins predominantly form at temperatures in excess of 1000°C and there are no published studies to confirm their absence in biochar products (Garcia-Perez, 2008).

The proliferation of PAH in secondary pyrolytic reactions above 700°C is well established (Ledesma et al., 2002), but smaller quantities may form in the temperature range of pyrolysis reactors (Garcia-Perez, 2008). Unpublished analyses of several biochar samples also found a PAH content no greater than that of bulk soil (Manning, pers. comm.); a single published study examined the full PAH profile (40 individual PAH compounds) in a number of synthetic char samples manufactured at relatively high heating rate concentrations (Brown, 2006). Total PAH concentration was  $3-16 \ \mu g \ g^{-1}$ , depending on peak temperature, compared to  $28 \ \mu g \ g^{-1}$  in char from a prescribed burn in pine forest. Information contained in PAH may

provide a measure of thermal history (Brown 2006), but empirical relationships to relate them to process parameters have not been defined.

The above analyses determine principally the total initial content. It is not clear over what timescale these compounds are altered in the soil, and most importantly, the bio-available component in soil is not known. However, it has been stated by Ahmed (1989) that whilst biochar should contain systems of PAH, existing evidence indicates that no leachable PAH is present.

No results of bio-assays using biochar in soil have been reported, nor have the appropriate biochar concentrations been defined in the context of the accumulations that might occur in water and marine sediments.

# 4. POLICY CONTEXT AND ANALYSIS

# 4.1. A framework to evaluate applications of biochar

The strategies for the use of biochar considered here are those that result in biochar being applied to soil on a significant scale. The strategies take a broad geographic perspective and look to avoid significant practical, regulatory or economic obstacles. They therefore are those situations where the benefits exceed the price of the biochar product; benefits may apply to the economy as a whole, arise from economic benefits for the individual enterprise or provide other non-monetary benefits from the use of biochar in soil. Non-monetary benefits include the opportunity cost to a biochar producer of not utilising the pyrolysis residue in combustion to realise its residual energy content.

However, the application of biochar to land must also be in accordance with regulatory frameworks and law and until relevant standards are defined, the direct costs to individual users in addressing these controls may be prohibitive. Although scenarios might involve large scale bioenergy and industrial agriculture, the same framework should be used to evaluate its potential contribution to subsistence or slash-and-burn agriculture. However, although these practices contrast quite starkly, like soil and climatic factors, farming practices occur over a continuum of different scales, and these examples sit at opposite extreme ends. As such, it will be highly advantageous to define a single framework for assessment and comparison of different biochar scenarios for their net carbon benefit and socio-economic impacts.

Separate evaluations should be made for the economic and environmental sustainability of alternative biochar scenarios. If the assured carbon-equivalent gain available using biochar is positive but the economic analysis for mainstream agriculture negative, then utilisation of economic instruments – most likely carbon trading or a subsidy that ensures biochar is used in soil rather than for combustion – is essential. The introduction, expansion or revision of such instruments that place a monetary value on the utilisation or disposal of organic waste, maintenance of soil quality and support for renewable and bioenergy as a whole may then be considered.

For any biochar scenario it is possible that the agronomic value for biochar is sufficient to render the economic evaluation positive, without resorting to carbon markets or Government incentives. Then concerted research effort will be sufficient to establish certainty around the extent and realisation of such benefits.

# 4.2. Scenarios for the uptake of biochar for use in soil

Even pending further research, biochar may be attractive to producers of high value crops, where certain characteristics of biochar (such as water storage) have high economic value. In these markets the price of biochar may be acceptable even in the absence of subsidy or payment. Some additional brand value may be derived from the carbon balance of the production system but would not be the driver of the system. Biochar could also be profitably

employed on recreational land or on sports turf. Such applications may increase recognition, but will not provide the extent of use required to contribute to climate change mitigation.

Currently, uncertainty around the expected benefits and potential returns at current prices is likely to limit widespread use in mainstream agriculture. This uncertainty stems from inadequate understanding or quantitative description of the underlying processes and the multiplicity of potential benefits and interactions.

Key biochar characteristics will vary according to the nature of the agricultural management system, soil and climate, and may not be static over time. The number of useful biochar properties and their relative importance will vary accordingly, but at the moment the understanding necessary to produce biochar optimised to deliver a particular balance of properties – especially in tandem with viable energy capture – does not yet exist. The complexity and diversity of decision making on farms, and the susceptibility of soil management strategies to commodity prices and external economic forces is important too.

To date, assessments of the benefits to be derived from applying biochar to soil have been made on the basis of very limited experimental evidence, and are often scoping studies based on generalised situations. The sensitivity of proposed scenarios to the spatial dimension presented by climate is improving but still inadequate in predictive terms. Comprehensive, whole-system life-cycle analyses (LCA) with full accounting are required in order to avoid unintended negative consequences. In such analysis it will be recognised that deliberate accentuation of one biochar characteristic may impact on the delivery of others, for example porosity versus nutrient value. Thus not only does the predictive capacity for biochar 'performance' not currently exist, but the feasibility of optimising multiple useful characteristics is not known. This is inhibiting realisation of other benefits to the wider system.

In the financial evaluation of biochar technologies it is important to consider not only current prices, which are known or can be determined, but also their likely future value. Given the current trajectory of global greenhouse gas emissions, the price of emissions as a tradable commodity will be increasingly important. The future price of fossil fuel and subsidy levels for renewable energy are difficult to predict. However, the indirect gains from the use of biochar will probably increase with the future price of fossil energy, reflecting the generally energy-intensive nature of the key inputs associated in mechanised agriculture, and possibly with finite supply of water (irrigation costs). There will be a corresponding increase in value of the residual energy in biochar as fossil energy prices rise. The price of bioenergy may also be enhanced by Government subsides designed to improve energy security and promote environmental goals. In many industrialised countries the opportunity cost associated with using biochar in soil is artificially enhanced by renewable energy subsidies. The future price of grains and other commodities is difficult to predict, but changing diet, a growing global population, and increasingly limited supply of new agricultural land is likely to increase demand relative to supply.

## 4.3. Market intervention and carbon trading

Markets for the sale of pyrolysis feedstocks are not currently accessible, and markets for potential feedstocks are ill-developed. A market for credits relating to 'avoided emissions' in which land managers could engage does not yet exist. In general, there also remains a lack of knowledge and awareness of bioenergy and carbon markets, how to access these markets, and particularly a way to accurately evaluate costs and benefits associated with the use of biochar in soil.

In the absence of research to support the optimisation of biochar and its agronomic evaluation, the viability of biochar-based soil management based on carbon-offsets alone is important. However, no framework exists within which the carbon sequestered in biochar can be certified as a tradable commodity. This barrier extends beyond carbon trading under the UN Clean Development Mechanism (CDM) to the voluntary carbon markets. To date the methodology required to recognise the stabilisation of degradable organic matter as an

'avoided emission' of  $CO_2$  has not been presented, although this is a current activity within the International Biochar Initiative.

