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Biochar Application to Soils

A Critical Scientific Review of Effects on Soil Properties, Processes and Functions

F. Verheijen, S. Jeffery, A.C. Bastos, M. van der Velde, I. Diafas



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Biochar Application to Soils

A Critical Scientific Review of Effects on Soil Properties, Processes and Functions

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EXECUTIVE SUMMARY

Biochar application to soils is being considered as a means to sequester carbon (C) while concurrently improving soil functions. The main focus of this report is providing a critical scientific review of the current state of knowledge regarding the effects of biochar application to soils on soil properties, processes and functions. Wider issues, including atmospheric emissions and occupational health and safety associated to biochar production and handling, are put into context. The aim of this review is to provide a sound scientific basis for policy development, to identify gaps in current knowledge, and to recommend further research relating to biochar application to soils. See Table 1 for an overview of the key findings from this report. Biochar research is in its relative infancy and as such substantially more data are required before robust predictions can be made regarding the effects of biochar application to soils, across a range of soil, climatic and land management factors.

Definition

In this report, biochar is defined as: "charcoal (biomass that has been pyrolysed in a zero or low oxygen environment) for which, owing to its inherent properties, scientific consensus exists that application to soil at a specific site is expected to sustainably sequester carbon and concurrently improve soil functions (under current and future management), while avoiding short- and long-term detrimental effects to the wider environment as well as human and animal health." Biochar as a material is defined as: "charcoal for application to soils". It should be noted that the term 'biochar' is generally associated with other co-produced end products of pyrolysis such as 'syngas'. However, these are not usually applied to soil and as such are only discussed in brief in the report.

Biochar properties

Biochar is an organic material produced via the pyrolysis of C-based feedstocks (biomass) and is best described as a 'soil conditioner'. Despite many different materials having been proposed as biomass feedstock for biochar (including wood, crop residues and manures), the suitability of each feedstock for such an application is dependent on a number of chemical, physical, environmental, as well as economic and logistical factors. Evidence suggests that components of the carbon in biochar are highly recalcitrant in soils, with reported residence times for wood biochar being in the range of 100s to 1,000s of years, i.e. approximately 10-1,000 times longer than residence times of most soil organic matter (SOM). Therefore, biochar addition to soil can provide a potential sink for C. It is important to note, however, that there is a paucity of data concerning biochar produced from feedstocks other than wood. Owing to the current interest in climate change mitigation, and the irreversibility of biochar application to soil, an effective evaluation of biochar stability in the environment and its effects on soil processes and functioning is paramount. The current state of knowledge concerning these factors is discussed throughout this report.

Pyrolysis conditions and feedstock characteristics largely control the physicochemical properties (e.g. composition, particle and pore size distribution) of the resulting biochar, which in turn, determine the suitability for a given application, as well as define its behaviour, transport and fate in the environment. Reported biochar properties are highly heterogeneous, both within individual biochar particles but mainly between biochar originating from different feedstocks and/or produced under different pyrolysis conditions. For example, biochar properties have been reported with cation exchange capacities (CECs) from negligible to approximately 40 cmolc g⁻¹, C:N ratios from 7 to 500 (or more). The pH is typically neutral to basic and as such relatively constant. While such heterogeneity leads to difficulties in identifying the underlying mechanisms behind reported effects in the scientific literature, it also provides a possible opportunity to engineer biochar with properties that are best suited to a particular site (depending on soil type, hydrology, climate, land use, soil contaminants, etc.).

Effects on soils

Biochar characteristics (e.g. chemical composition, surface chemistry, particle and pore size distribution), as well as physical and chemical stabilisation mechanisms of biochar in soils, determine the effects of biochar on soil functions. However, the relative contribution of each of these factors has been assessed poorly, particularly under the influence of different climatic and soil conditions, as well as soil management and land use. Reported biochar loss from soils may be explained to a certain degree by abiotic and biological degradation and translocation within the soil profile and into water systems. Nevertheless, such mechanisms have been quantified scarcely and remain poorly understood, partly due to the limited amount of long-term studies, and partly due to the lack of standardised methods for simulating biochar aging and long-term environmental monitoring. A sound understanding of the contribution that biochar can make as a tool to improve soil properties, processes and functioning, or at least avoiding negative effects, largely relies on knowing the extent and full implications of the biochar interactions and changes over time within the soil system.

Extrapolation of reported results must be done with caution, especially when considering the relatively small number of studies reported in the primary literature, combined with the small range of climatic, crop and soil types investigated when compared to possible instigation of biochar application to soils on a national or European scale. To try and bridge the gap between small scale, controlled experiments and large scale implementation of biochar application to a range of soil types across a range of different climates (although chiefly tropical), a statistical meta-analysis was undertaken. A full search of the scientific literature led to a compilation of studies used for a meta-analysis of the effects of biochar application to soils and plant productivity. Results showed a small overall, but statistically significant, positive effect of biochar application to soils on plant productivity in the majority of cases. The greatest positive effects were seen on acidic freedraining soils with other soil types, specifically calcarosols showing no significant effect (either positive or negative). There was also a general trend for concurrent increases in crop productivity with increases in pH up on biochar addition to soils. This suggests that one of the main mechanisms behind the reported positive effects of biochar application to soils on plant productivity may be a liming effect. However, further research is needed to confirm this hypothesis. There is currently a lack of data concerning the effects of biochar application to soils on other soil functions. This means that although these are qualitatively and comprehensively discussed in this report, a robust meta-analysis on such effects is as of yet not possible. Table 0.1 provides an overview of the key findings - positive, negative, and unknown - regarding the (potential) effects on soil, including relevant conditions.

Preliminary, but inconclusive, evidence has also been reported concerning a possible priming effect whereby accelerated decomposition of SOM occurs upon biochar addition to soil. This has the potential to both harm crop productivity in the long term due to loss of SOM, as well as releasing more CO₂ into the atmosphere as increased quantities of SOM is respired from the soil. This is an area which requires urgent further research.

Biochar incorporation into soil is expected to enhance overall sorption capacity of soils towards anthropogenic organic contaminants (e.g. polycyclic aromatic hydrocarbons - PAHs, pesticides and herbicides), in a mechanistically different (and stronger) way than amorphous organic matter. Whereas this behaviour may greatly mitigate toxicity and transport of common pollutants in soils through reducing their bioavailability, it might also result in their localised accumulation, although the extent and implications of this have not been fully assessed experimentally. The potential of biochar to be a source of soil contamination needs to be evaluated on a case-by-case basis, not only with concern to the biochar product itself, but also to soil type and environmental conditions.

Implications

As highlighted above, before policy can be developed in detail, there is an urgent need for further experimental research with regard to long-term effects of biochar application on soil functions, as well as on the behaviour and fate in different soil types (e.g. disintegration, mobility, recalcitrance), and under different management practices. The use of representative pilot areas, in different soil ecoregions, involving biochars produced from a representative range of feedstocks is vital. Potential research methodologies are discussed in the report. Future research should also include biochars from non-lignin-based feedstocks (such as crop residues, manures, sewage and green waste) and focus on their properties and environmental behaviour and fate as influenced by soil conditions. It must be stressed that published research is almost exclusively focused on (sub)tropical regions, and that the available data often only relate to the first or second year following biochar application.

Preliminary evidence suggests that a tight control on the feedstock materials and pyrolysis conditions might substantially reduce the emission levels of atmospheric pollutants (e.g. PAHs, dioxins) and particulate matter associated to biochar production. While implications to human health remain mostly an occupational hazard, robust qualitative and quantitative assessment of such emissions from pyrolysis of traditional biomass feedstock is lacking.

Biochar potentially affects many different soil functions and ecosystem services, and interacts with most of the 'threats to soil' outlined by the Soil Thematic Strategy (COM(2006) 231). It is because of the wide range of implications from biochar application to soils, combined with the irreversibility of its application that more interdisciplinary research needs to be undertaken before policy is implemented. Policy should first be designed with the aim to invest in fundamental scientific research in biochar application to soil. Once positive effects on soil have been established robustly for certain biochars at a specific site (set of environmental conditions), a tiered approach can be imagined where these combinations of biochar and specific site conditions are considered for implementation first. A second tier would then consist of other biochars (from different feedstock and/or pyrolysis conditions) for which more research is required before site-specific application is considered.

From a climate change mitigation perspective, biochar needs to be considered in parallel with other mitigation strategies and cannot be seen as an alternative to reducing emissions of greenhouse gases. From a soil conservation perspective, biochar may be part of a wider practical package of established strategies and, if so, needs to be considered in combination with other techniques.