Additional evidence for the portion of biochar that can be considered stable over the long term is required. Furthermore, research is required to determine whether the carbon-equivalent benefits of biochar application to soil extend beyond direct carbon sequestration or the avoidance of other greenhouse gas emissions. At the moment these effects are not fully understood or proven in the predictive sense, nor have the timescales over which they mainly occur been established (Section 3.1.5.). However, the existence of a current methodology for stabilisation of organic matter in avoidance of methane emission represents an important precedent (UNFCCC).

Various national Governments have implemented carbon trading schemes in order to meet emission reduction commitments under the Kyoto protocol. This has resulted in the European Union Greenhouse Gas Emission Trading Scheme and subsidiary schemes such as the UK Emissions Trading Scheme. More recently, Australia has announced plans for a Carbon Pollution Reduction Scheme (Anon, 2007c).

In these countries, their regional neighbours and in the USA there is a strong market for voluntary carbon trading carbon. Individuals or organisations engage outside of Government requirements in a market currently valued in excess of USD 30 billion yr<sup>-1</sup>. Offsets traded in the voluntary market are unregulated, and their credentials have been questioned. Biocharbased schemes should offer the opportunity to trade a more demonstrable offset (by virtue of the visibility and durability of biochar in soil), that has community as well as climate benefits through its impact on agriculture. However, there is an expectation within some NGOs that the inclusion of biochar into any carbon trading scheme will ultimately lead to large projects based around dedicated biomass crops that will not benefit agriculture and put additional pressure on rural livelihoods in developing countries as a consequence of land acquisition. Other major NGOs have not yet adopted a specific position on biochar.

Alongside the IBI, pressure groups such as the US-based Clean Air Task Force have been promoting biochar based offsets alongside other bioenergy schemes for trading in all carbon markets (Baum et al., 2006).

## 4.4. Market acceptability issues

There are significant organisational and institutional obstacles to the use of biochar in soil. Since biochar could be used on a wide scale and cannot be removed from soil once applied, there is a need to carefully assess any potential negatives in occupational health (possible inhalation risks from physical application to soil), environmental pollution (particulates travelling into water or air), water quality (impacts on aquatic life and water treatment) and food safety (surface and systemic contamination of food products). Since several sectors are involved – broadly water, waste and food safety – it requires a concerted effort to evaluate potential products, and ideally define product standards. Support for the use of biochar in meeting policy objectives will draw upon life-cycle analysis with full greenhouse accounting, backed by a body of experimental data. Where biochar is designated as a regulated waste material, land-users in many countries may be subject to a complex and expensive approval process pending defined standards.

However, the political and economic case for using food crops as feedstock for liquid biofuel production (bioethanol), or devoting large land areas to biomass production for bioenergy, is increasingly challenged in the context of rising commodity prices and increasing land pressure. Strategies based around pyrolysis with the use of biochar in soil are distinct from these, since productivity and sustainability of land is potentially enhanced. Globally, rising prices favour cash-crop farming, and the economic case for applying biochar to land is likely to improve.

The lack of mechanistic understanding as to the function of biochar and its interaction with already complex soil processes, mean predicting the return to an investment in biochar between locations in terms of extent, predictability and durability of benefits does not yet

exist. Providing a measure of certainty to the many possible benefits is a key challenge to be addressed by further research.

# 4.5. Research

To date there are a limited number of examples of large-scale publicly funded research initiatives that assess the use and optimisation of biochar for use in soil. In New Zealand the Massey University has a Biochar Research Initiative. In the UK the Engineering and Physical Sciences Research Council supports two established projects, one building capacity in technology for fast pyrolysis (as part of a wider bioenergy initiative, SUPERGEN) and testing by-products in soil, and the other developing Carbon Sequestration and Capture technology. Brazil has funded second and third tier levels within 'macro-programs' defined by the research organisation, EMBRAPA. These will extend field experimentation to create new *terra preta (terra preta nova*). At Federal Government level, the US has created the Farm Bill that supports 'biochar research development and demonstration' which seeks to enhance agricultural energy programs (Anon, 2007b). Biochar was specifically mentioned in the Garnaut Climate Change Review in Australia (Garnaut, 2008) and has been raised in Environment Select Committee discussions in the UK.

Currently much of our understanding of the long-term dynamics of biochar is based on studies of charcoal from natural fire, new charcoal produced using traditional methods or analogous procedures undertaken in the laboratory. Studies in Brazil use charcoal fines (waste) from industrially produced charcoal. However, only a small number of comprehensive studies using the products of commercial bioenergy plants currently exist, and although the conditions used to produce these products has been guided by preliminary studies, those conditions may not have been optimised for the soil into which they have been incorporated. The only full-scale field trials using biochar from slow pyrolysis energy plants are being conducted in NY, USA

(<http://www.css.cornell.edu/faculty/lehmann/research/biochar/biocharproject.html>).

5. RESEARCH PRIORITIES AND FUTURE CHALLENGES

Based on the results of this review, the following research priorities have been identified:

- 1) Determine a predictive relationship for properties and qualities of biochar and its manufacture such that it can be optimised for use in soil.
- 2) Examine how the possibility of adverse impacts on the soil and atmosphere can be eliminated with certainty.
- 3) Model the impact of alternate bioenergy systems on the carbon cycle at the global scale, and in the context of national targets, in order to support policy decisions and devise suitable market instruments.

Since the underlying context for biochar-based strategies is that of global climate change, research needs to provide answers that are applicable under diverse combinations of climate, agriculture and energy production systems. This requires a fundamental, mechanistic understanding of how biochar provides its unique functional characteristics, probably embodied in models, and would include its interactions with other living and non-living components of soil.

Globally coordinated research activity across a range of countries and climates is necessary if the global applicability of knowledge gained is to be rigorously assessed.

# 5.1. Fundamental mechanisms

The fundamental mechanisms by which biochar could provide beneficial function to soil and the wider function of the agro-ecosystem are poorly described in terms of providing the predictive capacity that is required.

In short-term experiments of months to a few years, biochar addition seems to generally enhance plant growth and soil nutrient status and decrease  $N_2O$  emissions. Yet surprisingly little is yet published concerning how these benefits occur, or particularly why the effects are quantitatively so variable according to crop, soil and application rate. Soil-biochar dynamics need to be investigated. The required understanding will have to be obtained in the following areas:

- a) Functional interactions with soil microbial communities. Biochar may modify the symbiotic relationships that exist in the rhizosphere, that is between plants and microbes in close proximity to the root. At the moment the net effect of physical protection provided to microbial colonies, and adequate access of the same colonies to labile and soluble carbon substrates is not yet known. The component of biochar stability provided by association of individual biochar particles and fine mineral particles has not been established, and the role of microbial and rhizosphere secretions in promoting them will be important. Fundamentally, the apparent conflict between high stability, soil organic matter accumulation and apparent enhancement of soil microbial activity needs to be resolved. Useful methods will separate indirect effects of increased water holding capacity or altered water release characteristics, pH effects, and allow for their potentially transitory nature.
- b) **Surface interactions.** It seems that as the exchange capacity of biochar surfaces develops over time, the contribution of feedstock and production parameters to the trajectory of its development will need to be established. Once the relative importance of biotic and abiotic processes in promoting this development are known, and the net effect of any simultaneous change in the ratio of external- to internal-surface resulting from physical disintegration under soil movement quantified, the net effect of climate might be predicted. Interaction of biochar with anions, most importantly phosphate, needs to be established, and the extent to which nutrient effects are internal, i.e. derived from within the biochar (finite), and external, supplied by the wider soil, must be determined.
- c) **Nutrient use efficiency.** Understanding the link between biochar function and its interaction with nutrient elements and crop roots may enable fertiliser use efficiency to be enhanced and diffuse pollution of watercourses and wetlands.
- d) Soil physical effects. The intrinsic contribution that biochar can make to the wetability of soil, water infiltration, water retention, macro-aggregation and soil stability is poorly understood yet should be of critical importance in tropical environments in combating erosion, mitigating drought and nutrient loss, and in general to enhance groundwater quality. The loss of biochar through vertical or lateral flow is not well understood; only recently have studies been initiated to examine movement down the soil profile.
- e) **Fate of biochar.** The stability of biochar carbon is intrinsic to fulfilling its role as a significant CO<sub>2</sub> sink, but in order to perform an agronomic role, it must also remain within the soil to which it is applied. The environmental role or impact of biochar once it has moved through a soil profile, or into watercourses, is yet to be assessed. Information on the extent to which physical breakdown of biochar changes the balance in its properties, particularly with respect to soil water dynamics, exchange capacity and soil micro-and macro-aggregation is lacking. Methods are urgently required to assess the long-term biological stability of specific biochar samples, possibly extrapolating from the dynamics of atypically high initial rates of decomposition.
- f) Impacts on soil N<sub>2</sub>O and CH<sub>4</sub> emission. Published data for the effect on trace gas emission is extremely limited, but has a potentially great impact on the net benefit of a biochar strategy. Good predictive models will be necessary for this to be reflected in future

accounting for biochar projects, and at the moment there is not a clear mechanism for the effect.

g) **Plant physiological responses** to biochar ultimately dictate impacts on growth and yield and need to be directly targeted in future work.

## 5.2. Properties, qualities and environmental risk assessment

As the mechanisms underlying biochar function in soil become understood, biochar products can be optimised to deliver specific benefits using a defined screening procedure based on relevant properties. Research tools for comparing different biochar products already exist from at least two decades of work on charcoal and other black carbon in soils: <sup>13</sup>C nuclear magnetic resonance spectroscopy has proved perhaps the most useful in revealing gross differences in composition at the functional group level. However, a screening approach should be defined by relevant properties rather than available measurement techniques. Also a cheap and rapid method procedure appropriate to routine analysis has not been identified. The following research is needed:

- a) Scoping. A comprehensive and systematic analysis of commercially available biochar products, including charcoal produced by industrial- and farm-scale carbonisation processes, to scope the boundaries of variation in compositional and functional characteristics of biochar. This should utilise all available techniques and link to a database recording the type of biomass from which the biochar was produced, and the type and details of the production process for correlative analysis.
- b) Benefits and risks. Thorough environmental and agronomic evaluation of biochar in soil will enhance its acceptability as a large-scale offsetting and sequestration strategy for CO<sub>2</sub>. However, the incorporation of biochar into soil is irreversible and therefore must be safe, with biochar products free of potentially harmful contaminants.
- a) Inventory. A systematic screening of biochar products is required, in tandem with the above, to establish the presence and absence of phytotoxic materials that could conceivably be formed during pyrolysis. This will establish the range of potentially harmful chemical contaminants present and their peak concentrations, providing evidence essential to the preparation of risk assessments. Key compounds will be polycyclic aromatic hydrocarbons, established products of partial combustion, and residual oils and acids.
- b) Air pollution. The environmental impact of vapours and gases produced in open combustion associated with traditional charcoal production and in sub-surface combustion, needs to be carefully evaluated, along with the technological developments required to address it. These emissions can cancel out carbon sequestration if not contained or used in the process.
- c) **Waste pyrolysis.** The potential for urban waste to be used in biochar production needs to be assessed. A risk-based approach may dictate that such materials are more suitable for gasification than pyrolysis if harmful compounds are abundant. It is not known whether the low quality biochar produced from these waste streams is suitable to deliver sequestration and soil benefits.
- d) Indirect impacts. The implications of rapid expansion in biomass pyrolysis on agricultural and natural land areas is a concern through, for example, the expansion of fast-growing plantation forest for production of feedstocks for biochar or charcoal production. There is also the possibility of increased deforestation if the technology is allowed to expand in an uncontrolled way.
- e) **Scrubbing air pollutants.** Biochar has been reported to scrub CO<sub>2</sub>, nitrous oxides and sulphur dioxide from fuel gas, creating a nitrogen-rich biochar product that could substitute conventionally produced chemical fertiliser. Since this approach addresses the practicality of application and offers added benefits, it needs to be pursued and refined.

# 5.3. Carbon cycle modelling

Two types of carbon modelling are required: static spreadsheet models to compare alternative scenarios for their relative carbon-equivalent gain, and mechanistic soil simulation models that capture information from short term experiments to predict longer-term impacts on soil function. In addition, socio-economic models that incorporate a spatial dimension are required to assess the workability of particular scenarios.

- a) Modelling net carbon gain. So far only generic, theoretical analyses have been published. Full assessment spreadsheet models based on improved experimental evidence are required to conduct 'what-if' comparisons of alternative strategies for specific feedstock streams and pyrolysis facilities, taking the spatial dimension of feedstock supply and biochar use into account.
- b) Mechanistic soil modelling. Modelling of the linked carbon and nitrogen cycles in soil with and without intervention using biochar is essential to understanding the fundamental mechanisms referred to above, and the impact on soil-based emissions of greenhouse gases. Modelling of soil carbon currently relies on conceptual pools, and essentially ignores black carbon from a mechanistic perspective. Progress in this area is dependent on improved quantification methods for biochar in soil.
- c) **Economic models.** Conceptual and actual geographic boundaries must be carefully set when assessing a particular scenario, accounting for the entire supply chain. Socioeconomic constraints relevant to the application of biochar must be recognised.
- d) **Audit.** A standard methodology for validation and audit of biochar application is required that ideally permits the source of a particular biochar application to be confirmed retrospectively.
- e) **Databases.** International support for a global system that enables optimal biochar products to be selected for application in a particular location and system. The only such database initiated to date is CharDB, at Terra Carbona (<<u>http://terracarbona.org/chardb/</u>>).

# 5.4. Beneficiaries

**Pyrolysis enterprises.** In areas where biochar may be produced for agricultural or environmental gain rather than energy production, NGOs may be interested in exploring the pyrolysis biochar technology. Market development would facilitate the dialogue between producers and investors as well as researchers and users. Currently the amount of biochar available for use as a soil amendment (and hence carbon sequestration) is limited to an extent where even assessment of products for non-energy use is limited.

**Charcoal producers.** Traditional producers may experience expansion in the market for charcoal if its use as a soil amendment is supported by land-users for carbon sequestration or enhancing soil fertility. There is a precedent for charcoal being produced on a commercial scale within Europe, with almond charcoal supplied to power companies in Spain.

**Water companies.** Larger scale production of activated charcoal from pyrolysis-derived biochar could reduce costs. Large scale use of biochar on agricultural land in intensively farmed areas may also reduce diffuse pollution and the need, and hence costs, for treatment of water.

**Land users.** Individual farms or farming consortia would benefit due to greater profitability as a result of savings on energy and fertilisers. Remediation of degraded or contaminated land using biochar could be supported through Government, engaging the agricultural community and supported by environmentally-oriented incentives and subsidy.

# 5.5. Commentary on likely barriers to the adoption of a large scale enterprises utilising Biochar

If the technical limitations described above are addressed and if biochar-related techniques are judged to be viable methods to address climate and agricultural problems, then it is likely that additional barriers to widespread adoption will remain. This section provides a commentary on these barriers.

The economics of biochar production will be fundamentally altered once methodology has been proposed and adopted with regard to carbon offset values, in the voluntary market, and as a longer-term possibility, certification under the United Nations Framework Convention on Climate Change (UNFCCC) clean development mechanism (CDM).

A streamlined regulatory framework may be essential to avoid stifling initial interest in the use of biochar products in mainstream agriculture. Government policies to help ensure continuity of feedstock supply to pyrolysis enterprises could assist in establishment of the industry; subsidy arrangements could be adopted that favour rather than discriminate against the use of biochar in soil.

A routine standard method to quantify biochar in soil is essential to realise the research agenda. Supply of biochar material from commercial pyrolysis facilities is currently extremely limited and localised, inhibiting research activity. Biochar is highly heterogeneous, so standards and quality control need to be defined and certified.

Association of pyrolysis with wider bioenergy technology and specifically the biofuel debate presents an image problem in the wake of diminished global grain stocks and rising commodity prices. However, this could also present forums where the principle and multiple benefits of biochar-based strategies can be discriminated and promoted.

The multi-disciplinary nature of the biochar concept seems to inhibit large-scale funding of the extensive research agenda, particularly the large sums required for long term trials. It also appears that assigning responsibility for researching biochar within Government and between public and private sectors is challenging. Funding for testing commercial products may be borne by companies producing the products, but such activities will need to be integrated with public sector science to address the wider climate change agenda.

# REFERENCES

- Ahmed, A., Pakdel, H., Roy, C., Kaliaguine, S., 1989. Characterization of the solid residues of vacuum pyrolysis of Papulus Tremuloides. Journal of Analytical and Applied Pyrolysis 14, 281-294.
- Anon, 2007a. Early action abatement incentives prior to the commencement of the Australian Emissions Trading Scheme. In: The Australian Government, Department of the Prime Minister and Cabinet, pp. 16.
- Anon, 2007b. Harvesting Energy Act of 2007. In: US Senate, United States of America.
- Anon, 2007c. Australia's climate change policy : our economy, our environment, our future. In: The Australian Government.
- Anon, 2008. Gasification: redefining clean energy. In: Gasification Technologies Council, Arlington, VA, pp. 25.
- Ansley, R.J., Boutton, T.W., Skjemstad, J.O., 2006. Soil organic carbon and black carbon storage and dynamics under different fire regimes in temperate mixed-grass savanna. Global Biogeochemical Cycles 20, B3006.
- Arias, B., Pevida, C., Fermoso, J., Plaza, M.G., Rubiera, F., Pis, J.J., 2008. Influence of torrefaction on the grindability and reactivity of woody biomass. Fuel Processing Technology 89, 169-175.
- Ascough, P.L., Bird, M.I., Brock, F., Higham, T.F.G., Meredith, W., Snape, C.E., Vane, C.H., 2008. Hydropyrolysis as a new tool for radiocarbon pretreatment and the quantification of black carbon.
- Baldock, J.A., Smernik, R.J., 2002. Chemical composition and bioavailability of thermally altered Pinus resinosa (Red pine) wood. Organic Geochemistry 33, 1093-1109.
- Bapat, H.D., Manahan, S.E., 1998. Chemchar gasification of hazardous wastes and mixed wastes on a biochar matrix. Abstracts of Papers of the American Chemical Society 215, U571-U571.
- Baskin, Y., 2006. Slash-and-char improves Amazonian soil. BioScience 56, 368.
- Baum, E., Weitner, S., 2006. Biochar application on soils and cellolosic ethanol production. In: Clean Air Task Force, Washington.
- Bhogal, A., Chambers, B.J., Whitmore, A.P., Powlson, D.S., 2007. The effects of reduced tillage practices and organic material additions on the carbon content of arable soils. In: Defra, London.
- Blanco-Canqui, H., Lal, R., 2008. No-tillage and soil-profile carbon sequestration: an on-farm assessment. Soil Science Society of America Journal 72, 693-701.

Bridgewater, A.V., 2004. Biomass fast pyrolysis. Thermal Science 8, 21-49.

Bridgewater, A.V., 2006. Biomass for energy. Journal of the Science of Food and Agriculture 86, 1755-1768.

- Brodowski, S., John, B., Flessa, H., Amelung, W., 2006. Aggregate-occluded black carbon in soil. European Journal of Soil Science 57, 539-546.
- Bruun, S., Luxhoi, J., 2008. Is biochar production really carbon-negative? Environmental Science & Technology 42, 1388-1388.
- Castro, M.S., Steudler, P.A., Melillo, J.M., Aber, J.D. and Bowden, R.D., 1995. Factors Controlling Atmospheric Methane Consumption by Temperate Forest Soils, Global Biogeochem. Cycles 9, 1–10.
- 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.
- Cheng, C.-H., Lehmann, J., Thies, J.E., Burton, S.D., Engelhard, M.H., 2006. Oxidation of black carbon by biotic and abiotic processes. Organic Geochemistry 37, 1477-1488.
- Cheng, C.-H., Lehmann, J., Engelhard, M.H., 2008. Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence. Geochimica et Cosmochimica Acta 72, 1598-1610.
- Coleman, K., Jenkinson, D.S., 1996. RothC-26.3 a model for the turnover of carbon in soil. In: Powlson, D.S., Smith, P., Smith, J.U. (Eds.), Evaluation of soil organic matter models. Springer Verlag, Berlin Heidelberg, pp. 237-246.
- Coleman, K., Jenkinson, D.S., Crocker, G.J., Grace, P.R., Klir, J., Korschens, M., Poulton, P.R., Richter, D.D., 1997. Simulating trends in soil organic carbon in long-term experiments using RothC-26.3. Geoderma 81, 29-44.
- Crutzen, P.J., 2006. Albedo enhancement by stratospheric sulfur injections: A contribution to resolve a policy dilemma?. Climatic Change 77, 211-219.
- Crutzen, P.J., Andreae, M.O., 1990. Biomass burning in the tropics: impact on atmospheric chemistry and biogeochemical cycles. Science 250, 1669-1678.
- Czimczik, C.I., Masiello, C.A., 2007. Controls on black carbon storage in soils. Global Biogeochemical Cycles 21, B3005.
- Czimczik, C.I., Schmidt, M.W.I., Schulze, E.D., 2005. Effects of increasing fire frequency on black carbon and organic matter in Podzols of Siberian Scots pine forests. European Journal of Soil Science. Blackwell Publishing, Oxford, UK 56, 417-428.
- Dai, X., Boutton, T.W., Glaser, B., Ansley, R.J., Zech, W., 2005. Black carbon in a temperate mixed-grass savanna. Soil Biology & Biochemistry 37, 1879-1881.
- Das, K.C., Garcia-Perez, M., Bibens, B., Melear, N., 2008. Slow pyrolysis of poultry litter and pine woody biomass: Impact of chars and bio-oils on microbial growth. Journal of Environmental Science and Health: Part A 43, 714-724.