Table 0.1 Overview of key findings (numbers in parentheses refer to relevant sections)

	Description	Conditions
es	Empirical evidence of charcoal in soils exists (long term)	Biochar analogues (pyrogenic BC and charcoal) are found in substantial quanities in soils of most parts of the world (1.2-1.4)
	The principle of improving soils has been tried successfully in the past	Anthrosols can be found in many parts of the world, although normally of very small spatial extent. Contemplation of Anthrosol generation at a vast scale requires more comprehensive, detailed and careful analysis of effects on soils as well as interactions with other environmental components before implementation (1.2-1.3 and throughout)
	Plant production has been found to increase significantly after biochar addition to soils	Studies have been reported almost exclusively from tropical regions with specific environmental conditions, and generally for very limited time periods, i.e. 1-2 yr. Some cases of negative effects on crop production have also been reported (3.3).
Positives	Liming effect	Most biochars have neutral to basic pH and many field experiments show an increase in soil pH after biochar application when the initial pH was low. On alkaline soils this may be an undesirable effect. Sustained liming effects may require regular applications (3.1.4)
	High sorption affinity for HOC may enhance the overall sorption capacity of soils towards these trace contaminants	Biochar application is likely to improve the overall sorption capacity of soils towards common anthropogenic organic compounds (e.g. PAHs, pesticides and herbicides), and therefore influence toxicity, transport and fate of such contaminants. Enhanced sorption capacity of a silt loam for diuron and other anionic and cationic herbicides has been observed following incorporation of biochar from crop residues (3.2.2)
	Microbial habitat and provision of refugia for microbes whereby they are protected from grazing	Biochar addition to soil has been shown to increase microbial biomass and microbial activity, as well as microbial efficieny as a measure of $\rm CO_2$ released per unit microbial biomass C. The degree of the response appears to be dependent on nutrient availability in soils

	Increases in mycorrhizal abundace which is linked to observed increases in plant productivity	Possibly due to: a) alteration of soil physico-chemical properties; b) indirect effects on mycorrhizae through effects on other soil microbes; c) plant–fungus signalling interference and detoxification of allelochemicals on biochar; or d) provision of refugia from fungal grazers (3.2.6)
	Increases in earthworm abundance and activity	Earthworms have been shown to prefer some soils amended with biochar than those soils alone. However, this is not true of all biochars, particularly at high application rates (3.2.6)
_	The use of biochar analogues for assessing effects of modern biochars is very limited	Charcoal in Terra Preta soils is limited to Amazonia and have received many diverse additions other than charcoal. Pyrogenic BC is found in soils in many parts of the world but are of limited feedstock types and pyrolysis conditions (Chapter 1)
	Soil loss by erosion	Top-dressing biochar to soil is likely to increase erosion of the biochar particles both by wind (dust) and water. Many other effects of biochar in soil on erosion can be theorised, but remain untested at present (4.1)
	Soil compaction during application	Any application carries a risk of soil compaction when performed under inappropriate conditions. Careful planning and management could prevent this effect (4.6)
Negatives	Risk of contamination	Contaminants (e.g. PAHs, heavy metals, dioxins) that may be present in biochar may have detrimental effects on soil properties and functions. The ocurrence of such compounds in biochar is likely to derive from either contaminated feedstocks or the use of processing conditions that may favour their production. Evidence suggests that a tight control over the type of feedstock used and lower pyrolysis temperatures (<500°C) may be sufficient to reduce the potential risk for soil contamination (3.2.4)
	Residue removal	Removal of crop residues for use as a feedstock for biochar production can forego incorporation of the crop residue into the soil, potentially leading to multiple negative effects on soils (3.2.5.5)
	Occupational health and fire hazards	Health (e.g. dust exposure) and fire hazards associated to the production, transport, application and storage of biochar need to be considered when determining the suitability for biochar application. In the context of occupational health, tight health and safety measures need to be put in place in order to reduce such risks. Some of these measures have already proved adequate (5.2)
	Reduction in earthworm survival rates (limited number of cases)	High biochar application rates of >67 t ha ⁻¹ (produced from poultry litter) were shown to have a negative effect on earthworm survival rates, possibly due to increases in pH or salt levels (3.2.6)
-	Empirical evidence is extremely scarce for many modern biochars in soils under modern arable management	Biochar analogues do not exist for many feedstocks, or for some modern pyrolysis conditions. Biochar can be produced with a wide variety of properties and applied to soils with a wide variety of properties. Some short term (1-2 yr) evidence exists, but only for a small set of biochar, environmental and soil management factors and almost no data is available on long term effect (1.2-1.4)
Jnknown	C Negativity	The carbon storage capacity of biochar is widely hypothesised, although it is still largely unquantified and depends on many factors (environmental, economic, social) in all parts of the life cycle of biochar and at the several scales of operation (1.5.2 and Chapter 5)
Unk	Effects on N cycle	$N_2 O$ emissions depend on effects of biochar addition on soil hydrology (water-filled pore volume) and associated microbial processes. Mechanisms are poorly understood and thresholds largely unknown $(1.5.2)$
	Biochar Loading Capacity (BLC)	BLC is likely to be crop as well as soil dependent leading to potential incompatibilities between the irreversibility of biochar once applied to soil and changing crop demands (1.5.1)
	Environmental behaviour	The extent and implications of the changes that biochar undergoes in soil remain largely unknown. Although biochar physical-chemical

mobility and fate

properties and stabilization mechanisms may explain biochar long mean residence times in soil, the relative contribution of each factor for its short- and long-term loss has been sparsely assessed, particularly when influenced by soil environmental conditions. Also, biochar loss and mobility through the soil profile and into the water resources has been scarcely quantified and transport mechanisms remain poorly understood (3.2.1)

Distribution and availability of contaminants (e.g. heavy metals, PAHs) within biochar

Very little experimental evidence is available on the short- and long-term occurrence and bioavailability of such contaminants in biochar and biochar-enriched soil. Full and careful risk assessment in this context is urgently required, in order to relate the bioavailability and toxicity of the contaminant to biochar type and 'safe' application rates, biomass feedstock and pyrolysis conditions, as well as soil type and environmental conditions (3.2.4)

Effect on soil organic matter dynamics

Various relevant processes are acknowledged but the way these are influenced by combinations of soil-climate-management factors remains largely unknown (Section 3.2.5)

Pore size and connectivity

Although pore size distribution in biochar may significantly alter key soil physical properties and processes (e.g. water retention, aeration, habitat), experimental evidence on this is scarce and the underlying mechanisms can only be hypothesised at this stage (2.3 and 3.1.3)

Soil water retention/availability

Adding biochar to soil can have direct and indirect effects on soil water retention, which can be short or long lived, and which can be negative or positive depending on soil type. Positive effects are dependent on high applications of biochar. No conclusive evidence was found to allow the establishment of an unequivocal relation between soil water retention and biochar application (3.1.2)

Soil compaction

Various processes associated with soil compaction are relevant to biochar application, some reducing others increasing soil compaction. Experimental research is lacking. The main risk to soil compaction could probably be reduced by establishing a guide of good practice regarding biochar application (3.1.1 and 4.6)

Priming effect

Some inconclusive evidence of a possible priming effect exists in the literature, but the evidence is relatively inconclusive and covers only the short term and a very restricted sample of biochar and soil types (3.2.5.4)

Effects on soil megafauna

Neither the effects of direct contact with biochar containing soils on the skin and respiratory systems of soil megafanua are known, nor the effects or ingestion due to eating other soil organisms, such as earthworms, which are likely to contain biochar in their guts (3.2.6.3)

Hydrophobicity

The mechnanisms of soil water repellency are understood poorly in general. How biochar might influence hydrophobicity remains largely untested (3.1.2.1)

Enhanced decomposition of biochar due to agricultural management

It is unknow how much subsequent agricultural management practices (planting, ploughing, etc.) in an agricultural soil with biochar may influence (accelerate) the disintegration of biochar in the soil, thereby potentially reducing its carbon storage potential (3.2.3)

Soil CEC

There is good potential that biochar can improve the CEC of soil. However, the effectiveness and duration of this effect after addition to soils remain understood poorly (2.5 and 3.1.4)

Soil Albedo

That biochar will lower the albedo of the soil surface is fairly well established, but if and where this will lead to a substantial soil warming effect is untested (3.1.3)