Day, D., Hawkins, B., 2007. Getting back to the garden. BioScience 57, 814-815.

Day, D., Evans, R.J., Lee, J.W., Reicosky, D., 2005. Economical CO2, SOx, and NOx capture from fossil-fuel utilization with combined renewable hydrogen production and large-scale carbon sequestration. Energy 30, 2558-2579.

- De la Rosa, J.M., Knicker, H., Lopez-Capel, E., Manning, D.A.C., Gonzalez-Perez, J.A., Gonzalez-Vila, F.J., 2008. Direct detection of black carbon in soils by Py-GC/MS, carbon-13 NMR spectroscopy and thermogravimetric techniques. Soil Science Society of America Journal 72, 258-267.
- Demirbas, A., 2004. Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. Journal of Analytical and Applied Pyrolysis 72, 243-248.
- Demirbas, A., 2006. Production and characterization of bio-chars from biomass via pyrolysis. Energy Sources Part A 28, 413-422.
- Demirbas, A., Pehlivan, E., Altun, T., 2006a. Potential evolution of Turkish agricultural residues as bio-gas, bio-char and bio-oil sources. International Journal of Hydrogen Energy 31, 613-620.
- Demirbas, A., Arslan, G., Pehlivan, E., 2006b. Recent studies on activated carbons and fly ashes from Turkish resources. Energy Sources Part A 28, 627-638.
- Edwards, R.D., Smith, K.R., Zhang, J., Yuqing, M., 2003. Models to predict emissions of health-damaging pollutants and global warming contributions of residential fuel/stove combinations in China. Chemosphere 50, 201-215.
- Falloon, P., Smith, P., Coleman, K., Marshall, S., 1998. Estimating the size of the inert organic matter pool from total soil organic carbon content for use in the Rothamsted carbon model. Soil Biology & Biochemistry 30, 1207-1211.
- Falloon, P.D., Smith, P., 2000. Modelling refractory soil organic matter. Biology and Fertility of Soils 30, 388-398.
- Fang, C., Smith, P., Smith, J.U., 2006. Is resistant soil organic matter more sensitive to temperature than the labile organic matter? Biogeosciences 3, 65-68.
- Fernandes, M.B., Brooks, P., 2003a. Characterization of carbonaceous combustion residues: II. Nonpolar organic compounds. Chemosphere 53, 447-458.
- Fernandes, M.B., Skjemstad, J.O., Johnson, B.B., Wells, J.D., Brooks, P., 2003b. Characterization of carbonaceous combustion residues: I. Morphological, elemental and spectroscopic features. Chemosphere 51, 785-795.
- Ferrio, J.P., Alonso, N., Voltas, J., Araus, J.L., 2006. Grain weight changes over time in ancient cereal crops: Potential roles of climate and genetic improvement. Journal of Cereal Science 44, 323-332.
- Forbes, M.S., Raison, R.J., Skjemstad, J.O., 2006. Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems. Science of the Total Environment 370, 190-206.
- Fowles, M., 2007. Black carbon sequestration as an alternative to bioenergy. Biomass and Bioenergy 31, 426-432.
- Friedl, A., Padouvas, E., Rotter, H., Varmuza, K., 2005. Prediction of heating values of biomass fuel from elemental composition. Analytica Chimica Acta 544, 191-198.

- Fushimi, C., Araki, K., Yamaguchi, Y., Tsutsumi, A., 2003. Effect of heating rate on steam gasification of biomass 2. Thermogravimetric-mass spectrometric (TG-MS) analysis of gas evolution. Industrial & Engineering Chemistry Research 42, 3929-3936.
- Garcia-Perez, M., 2008. The formation of polyaromatic hydrocarbons and dioxins during pyrolysis. In: Washington State University.
- Garnaut, R., 2008. The Garnaut Climate Change Review. ICambridge University Press, Port Melbourne, 680p. http://www.garnautreview.org.au/domino/Web Notes/Garnaut/garnautweb.nsf
- Gaskin, J.W., Speir, A., Morris, L.M., Ogden, L., Harris, K., Lee, D., Das, K.C., 2007.
   Potential for pyrolysis char to affect soil moisture and nutrient status of loamy sand soil.
   In: Georgia Water Resources Conference. University of Georgia.
- Gaunt, J.L., Lehmann, J., 2008. Energy balance and emissions associated with biochar sequestration and pyrolysis bioenergy production. Environmental Science & Technology 42, 4152-4158.
- Gercel, H.F. and Pułuin, E., 2002, Fast pyrolysis of sunflower-pressed bagasse: Effects of sweeping gas flow rate. Energy Sources 24, 451-460.
- Glaser, B., Balashov, E., Haumaier, L., Guggenberger, G., Zech, W., 2000. Black carbon in density fractions of anthropogenic soils of the Brazilian Amazon region. Organic Geochemistry 31, 669-678.
- Glaser, B., Haumaier, L., Guggenberger, G., Zech, W., 2001. The 'Terra Preta' phenomenon: a model for sustainable agriculture in the humid tropics. Naturwissenschaften, 37-41.
- Glaser, B., Lehmann, J., Zech, W., 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal a review. Biology and Fertility of Soils 35, 219-230.
- Graetz, R.D., Skjemstad, J.O., 2003. The charcoal sink of biomass burning on the Australian continent. In: CSIRO, Victoria, pp. 61.
- Gulde, S., Chung, H., Amelung, W., Chang, C., Six, J., 2008. Soil carbon saturation controls labile and stable carbon pool dynamics. Soil Science Society of America Journal 72, 605-612.
- Hamer, U., Marschner, B., Brodowski, S., Amelung, W., 2004. Interactive priming of black carbon and glucose mineralisation. Organic Geochemistry 35, 823-830.
- Hammes, K., Schmidt, M.W.I., Smernik, R.J., Currie, L.A., Ball, W.P., Nguyen, T.H., Louchouarn, P., Houel, S., Gustafsson, O., Elmquist, M., Cornelissen, G., Skjemstad, J.O., Masiello, C.A., Song, J., Peng, P., Mitra, S., Dunn, J.C., Hatcher, P.G., Hockaday, W.C., Smith, D.M., Hartkopf-Froder, C., Bohmer, A., Luer, B., Huebert, B.J., Amelung, W., Brodowski, S., Huang, L., Zhang, W., Gschwend, P.M., Flores-Cervantes, D.X., Largeau, C., Rouzaud, J.N., Rumpel, C., Guggenberger, G., Kaiser, K., Rodionov, A., Gonzalez-Vila, F.J., Gonzalez-Perez, J.A., Rosa, J.M.d.I., Manning, D.A.C., Lopez-Capel, E., Ding, L., 2007. Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. Global Biogeochemical Cycles 21, 1-18.

Harder, B., 2006. Smouldered earth policy. Science 169, 133.

- Haumaier, L., Zech, W., 1995. Black carbon possible source of highly aromatic components of soil humic acids. Organic Geochemistry 23, 191-196.
- Ishii, T., Kadoya, K., 1994. Effects of charcoal as a soil conditioner on citrus growth and vesicular-arbuscular mycorrhizal development. Journal of the Japanese Society for Horticultural Science 63, 529-535.
- Janik, L.J., Skjemstad, J.O., Shepherd, K.D., Spouncer, L.R., 2007. The prediction of soil carbon fractions using mid-infrared-partial least square analysis. Australian Journal of Soil Research 45, 73-81.
- Janzen, H.H., 2006. The soil carbon dilemma: Shall we hoard it or use it? Soil Biology & Biochemistry 38, 419-424.
- Ketterings, Q.M., Bigham, M., 2000. Soil color as an Indicator of slash-and-burn fire severity and soil fertility in Sumatra, Indonesia. Soil Science Society of America Journal 64, 1826-1833.
- Knicker, H., 2007. How does fire affect the nature and stability of soil organic nitrogen and carbon? A review. Biogeochemistry 85, 91-118.
- Krull, E.S., Baldock, J.A., Skjemstad, J.O., 2003. Importance of mechanisms and processes of the stabilisation of soil organic matter for modelling carbon turnover. Functional Plant Biology 30, 207-222.
- Krull, E.S., Skjemstad, J.O., Baldock, J.A., 2004. Functions of soil organic matter and the effect on soil properties. In: Grains Research and Development Corporation, pp. 129. http://www.grdc.com.au/uploads/documents/cso000291.pdf

Kuhlbusch, T.A.J., 1998. Black carbon and the carbon cycle. Science 280, 1903-1904.

- Kuhlbusch, T.A.J., Andreae, M.O., Cachier, H., Goldammer, J.G., Lacaux, J.P., Shea, R., Crutzen, P.J., 1996. Black carbon formation by savanna fires: Measurements and implications for the global carbon cycle. Journal of Geophysical Research 101, 23651– 23665.
- Kuwagaki, H., Tamura, K., 1990. Aptitude of wood charcoal to a soil improvement and other. non-fuel use. In: Mitigation and adaptation strategies for global change.
- Laird, A.D., 2008. The charcoal Vision: A win-win-win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. Agronomy Journal 100, 178-181.
- Lal, R., 1997. Residue management, conservation tillage and soil restoration for mitigating greenhouse effect by CO2-enrichment. Soil and Tillage Research 43, 81-107.
- Ledesma, E.B., Marsh, N.D., Sandrowitz, A.K., Wornat, M.J., 2002. Global kinetic rate parameters for the formation of polycyclic aromatic hydrocarbons from the pyrolysis of catechol, a model compound representative of solid fuel moieties. Energy and Fuels 16, 1331-1336.

Lehmann, J., 2007a. A handful of carbon. Nature 447, 143-144.

Lehmann, J., 2007b. Bio-energy in the black. Frontiers in Ecology and the Environment 5, 381-387.

- Lehmann, C.J. and Rondon, M., 2006. Bio-char soil management on highly-weathered soils in the tropics. In: Uphoff, N.T. (Ed.), Biological Approaches to Sustainable Soil Systems. CRC Press, Boca Raton, pp. 517-530.
- Lehmann, C.J. and Sohi, S.P., 2008. Comment on "Fire-derived charcoal causes loss of forest humus". Science 321, 1295c.
- Lehmann, C.J. and Joseph, S., 2009a. Biochar systems. In: Lehmann, C.J., Joseph, S. (Eds.), Biochar for environmental management: science and technology. Earthscan.
- Lehmann, J. and Joseph, S., 2009b. Biochar for environmental management: science and technology. In: Earthscan, London.
- Lehmann, C.J., da Silva Jr, J.P., Rondon, M., C.M., D.S., Greenwood, J., Nehls, T., Steiner, C., Glaser, B., 2002. Slash-and-char a feasible alternative for soil fertility management in the central Amazon? In: 17th World Congress of Soil Science. Bangkok.
- Lehmann, J., da Silva Jr, J.P., Steiner, C., Nehls, T., Zech, W., Glaser, B., 2003. Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: fertilizer, manure and charcoal amendments. Plant & Soil 249, 343-357.
- Lehmann, J., Kern, D.C., Glaser, B. and Woods, W.I. 2003. Amazonian Dark Earths: Origin, Properties, Management. Kluwer Academic Publishers, The Netherlands, 523p.
- Lehmann, C.J., Czimczik, C.I., Sohi, D.L.S.P., 2009. Stability of biochar in soil ecosystems. In: Lehmann, C.J., Joseph, S. (Eds.), Biochar for environmental management: science and technology.
- Lehmann, J., Gaunt, J., Rondon, M., 2005a. Bio-char sequestration in terrestrial ecosystems a review. Mitigation and adaptation strategies for global change.
- Lehmann, J., Liang, B.Q., Solomon, D., Lerotic, M., Luizao, F., Kinyangi, J., Schafer, T., Wirick, S., Jacobsen, C., 2005b. Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy for mapping nano-scale distribution of organic carbon forms in soil: Application to black carbon particles. Global Biogeochemical Cycles 19.
- Lehmann, J., Skjemstad, J., Sohi, S., Carter, J., Barson, M., Falloon, P., Coleman, K., Woodbury, P., Krull, E., 2008. Australian climate-carbon cycle feedback reduced by soil black carbon. Nature Geoscience 1: 832-835.
- Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J.O., Thies, J., Luizao, F.J., Petersen, J., Neves, E.G., 2006. Black Carbon increases cation exchange capacity in soils. Soil Science Society of America Journal 70, 1719-1730.

Marris, E., 2006. Black is the new green. Nature 442, 624-626.

- Masiello, C.A., 2004. New directions in black carbon organic geochemistry. Marine Chemistry 92, 201-213.
- Masiello, C.A., Druffel, E.R.M., 1998. Black carbon in deep-sea sediments Science 280, 1911-1913.

Matthews, J.A., 2008. Carbon negative biofuels. Energy Policy 36, 940-945.