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	4
EXECUTIVE SUMMARY	5
TABLE OF CONTENTS	11
LIST OF FIGURES	15
LIST OF TABLES	17
LIST OF ACRONYMS	19
LIST OF UNITS	21
LIST OF CHEMICAL ELEMENTS AND FORMULAS	23
LIST OF KEY TERMS	25
1. BACKGROUND AND INTRODUCTION	29
1.1 Biochar in the attention	31
1.2 Historical perspective on soil improvement	33
1.3 Different solutions to similar problems	35
1.4 Biochar and pyrogenic black carbon	35
1.5 Carbon sequestration potential	36
1.5.1 Biochar loading capacity	38
1.5.2 Other greenhouse gasses	39
1.6 Pyrolysis	40
1.6.1 The History of Pyrolysis	41
1.6.2 Methods of Pyrolysis	41
1.7 Feedstocks	43
1.8 Application Strategies	47
1.9 Summary	48
2. PHYSICOCHEMICAL PROPERTIES OF BIOCHAR	49
2.1 Structural and Chemical Composition	49
2.1.1 Structural composition	49
2.1.2 Chemical composition and surface chemistry	50
2.2 Particle size distribution	52
2.2.1 Biochar dust	54
2.3 Pore size distribution and connectivity	54
2.4 Thermodynamic stability	56
2.5 CEC and pH	56
2.6 Summary	56
3. EFFECTS ON SOIL PROPERTIES, PROCESSES AND	
FUNCTIONS	59
3.1 Properties	59
3.1.1 Soil Structure	59
3.1.1.1 Soil Density	59
3.1.1.2 Soil pore size distribution	61
3.1.2 Water and Nutrient Retention	62
3.1.2.1 Soil water repellency 3.1.3 Soil colour, albedo and warming	64 65
3.1.4 CFC and pH	66 66

3.2 Soil Processes	67
3.2.1 Environmental behaviour, mobility and fate	67
3.2.2 Sorption of Hydrophobic Organic Compounds (HOCs)	70
3.2.3 Nutrient retention/availability/leaching	74
3.2.4 Contamination	76
3.2.5 Soil Organic Matter (SOM) Dynamics	79
3.2.5.1 Recalcitrance of biochar in soils	79
3.2.5.2 Organomineral interactions	80
3.2.5.3 Accessibility	81
3.2.5.4 Priming effect	81
3.2.5.5 Residue Removal	83
3.2.6 Soil Biology 3.2.6.1 Soil microbiota	83 85
3.2.6.2 Soil meso and macrofauna	87
3.2.6.3 Soil megafauna	88
3.3 Production Function	89
3.3.1 Meta-analysis methods	89
3.3.2 Meta-analysis results	91
3.3.3 Meta-analysis recommendations	96
3.3.4 Other components of crop production function	96
3.4 Summary	96
4. BIOCHAR AND 'THREATS TO SOIL'	99
4.1 Soil loss by erosion	99
4.2 Decline in soil organic matter	101
4.3 Soil contamination	101
4.4 Decline in soil biodiversity	103
4.6 Soil compaction	104
4.7 Soil salinisation	104
4.8 Summary	105
5. WIDER ISSUES	103 107
	107
5.1 Emissions and atmospheric pollution	107
5.2 Occupational health and safety	
5.3 Monitoring biochar in soil	111
5.4 Economic Considerations	111
5.4.1 Private costs and benefits	111
5.4.2 Social costs and benefits	113
5.5 Is biochar soft geo-engineering?	114
5.6 Summary	116
6. KEY FINDINGS	117
6.1 Summary of Key Findings	117
6.1.1 Background and Introduction	120
6.1.2 Physicochemical properties of Biochar	120
6.1.3 Effects on soil properties, processes and functions	121
6.1.4 Biochar and soil threats	123
6.1.5 Wider issues	123
6.2 Synthesis	124
6.2.1 Irreversibility	124
6.2.2 Quality assessment	124
6.2.3 Scale and life cycle	125

6.2.4 Mitigation/adaptation	125
6.3 Knowledge gaps	127
6.3.1 Safety	127
6.3.2 Soil organic matter dynamics	127
6.3.3 Soil biology	128
6.3.4 Behaviour, mobility and fate	128
6.3.5 Agronomic effects	129
References	131

LIST OF FIGURES

Figure	1.1	Google Trends [™] result of "biochar", " <i>Terra Preta</i> " and "black earth". The scale is based on the average worldwide traffic of "biochar" from January 2004 until June 2009 (search performed on 04/12/2009)	
Figure	1.2	Google Trends [™] geographical distribution of the search volume index of "biochar" of the last 12 months from June 2008 to June 2009 (search performed on 16/09/2009). Data is normalised against the overall search volume by country	32
Figure	1.3	Scientific publications registred in Thompson's ISI Web of Science indexed for either biochar or bio-char including those articles that mention charcoal (search performed on 4/12/2009)	33
Figure	1.4	Distribution of Anthrosols in Amazonia (left; Glaser et al., 2001) and Europe (middle and right; Toth et al., 2008; Blume and Leinweber, 2004)	33
Figure	1.5	Comparing tropical with temperate Anthrosols. The left half shows a profile of a fertile Terra Preta (Anthrosol with charcoal) created by adding charcoal to the naturally-occurring nutrient poor Oxisol (far left; photo courtesy of Bruno Glaser). The right half (far right) is a profile picture of a fertile European Plaggen Soil (Plaggic Anthrosol; photo courtesy of Erica Micheli) created by adding peat and manure to the naturally-occurring nutrient poor sandy soils (Arenosols) of The Netherlands	
Figure	1.6	Terms and properties of pyrogenic BC (adopted from Preston and Schmidt, 2006)	36
Figure	1.7	Diagram of the carbon cycle. The black numbers indicate how much carbon is stored in various reservoirs, in billions of tons (GtC = Gigatons of Carbon and figures are circa 2004). The purple numbers indicate how much carbon moves between reservoirs each year, i.e. the fluxes. The sediments, as defined in this diagram, do not include the ~70 million GtC of carbonate rock and kerogen (NASA, 2008)	
Figure	1.9	A graph showing the relative proportions of end products after fast pyrolysis of aspen poplar at a range of temperatures (adapted from IEA, 2007)	42
Figure	2.1	Putative structure of charcoal (adopted from Bourke et al., 2007). A model of a microcristalline graphitic structure is shown on on the left and an aromatic structure containing oxygen and carbon free radicals on the right	49

- Figure 3.1 Typical representation of the soil water retention curve as provided by van Genuchten (1980) and the hypothesized effect of the addition of biochar to this soil
- Figure 3.2 The percentage change in crop productivity upon application of biochar at different rates, from a range of feedstocks along with varying fertiliserco-amendments. Points represent mean and bars represent 95% confidence intervals. Numbers next to bars denote biochar application rates (t ha⁻¹). Numbers in the two columns on the right show number of total 'replicates' upon which the statistical analysis is based (bold) and the number of 'experimental treatments' which have been grouped for each analysis (italics)
- Figure 3.3 Percentage change in crop productivity upon application of biochar at different rates along with varying fertiliserco-amendments grouped by change in pH caused by biochar addition to soil. Points represent mean and bars represent 95% confidence intervals. Values next to bars denote change in pH value. Numbers in the two columns on the right show number of total 'replicates' upon which the statistical analysis is based (bold) and the number of 'experimental treatments' which have been grouped for each analysis (italics)
- Figure 3.4 The percentage change in crop productivity o upon application of biochar at different rates along with varying fertiliserco-amendments to a range of different soils. Points shows mean and bars so 95% confidence intervals. Numbers in the two columns on the right show number of total 'replicates' upon which the statistical analysis is based (bold) and the number of 'experimental treatments' which have been grouped for each analysis (italics)
- Figure 3.5 The percentage change in crop productivity of either the biomass or the grain upon application of biochar at different rates along with varying fertiliserco-amendments. Points shows mean and bars so 95% confidence intervals. Numbers in the two columns on the right show number of total 'replicates' upon which the statistical analysis is based (bold) and the number of 'experimental treatments' which have been grouped for each analysis (italics)
- Figure 3.6 The percentage change in crop productivity upon application of biochar along with a co-amendment of organic fertiliser(o), inorganic fertiliser(I) or no fertiliser(none). Points shows mean and bars so 95% confidence intervals. Numbers in the two columns on the right show number of total 'replicates' upon which the statistical analysis is based (bold) and the number of 'experimental treatments' which have been grouped for each analysis (italics)