- McConnell, J.R., Edwards, R., Kok, G.L., Flanner, M.G., Zender, C.S., Saltzman, E.S., Banta, J.R., Pasteris, D.R., Carter, M.M., Kahl, J.D.W., 2007. 20th-century industrial black carbon emissions altered arctic climate forcing. Science.
- McGill, W.B., 1996. Review and classification of ten soil organic matter (SOM) models. In: Powlson, D.S., Smith, P., Smith, J.U. (Eds.), Evaluation of soil organic matter models. Springer Verlag, Berlin Heidelberg, pp. 111-132.
- McHenry, M. P., 2009. Agricultural bio-char production, renewable energy generation and farm carbon sequestration in Western Australia: Certainty, uncertainty and risk. Agriculture, Ecosystems & Environment 129, 1-7.
- Mouillot, F., Field, C.B., 2005. Fire history and the global carbon budget: a 1 degrees x 1 degrees fire history reconstruction for the 20th century. Global Change Biology 11, 398-420.
- Murage, E.W., Voroney, P., Beyaert, R.P., 2007. Turnover of carbon in the free light fraction with and without charcoal as determined using the 13C natural abundance method. Geoderma 138, 133-143.
- Nishio, M., 1996. Microbial fertilizers in Japan. In: National Institute of Agro-Environmental Sciences, Ibaraki, Japan.
- Ogawa, M., 1994. Tropical agriculture using charcoal. Farming Japan 28, 21–35.
- Ogawa, M., Okimori, Y., Takahashi, F., 2006. Carbon sequestration by carbonization of biomass and forestation: three case studies. Mitigation and adaptation strategies for global change 11, 429-444.
- Oguntunde, P.G., Abiodun, B.J., Ajayi, A.E., van de Giesen, N., 2008. Effects of charcoal production on soil physical properties in Ghana. Journal of Plant Nutrition and Soil Science 171, 591-596.
- Okimori, Y., Ogawa, M., Takahashi, F., 2003. Potential of CO2 emission reductions by carbonizing biomass waste from industrial tree plantation in south Sumatra , Indonesia. Mitigation and adaptation strategies for global change 8, 261-280.
- Özçimen, D. and Karaosmanoglu, F., 2004. Production and characterization of bio-oil and biochar from rapeseed cake. Renewable Energy 29,779-787
- Palm, C.A., Gachengo, C.N., Delve, R.J., Cadisch, G., Giller, K.E., 2001. Organic inputs for soil fertility management in tropical agro ecosystems: application of an organic resource database. Agriculture, Ecosystems and Environment 16, 27-42.
- Pekrun, C., Kaul, H.-P., Claupein, W., 2003. Soil tillage for sustainable nutrient management. In: El Titi, A. (Ed.), Soil tillage in agroecosystems. CRC Press.
- Preston, C.M., Schmidt, M.W.I., 2006. Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions. Biogeosciences Discussions 3, 397-420.
- Prins, M.J., Ptasinski, K.J., Janssen, F.J.J.G., 2006. Torrefaction of wood Part 2. Analysis of products. Journal of Analytical and Applied Pyrolysis 77, 35-40.

- Pułuin, A.E., Biomass to bio-oil via fast pyrolysis of cotton straw and stalk, 2002. Energy Sources 24: 275-285.
- Quénéa, K., Derenne, S., Rumpel, C., Rouzaud, J.-N., Gustafsson, O., Carcaillet, C., Mariotti, A., Largeau, C., 2006. Black carbon yields and types in forest and cultivated sandy soils (Landes de Gascogne, France) as determined with different methods: Influence of change in land use. Organic Geochemistry 37, 1185-1189.
- Ramanathan, V., Carmichael, G., 2008. Global and regional climate changes due to black carbon. Nature Geoscience 1, 221-227.
- Ramankutty, N., Evan, A.T., Monfreda, C., Foley, J.A., 2008. Farming the planet: 1. Geographic distribution of global agricultural lands in the year 2000. Global Biogeochemical Cycles 22, Online.
- Renner, R., 2007. Rethinking biochar. Environmental Science & Technology 41, 5932-5933.
- Rhodes, A.H., Carlin, A., Semple, K.T., 2008. Impact of black carbon in the extraction and mineralization of phenanthrene in soil. Environmental Science & Technology 42, 740-745.
- Rokityanskiy, D., Benítez, P.C., Kraxner, F., McCallum, I., Obersteiner, M., Rametsteiner, E., Yamagata, Y., 2007. Geographically explicit global modeling of land-use change, carbon sequestration, and biomass supply. Technological Forecasting & Social Change 74, 1057-1082.
- Rondon, M.A., Lehmann, J., Ramirez, J., Hurtado, M., 2007. Biological nitrogen fixation by common beans (Phaseolus vulgaris L.) increases with bio-char additions. Biology and Fertility of Soils 43, 699-708.
- Schlesinger, W.H., 2000. Carbon sequestration in soils: some cautions amidst optimism. Agriculture Ecosystems & Environment 82, 121-127.
- Schmidt, M., 2004. Carbon budget in the black. Nature 427, 305-307.
- Schmidt, M.W.I. and Noack, A.G., 2000. Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges. Global Biogeochemical Cycles 14, 777-793.
- Schmidt, M.W.I., Skjemstad, J.O., Gehrt, E., Kogel-Knabner, I., 1999. Charred organic carbon in German chernozemic soils. European Journal of Soil Science 50, 351-365.
- Schmidt, M.W.I., Skjemstad, J.O., Czimczik, C.I., Glaser, B., Prentice, K.M., Y.Gelinas, Kuhlbusch, T.A.J., 2001. Comparative analysis of black carbon in soils. Global Biogeochemical Cycles 15, 163-167.
- Schneur, E.A., 1966. Oxidation of graphitic carbon in certain soils. Science 151, 991-992.
- Schulze, E.-D., Wirth, C., Heimann, M., 2000. Managing forests after Kyoto. Science 289, 2058-2059.
- Scott, A. C., Cripps, J. A., Collinson, M. E. and Nichols, G. J. (2000) The taphonomy of charcoal following a recent heathland fire and some implications for the interpretation of fossil charcoal deposits. Palaeogeography, Palaeoclimatology and Palaeoecology, 164, 1-31.

- Searchinger, T., Heimlich, R., Houghton, R.A., Dong, F., Elobeid, A., Fabiosa, J., Tokgoz, S., Hayes, D., Yu, T.-H., 2008. Use of U.S. croplands for biofuels increases greenhouse gases through emissions from land-use change. Science 213, 1238-1240.
- Seifritz, W., 1993. Should we store carbon in charcoal? International Journal of Hydrogen Energy 18, 405-407.
- Seiler, W., Crutzen, P.J., 1980. Estimates of gross and net fluxes of carbon between the biosphere and the atmosphere from biomass burning. Climatic Change 2, 207-247.
- Sensöz, S., 2003, Slow pyrolysis of wood barks from Pinus brutia Ten. and product compositions. Bioresource Technology 89, 307-311
- Shinogi, Y., Yoshida, H., Koizumi, T., Yamaoka, M., Saito, T., 2002. Basic characteristics of low-temperature carbon products from waste sludge. Advances in Environmental Research 7, 661-665.
- Simpson, M.J. and Hatcher, P.G., 2004a. Determination of black carbon in natural organic matter by chemical oxidation and solid-state 13C nuclear magnetic resonance spectroscopy. Organic Geochemistry 35, 923-935.
- Simpson, M.J. and Hatcher, P.G., 2004b. Overestimates of black carbon in soils and sediments. Naturwissenschaften 91, 436-440.
- Skjemstad, J.O., Taylor, J.A., Smernik, R.J., 1999. Estimation of charcoal (char) in soils. Communications in Soil Science and Plant Analysis 30, 2283-2298.
- Skjemstad, J.O., Dalal, R.C., Janik, L.J., McGowan, J.A., 2001. Changes in chemical nature of soil organic carbon in Vertisols under wheat in south-eastern Queensland. Australian Journal of Soil Research 39, 343-359.
- Skjemstad, J.O., Spouncer, L.R., Cowie, B., Swift, R.S., 2004a. Calibration of the Rothamsted organic carbon turnover model (RothC ver. 26.3), using measurable soil organic carbon pools. Australian Journal of Soil Research. CSIRO Publishing, Collingwood, Australia 42, 79-88.
- Skjemstad, J.O., Spouncer, L.R., Cowie, B., Swift, R.S., 2004b. Calibration of the Rothamsted organic carbon turnover model (RothC ver. 26.3) using measurable soil organic carbon pools. Australian Journal of Soil Research 42, 79-88.
- Smernik, R.J. and Oades, J.M., 2000. The use of spin counting for determining quantitation in solid state <sup>13</sup>C NMR spectra of natural organic matter: 2. HF-treated soil fractions. Geoderma 96, 159-171.
- Smernik, R.J., Skjemstad, J.O., Oades, J.M., 2000. Virtual fractionation of charcoal from soil organic matter using solid state 13C NMR spectral editing. Australian Journal of Soil Research 38, 665-683.
- Smernik, R.J., Baldock, J.A., Oades, J.M., Whittaker, A.K., 2002. Determination of T1ph relaxation rates in charred and uncharred wood and consequences for NMR quantitation. Solid State Nuclear Magnetic Resonance 22, 50-70.
- Smith, N.J.H., 1999. The Amazon River forest: a natural history of plants, animals, and people. Oxford University Press, New York.