94

64

91

92

LIST OF TABLES

Table	0.1	Overview of key findings	
Table	1.1	The mean post-pyrolysis feedstock residues resulting from different temperatures and residence times (adapted from IEA, 2007)	
Table	1.2	Summary of key components (by weight) in biochar feedstocks (adapted from Brown et al., 2009)	44
Table	1.3	Examples of the proportions of nutrients (g kg ⁻¹) in feedstocks (adapted from Chan and Xu, 2009)	45
Table	2.1	Relative proportion range of the four main components of biochar (weight percentage) as commonly found for a variety of source materials and pyrolysis conditions (adapted from Brown, 2009; Antal and Gronli, 2003)	
Table	2.2	Summary of total elemental composition (C, N, C:N, P, K, available P and mineral N) and pH ranges and means of biochars from a variety of feedstocks (wood, green wastes, crop residues, sewage sludge, litter, nut shells) and pyrolysis conditions (350-500°C) used in various studies (adapted from Chan and Xu, 2009)	•
Table	3.1	Pore size classes in material science vs. soil science	61
Table	6.1	Overview of key findings	117

LIST OF ACRONYMS

BC Black carbon

CEC Cation Exchange Capacity
DOM Dissolved Organic Matter

HOCs Hydrophobic Organic Compounds NOM Natural (or Native) Organic Matter

NPs Nanoparticles OM Organic Matter

PAHs Polycyclic Aromatic Hydrocarbons

PCDD/PCDFs Dioxins and furans
(S)OC (Soil) Organic Carbon
SOM Soil Organic Matter
SWR Soil Water Repellency

VOCs Volatile Organic Compounds

LIST OF UNITS

Micrometer (= 10⁻⁶ m) μm

1 bar = 100 kPa = 0.987 atmBar

Centimol of charge (1 cmol kg⁻¹ = 1 meq 100g⁻¹) per Cmol_c g⁻¹

gram

Gt y⁻¹ Gigatonnes per year

Joule (1J = 1 kg m^2 sec⁻²) per gram per Kelvin

J g⁻¹ K⁻¹ J g⁻¹ K⁻¹ Joule per gram per Kelvin Kelvin (1 K = $^{\circ}$ C + 273,15) K

Kilojoule (= 10^3 J) per mole (1 mol $\approx 6.022 \times 10^{23}$ atoms kJ mol⁻¹

or molecules of the pure substance measured)

Megagram (= 10⁶ g) *per* hectare Nanometer (= 10⁻⁹ m) Mg ha⁻¹

nm

°C sec⁻¹ Degrees Celsius per second (rate of temperature

increase)

t ha⁻¹ Tonnes per hectare

 $v v^{-1}$ Volume per volume (e.g. 1 ml per 100 ml) $w w^{-1}$ Weight per weight (e.g. 1 g per 100 g)

LIST OF CHEMICAL ELEMENTS AND FORMULAS

Al Aluminium
Ar Arsenic
C Carbon

CaCO₃ Calcium carbonate
CaO Calcium oxide
CH₄ Methane

 CH_4 Methane CI Chlorine

CO₂ Carbon dioxide
Cr Chromium
Cu Copper
H Hydrogen
H₂ Hydrogen gas
Hg Mercury
K Potassium

K2OPotassium oxideMgMagnesiumNNitrogenN2ONitrous oxideNa2OSodium oxideNH4+Ammonium (ion)

Ni Nickel
NO3 Nitrate (ion)
O Oxygen
P Phosphorus

Pb Lead Sulphur Si Silicon

SiO₂ Silica (silicon dioxide)

Zn Zinc

LIST OF KEY TERMS

Accelerated soil erosion

Soil erosion, as a result of anthropogenic activity, in excess of natural soil formation rates causing a deterioration or loss of one or more soil functions

Activated carbon

(noun) Charcoal produced to optimise its reactive surface area

(e.g. by using steam during pyrolysis)

Anthrosol

(count noun) A soil that has been modified profoundly through human activities, such as addition of organic materials or household wastes, irrigation and cultivation (WRB, 2006)

Biochar

i) (Material) charcoal for application to soilii) (Concept) "charcoal (biomass that has b

(Concept) "charcoal (biomass that has been pyrolysed in a zero or low oxygen environment) for which, owing to its inherent properties, scientific consensus exists that application to soil at a specific site is expected to sustainably sequester carbon and concurrently improve soil functions (under current and future management), while avoiding short- and long-term detrimental effects to the wider environment as well as human and animal health."

Black carbon

(noun) All C-rich residues from fire or heat (including from coal,

gas or petrol)

Black Earth

(mass noun) Term synonymous with Chernozem used (e.g. in Australia) to describe self-mulching black clays (SSSA, 2003) (mass noun) 1. Synonym of 'charcoal'; 2. charred organic matter

Char

as a result of wildfire (Lehmann and Joseph, 2009)

(verb) synonym of the term 'pyrolyse' (mass noun) charred organic matter

Charcoal Chernozem

(count noun) A black soil rich in organic matter; from the Russian

'chernij' meaning 'black' and 'zemlja' meaning 'earth' or 'land'

(WRB, 2006)

Coal

(mass noun) Combustible black or dark brown rock consisting chiefly of carbonized plant matter, found mainly in underground

seams and used as fuel (OED, 2003)

Combustion

(mass noun) chemistry Rapid chemical combination of a substance with oxygen, involving the production of heat and light

(OED, 2003)

Decline in soil biodiversity

(soil threat) Reduction of forms of life living in the soil (both in terms of quantity and variety) and of related functions, causing a

deterioration or loss of one or more soil functions

Decline in soil organic matter

(soil threat) A negative imbalance between the build-up of SOM and rates of decomposition leading to an overall decline in SOM contents and/or quality, causing a deterioration or loss of one or

more soil functions

(SOM)

Desertification (soil threat) land degradation in arid, semi-arid and dry sub-humid

areas resulting from various factors, including climatic variations and human activities, causing a deterioration or loss of one or

more soil functions

Dust

The finest fraction of biochar, rather than the particulate matter emitted during pyrolysis. This fraction comprises distinct particle

sizes within the micro- and nano-size range.

Ecosystem functions Feedstock Landslides

The capacity of natural processes and components to provide goods and services that satisfy human needs, directly or indirectly

(noun) Biomass that is pyrolysed in order to produce biochar The movement of a mass of rock, debris, artificial fill or earth down

a slope, under the force of gravity

Nanoparticle

(noun) Any particle with at least one dimension smaller than 100 nm (e.g. fullerenes or fullerene-like structures, crystalline forms of

silica, cristobalite and tridymite)

(noun) biology C that was originally part of an organism; Organic carbon (chemistry) C that is bound to at least one hydrogen (H) atom

(mass noun) The thermal degradation of biomass in the absence

of oxygen leading to the production of condensable vapours,

gases and charcoal

(mass noun) The unconsolidated mineral or organic matter on the surface of the earth that has been subjected to and shows effects of genetic and environmental factors of: climate (including water and temperature effects), and macro- and microorganisms, conditioned by relief, acting on parent material over a period of

time (ENVASSO, 2008).

(count noun) a spatially explicit body of soil, usually differentiated vertically into layers formed naturally over time, normally one of a specific soil class (in a specified soil classification system) surrounded by soils of other classes or other demarcations like hard rock, a water body or artificial barriers (ENVASSO, 2008) (soil threat) The densification and distortion of soil by which total and air-filled porosity are reduced, causing a deterioration or loss

of one or more soil functions

(soil threat) The accumulation of pollutants in soil above a certain Soil contamination

level, causing a deterioration or loss of one or more soil functions. (soil threat) The wearing away of the land surface by physical forces such as rainfall, flowing water, wind, ice, temperature change, gravity or other natural or anthropogenic agents that abrade, detach and remove soil or geological material from one point on the earth's surface to be deposited elsewhere. When the term 'soil erosion' is used in the context of it representing a soil

threat it refers to 'accelerated soil erosion'.

A subset of ecosystem functions: those ecosystem functions that Soil functions are maintained by soil

Usage:

Most soil function systems include the following:

Habitat function

2) Information function

3) **Production** function

4) **Engineering function**

Regulation function 5)

(noun) The organic fraction of the soil exclusive of undecayed Soil organic matter plant and animal residues (SSSA, 2001)

(soil threat) Accumulation of water soluble salts in the soil, causing

a deterioration or loss of one or more soil functions.

(soil threat and key issue) The destruction or covering of soil by buildings, constructions and layers, or other bodies of artificial material which may be very slowly permeable to water (e.g. asphalt, concrete, etc.), causing a deterioration or loss of one or more soil functions

A phenomenon that causes a deterioration or loss of one or more soil functions.

Usage:

Eight main threats to soil identified by the EC (2002) with the addition of desertification:

- Soil erosion 1.
- 2. Decline in soil organic matter
- 3. Soil contamination
- 4. Soil sealing
- 5. Soil compaction
- Decline in soil biodiversity 6.
- 7. Soil salinisation
- Landslides

Soil compaction

Soil erosion

Pyrolysis

Soil

Soil salinisation

Soil sealing

Soil threats

Soil water repellency

Terra Preta

9. Desertification

the reduction of the affinity of soils to water such that they resist wetting for periods ranging from a few seconds to hours, days or weeks (King, 1981)

weeks (King, 1981)
(noun) Colloquial term for a kind of Anthrosol where charcoal (or biochar) has been applied to soil along with many other materials, including pottery shards, turtle shells, animal and fish bones, etc. Originally found in Brazil. From the Portuguese 'terra' meaning 'earth' and 'preta' meaning 'black'.

1. BACKGROUND AND INTRODUCTION

Biochar is commonly defined as charred organic matter, produced with the intent to deliberately apply to soils to sequester carbon and improve soil properties (based on: Lehmann and Joseph, 2009). The only difference between biochar and charcoal is in its utilitarian intention; charcoal is produced for other reasons (e.g. heating, barbeque, etc.) than biochar. In a physicochemical sense, biochar and charcoal are essentially the same material. It could be argued that biochar is a term that is used for other purposes than scientific, i.e. to re-brand charcoal into something more attractive-sounding to serve a commercial purpose. However, from a soil science perspective it is useful to be able to distinguish between any charcoal material and those charcoal materials where care has been taken to avoid deleterious effects on soils and to promote beneficial ones. As this report makes clear, the wide variety of soil groups and associated properties and processes will require specific charcoal properties for specific soils in order to meet the intention of biochar application. Considering the need to make this distinction, a new term is required and since biochar is the most common term currently used, it was selected for this report. The definition of the concept of biochar used in this report is:

"charcoal (biomass that has been pyrolysed in a zero or low oxygen environment) for which, owing to its inherent properties, scientific consensus exists that application to soil at a specific site is expected to sustainably sequester carbon and concurrently improve soil functions (under current and future management), while avoiding short- and long-term detrimental effects to the wider environment as well as human and animal health." As a material, biochar is defined as: "charcoal for application to soil".

The distinction between biochar as a concept and as a material is important. For example, a particular biochar (material) may comply with all the conditions in the concept of biochar when applied to field A, but not when applied to field B. This report investigates the evidence for when, where and how actual biochar application to soil complies with the concept, or not.

The terms 'charcoal' and 'pyrogenic black carbon (BC)' are also used in this report when appropriate according to their definitions above and in the List of Key Terms. Additionally, BC refers to C-rich residues from fire or heat (including from coal, gas or petrol).

This report aims to review the state-of-the-art regarding the interactions between biochar application to soil and its effects on soil properties, processes and functioning. A number of recent publications have addressed parts of this objective as well (Sohi et al., 2009; Lehmann and Joseph, 2009; Collison et al., 2009). This report sets itself apart by i) addressing the issue from an EU perspective, ii) inclusion of quantitative meta-analyses of selected effects, and iii) a discussion of biochar for the threats to soil as identified by the Thematic Strategy for Soil Protection (COM(2006) 231). In addition, this report is independent, objective and critical.

Biochar is a stable carbon (C) compound created when biomass (feedstock) is heated to temperatures between 300 and 1000°C, under low (preferably zero) oxygen concentrations. The objective of the biochar concept is to abate

the enhanced greenhouse effect by sequestering C in soils, while concurrently improving soil quality. The proposed concept through which biochar application to soils would lead to C sequestration is relatively straightforward. Carbondioxide from the atmosphere is fixed in vegetation through photosynthesis. Biochar is subsequently created through pyrolysis of the plant material thereby potentially increasing its recalcitrance with respect to the original plant material. The estimated residence time of biochar-carbon is in the range of hundreds to thousands of years while the residence time of carbon in plant material is in the range of decades. Consequently, this would reduce the CO2 release back to the atmosphere if the carbon is indeed persistently stored in the soil. The carbon storage potential of biochar is widely hypothesised, although it is still largely unquantified, particularly when also considering the effects on other greenhouse gasses (see Section 1.3), and the secondary effects of large-scale biochar deployment. Concomitant with carbon sequestration, biochar is intended to improve soil properties and soil functioning relevant to agronomic and environmental performance. Hypothesised mechanisms that have been suggested for potential improvement are mainly improved water and nutrient retention (as well as improved soil structure, drainage).

Considering the multi-dimensional and cross-cutting nature of biochar, an imminent need is anticipated for a robust and balanced scientific review to effectively inform policy development on the current state of knowledge with reference to biochar application to soils.

How to read this report?

Chapter 1 introduces the concept of biochar and its origins, including a comparison with European conditions/history.

Chapter 2 reviews the range of physical and chemical properties of biochars that are most relevant to soils.

Chapter 3 focuses on the interactions between biochar application to soil and soil properties, processes and functions.

Chapter 4 outlines how biochar application can be expected to influence threats to soils.

Chapter 5 discusses some key issues regarding biochar that are beyond the scope of this report.

Chapter 6 summarises the main findings of the previous chapters, synthesises between these and identifies the key findings. Suggestions for further reading are inserted where appropriate.

1.1 Biochar in the attention

The concept of biochar is increasingly in the attention in both political and academic arenas, with several countries (e.g. UK, New Zealand, U.S.A.) establishing 'biochar research centres'; as well as in the popular media where it is often portrayed as a miracle cure (or as a potential environmental disaster). The attention of the media and public given to biochar can be illustrated by contrasting a GoogleTM search for 'biochar' with a search for 'biofuels'. A Google search for biochar yields 185,000 hits while biofuels yields 5,210,000 hits. Another illustration is given by comparing the search volumes of 'biochar', '*Terra Preta*' and 'black earth' over the last years, testifying the recent increase in attention in and exposure of biochar (Figure 1.1, made with Google TrendsTM).

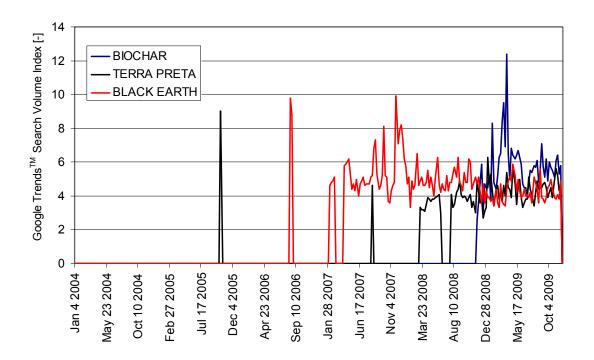


Figure 1.1 Google Trends TM result of "biochar", "Terra Preta" and "black earth". The scale is based on the average worldwide traffic of "biochar" from January 2004 until June 2009 (search performed on 04/12/2009)

The geographical interest in biochar can be explored further by using the search volume index of biochar; the total number of searches normalised by the overall search volume by country. Over the last 12 months the search volume index for biochar was highest in Australia and New Zealand (Figure 1.2). The actual attention for biochar in Australia may even be higher, since in Australia biochar is also referred to as 'Agrichar', one of its trade names.

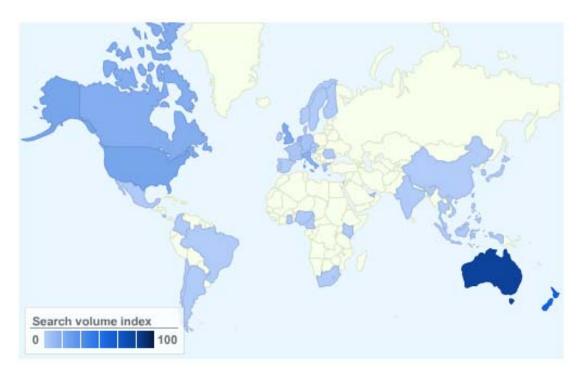


Figure 1.2 Google TrendsTM geographical distribution of the search volume index of "biochar" of the last 12 months from June 2008 to June 2009 (search performed on 16/09/2009). Data is normalised against the overall search volume by country

An indication for the attention devoted to biochar by the scientific community is provided by performing a search in the scientific literature search engines Thompson's ISI Web of Science and Google ScholarTM. A search in Google ScholarTM yielded 724 hits for biochar and 48,600 hits for biofuels (searches undertaken on 16/09/2009). If we consider 'Terra Preta' - a Hortic Anthrosol found in Amazonia – in comparison to biochar, a search yielded 121,000 hits on Google and 1,490 on Google Scholar. A search in the ISI Web of Science for those articles indexed for either biochar or bio-char yielded a total of 81 articles (Figure 1.3). Three authors are independently involved in 22 articles (~25%) of these 81 articles (Lehmann (9); Derimbas (8); Davaajav (8)). Out of the 81 articles 27 articles include a reference to charcoal (Figure 1.3). This is an indication of the relative small number of scientists currently involved in biochar research, although the number of articles is rapidly increasing (Figure 1.3). Finally, the oldest paper appearing in either ISI Web of Science[™] or ScopusTM dealing with 'biochar', 'Terra Preta' or 'black earth' dates from 1998, 1984 and 1953, respectively.