- Smith, P., Powlson, D.S., Glendining, M.J., Smith, J.U., 1998. Preliminary estimates of the potential for carbon mitigation in European soils through no-till farming. Global Change Biology 4, 679-685.
- Smith, P., Milne, R., Powlson, D.S., Smith, J.U., Falloon, P., Coleman, K., 2000. Revised estimates of the carbon mitigation potential of UK agricultural land. Soil Use and Management 16, 293-295.
- Smittenberg, R.H., Eglinton, T.I., Schouten, S., Sinninghe Damsté, J.S., 2006. Ongoing build-up of refractory organic carbon in boreal soils during the Holocene. Science 314, 1283-1286.
- Sohi, S.P., Yates, H.C., Lehmann, J., Liang, B., Gaunt, J.L., 2006. Evaluating C dynamics in terra preta. In: World Soils Congress. Philadelphia.
- Solomon, D., Lehmann, J., Thies, J., Schäfer, T., Liang, B., Kinyangi, J., Neves, E., Petersen, J., Luizo, F. and Skjemstad, J., 2007. Molecular signature and sources of biochemical recalcitrance of organic C in Amazonian Dark Earths. Geochimica et Cosmochimica Acta 71: 2285-2298. DOI 10.1016/j.gca.2007.02.014 3.6/0
- Steiner, C., Teixeira, W., Lehmann, J., Zech, W., 2003. Microbial response to charcoal amendments of highly weathered soils and Amazonian Dark Earths in Central Amazonia preliminary results. In: Lehmann, J., Kern, D.C., Glaser, B., Woods, W.I. (Eds.), Amazonian dark earths: origin, properties, management. Kluwer Academic Publishers, Dordrecht.
- Steiner, C., Teixeira, W.G., Lehmann, J., Nehls, T., MacêDo, J.L.V., Blum, W.E.H., Zech, W., 2007. Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. Plant and Soil 291, 275-290.
- Steiner, C., Keshav, C.D., Garcia, M., Forster, B., Zech, W., 2008. Charcoal and smoke extract stimulate the soil microbial community in a highly weathered xanthic Ferralsol. Pedobiologia 51, 359-356.
- Stewart, C.E., Paustian, K., Conant, R.T., Plante, A.F., Six, J., 2007. Soil carbon saturation: concept, evidence and evaluation. Biogeochemistry 86, 19-31.
- Streets, D.G., Bond, T.C., Lee, T., Jang, C., 2004. On the future of carbonaceous aerosol emissions. Journal of Geophysical Research-Atmospheres 109, 19.
- Tanaka, S., 1963. Fundamental study on wood carbonization. In: Bulletin of Experimental Forest of Hokkaido University.
- The Royal Society, 2008. Sustainable biofuels: prospects and challenges. In: The Royal Society, London, pp. 84.
- Thonicke, K., Venevsky, S., Sitch, S., Cramer, W., 2001. The role of fire disturbance for global vegetation dynamics: coupling fire into a Dynamic Global Vegetation Model. Global Ecology and Biogeography 10, 661-677.
- Tomaszewski, J.E., Werner, D., Luthy, R.G., 2007. Activated carbon amendment as a treatment for residual DDT in sediment from a superfund site in San Francisco Bay, Richmond, California, USA. Environmental Toxicology and Chemistry, 2143–2150.

- Ueno, M., Kawamitsu, Y., Komiya, Y., Sun, L., 2007. Carbonisation and gasification of bagasse for effective utilisation of sugarcane biomass. International Sugar Journal 110, 22-26.
- UNFCCC, Indicative simplified baseline and monitoring methodologies for selected smallscale CDM project activity categories. In: Board, C.E. (Ed.), Avoidance of methane production from biomass decay through controlled pyrolysis. United Nations.
- Wang, X., K.R., S., 1999. Secondary benefits of greenhouse gas control: health impacts in China. Environmental Science & Technology 33, 3056-3061.
- Wardle, D.A., Nilsson, M.-C., Zackrisson, O., 2008. Fire-derived charcoal causes loss of forest humus. Science 320, 629.
- Warnock, D.D., Lehmann, J., Kuyper, T.W., Rillig, M.C., 2007. Mycorrhizal responses to biochar in soil concepts and mechanisms. Plant & Soil 300, 9-20.
- Watts, C.W., Whalley, R.W., Brookes, P.C., Devonshire, B.J., Whitmore, A.P., 2005. Biological and physical processes that mediate micro-aggregation of clays. Soil Science 170, 573-583.
- Winsley, P., 2007. Biochar and bioenergy production for climate change mitigation. New Zealand Science Review 64, 1-10.
- Woolf, D., 2008. Biochar as a soil amendment: A review of the environmental implications. In: Swansea.
- Yaman, S., 2004. Pyrolysis of biomass to produce fuels and chemical feedstocks. Energy Conversion and Management 45 651-671.
- Yamato, M., Okimori, Y., Wibowo, I.F., Anshori, S., Ogawa, M., 2006. Effects of the application of charred bark of Acacia mangium on the yield of maize, cowpea and peanut, and soil chemical properties in South Sumatra, Indonesia. Soil Science and Plant Nutrition 52, 489 - 495.
- Yanai, Y., Toyota, K., Okazaki, M., 2007. Effects of charcoal addition on N2O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments. Soil Science and Plant Nutrition 53, 181-188.
- Young, A., 1804. Paring and burning. In: . (Ed.), The farmers calendar. Richard Phillips, London, pp. 171-182.
- Yu, X.-Y., Ying, G.-G., Kookana, R.S., 2006. Sorption and desorption dehaviors of diuron in soils amended with charcoal. Journal of Agricultural and Food Chemistry 54, 8545–8550.

Contact Us Phone: 1300 363 400 +61 3 9545 2176 Email: enquiries@csiro.au Web: www.csiro.au

#### Your CSIRO

Australia is founding to future on advance and innovation. Its mational advance agency, CSIRO, is a powerhouse of ideas, technologies and static for building prospering growth, builds and sustainability. It surves governments, industries, business and communities across the ration.