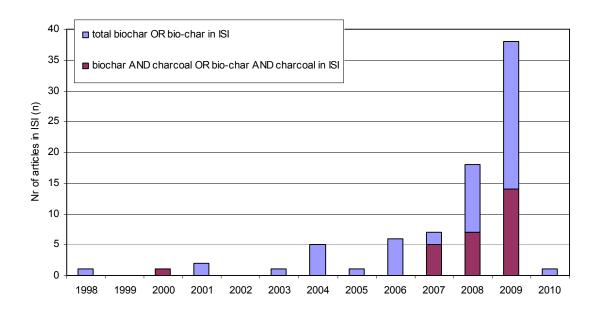


Figure 1.3 Scientific publications registred in Thompson's ISI Web of Science indexed for either biochar or bio-char including those articles that mention charcoal (search performed on 4/12/2009)

1.2 Historical perspective on soil improvement

Man-made soils (Anthrosols) enriched with charcoal are found as small pockets (10s – 200 m in diameter) close to both current and historic human settlements throughout Amazonia (see Figure 1.4) which are estimated to cover a total area of 6,000 – 18,000 km² (Sombroek and Carvalho de Souza, 2000). A rapidly expanding body of scientific literature has reached the consensus that these soils were created by indigenous people, as far back as 10,000 yr BP (Woods et al., 2009), with varying depth (down to 1 m).

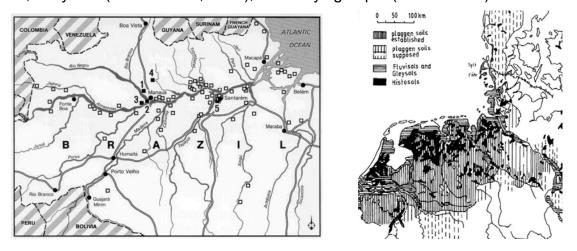


Figure 1.4 Distribution of Anthrosols in Amazonia (left; Glaser et al., 2001) and Europe (right; Blume and Leinweber, 2004)

The first Anthrosols in Europe, which are mostly enriched with organic material from peatlands and heathlands, have been dated to 3,000 vr BP on

the German island of Sylt (Blume and Leinweber, 2004). The largest expanse, from a 3,500 km² total European area of man-made soils (Plaggic Anthrosols), was created during the Middle Ages in the nutrient poor, dry sandy soils (Arenosols) of The Netherlands, northern Belgium and northwestern Germany (Figure 1.4) to similar depths as their Amazonian counterparts (i.e. down to 1 m).

Such a vast single area of Anthrosols is rare, if not unique, and may be explained by the relatively high population density (and subsequent food demand) combined with environmental factors, i.e. the presence of extensive peat deposits in close proximity to the nutrient poor free-draining soil. Much more common are small scale Anthrosols, pockets of man-made soils close to settlements, as an inevitable consequence or planned soil conditioning, by a 'permanent' human settlement that continuously produces organic waste. Many Anthrosols do not appear on the EU soil distribution map because of their small size in relation to the 1:1,000,000 scale of the Soil Geographical Database of Eurasia, which is the basis of the map (Toth et al., 2008). However, numerous small scale Anthrosols have been reported across the European continent, e.g. Scotland (Meharg et al., 2006; Davidson et al., 2006), Ireland, Italy, Spain and northwest Russia (Giani et al., 2004). Based on their formation, it can be assumed that Anthrosols exist in other parts of Europe as well, but data are lacking.

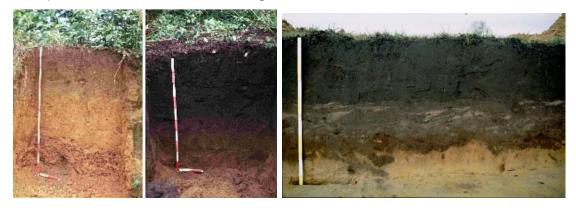


Figure 1.5 Comparing tropical with temperate Anthrosols. The left half shows a profile of a fertile Terra Preta (Anthrosol with charcoal) created by adding charcoal to the naturally-occurring nutrient poor Oxisol (far left; photo courtesy of Bruno Glaser). The right half (far right) is a profile picture of a fertile European Plaggen Soil (Plaggic Anthrosol; photo courtesy of Erica Micheli) created by adding peat and manure to the naturally-occurring nutrient poor sandy soils (Arenosols) of The Netherlands

Although both European and Amazonian Anthrosols were enriched to increase their agricultural performance, there is an important distinction between the Plaggic Anthrosols of Europe and the Hortic Anthrosols of Amazonia (Figure 1.5). Plaggic is from the Dutch 'Plag' meaning a cut out section of the organic topsoil layer, including vegetation (grass or heather) while Hortic Anthrosol translates freely into 'kitchen soil'. These names are reflected in their composition, i.e. Plaggic Anthrosols were made by adding organic topsoil material and peat (early Middle Ages) and mixed with manure (late Middle Ages) while Hortic Anthrosols were created by a wide variety of organic and mineral materials, ranging from animal bones to charcoal and pottery fragments. What sets the Terra Preta apart from other Hortic

Anthrosols is the high proportion of charcoal. It is assumed that the charcoal was made deliberately for application to soil, i.e. not just charred remains from clearing and burning the forest.

1.3 Different solutions to similar problems

The challenges faced by the people of two very different environments (tropical rain forest vs. temperate climate on largely open or partially deforested land) appear similar in the sense of needing to grow crops on soils that naturally had low nutrient and water retention. One can only speculate as to what exactly the reasons were for the people living at the time to either add or not add charcoal to their soils. In addition to the available supply of organic materials, possible explanations may be related to the relative value of the different organic materials and contrasting residence times of SOM. In a simplified scenario, the colder climate in Europe means that microbial decomposition occurs much more slowly than in the tropics, leading to much longer residence times of organic matter. The recalcitrance of the peat and plaggen that were added to the soil meant that the benefits from increased water and (to a lesser degree) nutrient retention lasted long enough to make it worth the investment. In tropical soils, however, the recalcitrance of the organic matter that was added to the soil needed to be greater to get a return that was worth the investment. Charring organic matter may have been a conscious policy to achieve this. Of course, wood and charcoal were being produced in Europe at the time as well. However, other uses of these materials were likely to be more valuable, e.g. the burning of wood in fire places to heat living accommodations and the use of charcoal to achieve high enough temperatures for extracting metals from ores.

Because of the relatively small areal extent of Anthrosols, many of their locations may not be known or recognised presently. It is possible that small pockets of Anthrosols exist in Europe, created at different times in history, where greater amounts of charcoal are present than in the Plaggic Anthrosols. Potentially, identification and study of these sites (including chronosequences) could provide valuable information regarding the interactions between charcoal and environmental factors prevalent in Europe.

1.4 Biochar and pyrogenic black carbon

A potential analogue for biochar may be found in the charcoal produced by wildfires (or pyrogenic black carbon – BC – as it is often referred to) found naturally in soils across the world, and in some places even makes up a larger proportion of total organic C in the soil than in some Terra Preta soils. Preston and Schmidt (2006) showed an overview of studies on non-forested sites in different parts of the world with BC making up between 1 and 80% of total SOC. For example, BC was found to constitute 10-35% of the total SOC content for five soils from long-term agricultural research sites across the U.S.A. (Skjemstad et al., 2002). Schmidt et al. (1999) studied pyrogenic BC contents of chernozemic soils (Cambisol, Luvisol, Phaeozem, Chernozem and Greyzem) in Germany and found BC to make up 2-45% of total SOC (mean of 14%).

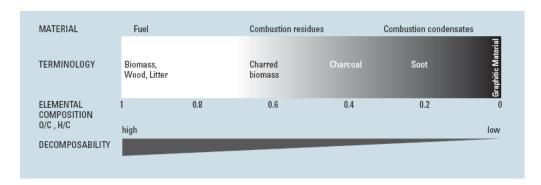


Figure 1.6 Terms and properties of pyrogenic BC (adopted from Preston and Schmidt, 2006)

However, it is important to bear in mind that, while the range of BC materials produced by wildfire overlaps with the range of biochar materials (i.e. the continuum from charred biomass to soot and graphite; Figure 1.6), the composition and properties of biochar can be very different to pyrogenic BC (see Chapter 2). The two main responsible factors are feedstock and pyrolysis conditions. In a wildfire, the feedstock is the aboveground biomass (and sometimes peat and roots) while for biochar any organic feedstock can theoretically be used from wood and straw to chicken manure (Chapter 2). In a pyrolysis oven, the pyrolysis conditions can be selected and controlled, including maximum temperature and duration but also the rate of temperature increase, and inclusion of steam, or e.g. KOH, activation and oxygen conditions.

1.5 Carbon sequestration potential

Globally, soil is estimated to hold more organic carbon (1,100 Gt; 1 Gt=1,000,000,000 tonnes) than the atmosphere (750 Gt) and the terrestrial biosphere (560 Gt) (Post et al., 1990; Sundquist, 1993). In the Kyoto Protocol on Climate Change of 1997, which was adopted in the United Nations Framework Convention on Climate Change, Article 3.4 allows organic carbon stored in arable soils to be included in calculations of net carbon emissions. It speaks of the possibility of subtracting the amounts of CO₂ removed from the atmosphere into agricultural sinks, from the assigned target reductions for individual countries. SOC sequestration in arable agriculture has been researched (Schlesinger, 1999; Smith et al., 2000a, b; Freibauer et al., 2002; West & Post, 2002; Sleutel et al., 2003; Janzen, 2004; King et al., 2004; Lal, 2004) against the background of organic carbon (OC) credit trading schemes (Brown et al., 2001; Johnson & Heinen, 2004). However, fundamental knowledge on attainable SOC contents (relative to variation in environmental factors) is still in its infancy, and it is mostly approached by modelling (Falloon et al., 1998; Pendall et al., 2004).

The principle of using biochar for carbon (C) sequestration is related to the role of soils in the C-cycle (Figure 1.7). As Figure 1.7 shows, the global flux of CO_2 from soils to the atmosphere is in the region of 60 Gt of C per year. This CO_2 is mainly the result of microbial respiration within the soil system as the microbes decompose soil organic matter (SOM). Components of biochar are proposed to be considerably more recalcitrant than SOM and as such are only decomposed very slowly, over a time frame which can be measured in

hundreds or thousands of years. This means that biochar allows carbon input into soil to be increased greatly compared to the carbon output through soil microbial respiration, and it is this that is the basis behind biochar's possible carbon negativity and hence its potential for climate change mitigation.

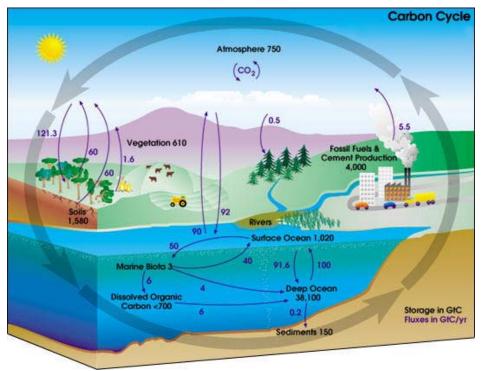


Figure 1.7 Diagram of the carbon cycle. The black numbers indicate how much carbon is stored in various reservoirs, in billions of tons (GtC = Gigatons of Carbon and figures are circa 2004). The purple numbers indicate how much carbon moves between reservoirs each year, i.e. the fluxes. The sediments, as defined in this diagram, do not include the \sim 70 million GtC of carbonate rock and kerogen (NASA, 2008)

Although Figure 1.7 is clearly a simplification of the C-cycle as it occurs in nature, the numbers are well established (NASA, 2008) and relatively uncontroversial. A calculation of the fluxes, while being more a 'back of the envelope' calculation, than precise mathematics, is highly demonstrative of the anthropogenic influence on atmospheric CO₂ levels. When all of the sinks are added together (that is the fluxes of CO₂ leaving the atmosphere) the total amount of C going into sinks is found to be in the region of 213.35 Gt per year. Conversely, when all of the C fluxes emitted into the atmosphere from non-anthropogenic (natural) sources are added, they total 211.6 Gt per year. This equates to a net loss of carbon from the atmosphere of 1.75 Gt C.

It is for this reason that the relatively small flux of CO_2 from anthropogenic sources (5.5 Gt C per year) is of such consequence as it turns the overall C flux from the atmosphere from a *loss* of 1.75 Gt per year, to a *net gain* of 3.75 Gt C per year. This is in relatively close agreement with the predicted rate of CO_2 increase of about 3 Gt of C per year (IPCC, 2001). It is mitigation of this net gain of CO_2 to the atmosphere that biochar's addition to soil is posited for.

Lehmann et al. (2006) estimate a potential global C-sequestration of 0.16 Gt yr⁻¹ using current forestry and agricultural wastes, such as forest residues, mill residues, field crop residues, and urban wastes for biochar production. Using

projections of renewable fuels by 2100, the same authors estimate sequestration to reach a potential range of 5.5-9.5 Gt yr⁻¹, thereby exceeding current fossil fuel emissions. However, the use of biochar for climate change mitigation is beyond the scope of this report that focuses on the effects of biochar addition to soils with regard to physical, chemical and biological effects, as well as related effects on soil and ecosystem functioning.

1.5.1 Biochar loading capacity

Terra Preta soils have been shown to contain about 50 t C ha⁻¹ in the form of BC, down to a depth of approximately 1 meter (approximately double the amount relative to pre-existing soil), and these soils are highly fertile when compared to the surrounding soils. This has lead to the idea of biochar being applied to soil to sequester carbon and maintain or improve the soil production function (e.g. crop yields), as well as the regulation function and habitat function of soils. Controlled experiments have been undertaken to look at the effects of different application rates of biochar to soils.

At present, however, it is not clear whether there is a maximum amount of C, in the form of biochar, which can be safely added to soils without compromising other soil functions or the wider environment; that is, what is the 'biochar loading capacity' (BLC) of a given soil? It will be important to determine if the BLC varies between soil types and whether it is influenced by the crop type grown on the soil. In order to maximise the amount of biochar which can be stored in soils without impacting negatively on other soil functions, the biochar loading capacity of different soils exposed to different environmental and climatic conditions specific to the site will have to be quantified for different types of biochar.

The organic matter fractions of some soils in Europe have been reported to consist of approximately 14% (up to 45%) BC or charcoal (see Section 1.4), which are both analogues of biochar as previously discussed. Lehmann and Rondon (2005) reported that at loadings up to 140 t C ha⁻¹ (in a weathered tropical soil) positive yield effects still occurred. However, it should be noted that some experiments report that some crops experience a loss of the positive effects of biochar addition to soil at a much lower application rate. For example, Rondon et al. (2007) reported that the beans (*Phaseolus vulgaris* L.) showed positive yield effects on biochar application rates up to 50 t C ha⁻¹ that disappeared at an application rate of 60 t C ha⁻¹ with a negative effect on yield being reported at application rates of 150 t C ha⁻¹. This shows that the BLC is likely to be crop dependent as well as probably both soil and climate dependent. Combined with the irreversibility of biochar application to soil, this highlights the complex nature of calculating a soil's BLC as future croppings should be taken into account to ensure that future crop productivity is not compromised if the crop type for a given field is changed. Apart from effects on plant productivity, it can be imagined that other effects, on for example soil biology or transport of fine particles to ground and surface water, should be taken into account when 'calculating' or deriving the BLC for a specific site. Also, the BLC concept would need to be developed for both total (final) amount and the rate of application, i.e. the increase in the total amount over time. The rate of application would need to consist of a long term rate (i.e. t ha⁻¹ yr⁻¹ over 10 or 100 years) as well as a 'per application' rate, both

determined by evidence of direct and indirect effects on soil and the wider environment.

Another consideration regarding the biochar loading capacity of a soil is the risk of smouldering combustion. Organic soils that dry out sufficiently are capable of supporting below ground smouldering combustion that can continue for long time periods (years in some cases). It is feasible that soils which experience very high to extreme loading rates of biochar and are subject to sufficiently dry conditions could support smouldering fires. Ignition of such fires could occur both naturally, e.g. by lightening strike, or anthropogenically. What the biochar content threshold would be, how the threshold would change according to environmental conditions, and how much a risk this would be in non-arid soils remains unclear, but is certainly worthy of thought and future investigation.

1.5.2 Other greenhouse gasses

Carbon dioxide is not the only gas emitted from soil with the potential to influence the climate. Methane (CH₄) production also occurs as a part of the carbon cycle. It is produced by the soil microbiota under anaerobic conditions through a process known as methanogenesis and is approximately 21 times more potent as a greenhouse gas than CO₂ over a time horizon of 100 years.

Nitrous oxide (N_2O) is produced as a part of the nitrogen (N) cycle through process known as nitrification and denitrification which are carried out by the soil microbiota. Nitrous oxide is 310 times more potent as a greenhouse gas than CO_2 over a time horizon of 100 years (U.S. Environmental Protection Agency, 2002).

Whilst these gases are more potent greenhouse gases than CO_2 , only approximately 8% of emitted greenhouse gases are CH_4 and only 5% are N_2O , with CO_2 making up approximately 83% of the total greenhouse gases emitted. Eighty percent of N_2O and 50% of CH_4 emitted are produced by soil processes in managed ecosystems (US Environmental Protection Agency, 2002). It should be noted that these figures detail total proportions of each greenhouse gas and are not weighted to account for climatic forcing.

In one study, biochar addition to soils has been shown to reduce the emission of both CH_4 and N_2O . Rondon et al. (2005) reported that a near complete suppression of methane upon biochar addition at an application rate of 2% w w⁻¹ to soil. It was hypothesised that the mechanism leading to reduced emission of CH_4 is increased soil aeration leading to a reduction in frequency and extent of anaerobic conditions under which methanogenesis occurs. Pandolfo et al. (1994) investigated CH_4 adsorption capacity of several activated carbons (from coconut feedstock) in a series of laboratory experiments. Their results showed increased CH_4 'adsoprtion' with increase surface area of the activated carbon, particularly for micropores (<2 μ m). These charcoal materials were activated using steam or KOH, however, and it remains to be tested how different biochar materials added to soils in the field will interact with methane dynamics. The influence of biochar on SOM dynamics are discussed later in this report (Section 3.2.5).

A reduction in N_2O emissions of 50% in soybean plantations and 80% in grass stands was also reported (Rondon et al. 2005). The authors

hypothesised that the mechanism leading to this reduction in N₂O emissions was due to slower N cycling, possibly as a result of an increase in the C:N ratio. It is also possible that the N that exists within the biochar is not bioavailable when introduced to the soil as it is bound up in heterocyclic form (Camps, 2009; Personal communication). Yanai et al. (2007) measured N₂O emissions from soils after rewetting in the laboratory and found variable results, i.e. an 89% suppression of N₂O emissions at 73-78% water-filled pore space contrasting to a 51% increase at 83% water-filled pore space. These results indicate that the effect of biochar additions to soils on the N cycle depend greatly on the associated changes in soil hydrology and that thresholds of water content effects on N₂0 production may be very important and would have to be studied for a variety of soil-biochar-climate conditions. Furthermore, if biochar addition to soil does slow the N-cycle, this could have possible consequences on soil fertility in the long term. This is because nitrate production in the soil may be slowed beyond the point of plant uptake, meaning that nitrogen availability, often the limiting factor for plant growth in soils, may be reduced leading to concurrent reduction in crop productivity. Yanai et al. (2007) reported that this effect did change over time, but their experiment only ran for 5 days and so extrapolation of the results to the time scales at which biochar is likely to persist in soil is not possible. Further research is therefore needed to better elucidate the effects and allow extrapolation to the necessary time scales.

1.6 Pyrolysis

Pyrolysis is the chemical decomposition of an organic substance by heating in the absence of oxygen. The word is derived from Greek word 'pyro' meaning fire and "lysis" meaning decomposition or breaking down into constituent parts. In practice it is not possible to create a completely oxygen free environment and as such a small amount of oxidation will always occur. However, the degree of oxidation of the organic matter is relatively small when compared to combustion where almost complete oxidation of organic matter occurs, and as such a substantially larger proportion of the carbon in the feedstock remains and is not given off as CO₂. However, with pyrolysis much of the C from the feedstock is still not recovered in charcoal form, but converted to either gas or oil.

Pyrolysis occurs spontaneously at high temperatures (generally above approximately 300°C for wood, with the specific temperature varying with material). It occurs in nature when vegetation is exposed to wildfires or comes into contact with lava from volcanic eruptions. At its most extreme, pyrolysis leaves only carbon as the residue and is called carbonization. The high temperatures used in pyrolysis can induce polymerisation of the molecules within the feedstocks, whereby larger molecules are also produced (including both aromatic and aliphatic compounds), as well as the thermal decomposition of some components of the feedstocks into smaller molecules. This is discussed in more detail in Section 3.2.5.1.

The process of pyrolysis transforms organic materials into three different components, being gas, liquid or solid in different proportions depending upon both the feedstock and the pyrolysis conditions used. Gases which are produced are flammable, including methane and other hydrocarbons which

can be cooled whereby they condense and form an oil/tar residue which generally contains small amounts of water. The gasses (either condenses or in gaseous form) and liquids can be upgraded and used as a fuel for combustion.

The remaining solid component after pyrolysis is charcoal, referred to as biochar when it is produced with the intention of adding it to soil to improve it (see List of Key terms). The physical and chemical properties of biochar are discussed in more detail in Chapter 2.

The process of pyrolysis has been adopted by the chemical industry for the production of a range of compounds including charcoal, activated carbon, methanol and syngas, to turn coal into coke as well as producing other chemicals from wood. It is also used for the breaking down, or 'cracking' of medium-weight hydrocarbons from oil to produce lighter hydrocarbons such as petrol.

A range of compounds in the natural environment are produced by both anthropogenic and non-anthropogenic pyrolysis. These include compounds released from the incomplete burning of petrol and diesel in internal combustion engines, through to particles produced from wood burned in forest fires, for example. These substances are generally referred to as black carbon (see List of Key terms) in the scientific literature and exist in various forms ranging form small particulate matter found in the atmosphere, through to a range of sizes found in soils and sediments where it makes up a significant part of the organic matter (Schmidt et al., 1999; Skjemstad et al., 2002; Preston et al., 2006; Hussain et al. 2008).

1.6.1 The History of Pyrolysis

While it is possible that pyrolysis was first used to make charcoal over 7,000 years ago for the smelting of copper, or even 30,000 years ago for the charcoal drawings of the Chauvet cave (Antal, 2003), the first definitive evidence of pyrolysis for charcoal production comes from over 5,500 years ago in Southern Europe and the Middle East. By 4,000 years ago, the start of the Bronze Age, pyrolysis use for the production of charcoal must have been widespread. This is because only burning charcoal allowed the necessary temperatures to be reached to smelt tin with copper and so produce bronze (Earl, 1995).

A range of compounds can be found in the natural environment that is produced by both anthropogenic and non-anthropogenic pyrolysis. These include compounds released from the incomplete burning of petrol and diesel in internal combustion engines, through to being produced from wood in forest fires for example.

1.6.2 Methods of Pyrolysis

Although the basic process of pyrolysis, that of heating a C-containing feedstock in an limited oxygen environment, is always the same, different methodologies exist, each with different outputs.

Apart from the feedstocks used, which are discussed further is Section 1.7, the main variables that are often manipulated are pyrolysis temperature, and

the residence time of the feedstock in the pyrolysis unit. Temperature itself can have a large effect on the relative proportions of end product from a feedstock (Fig. 1.9).

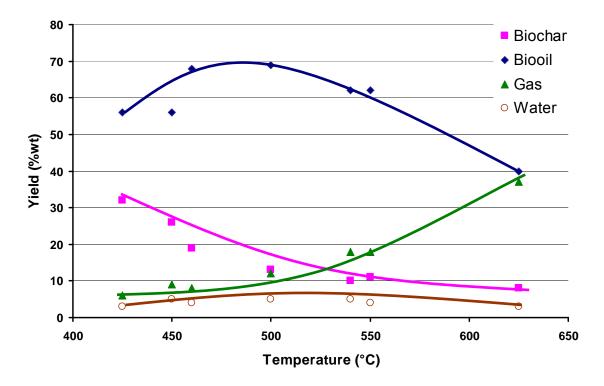


Figure 1.8 A graph showing the relative proportions of end products after fast pyrolysis of aspen poplar at a range of temperatures (adapted from IEA, 2007)

Residence times of both the solid constituents and the hot vapor produced under pyrolysis conditions can also have a large effect on the relative proportions of each end product of pyrolysis (Table 1.1). In the nomenclature, four different types of pyrolysis are generally referred to, with the difference between each being dependent on temperature and residence time of solid or vapour in the pyrolysis unit, or a combination of both. The four different types of pyrolysis are fast, intermediate and slow pyrolysis (with slow pyrolysis often referred to as "carbonisation" due to the relatively high proportion of carbonaceous material it produces: biochar) along with gasification (due to the high proportion of syngas produced).

Table 1.1 shows that different pyrolysis conditions lead to different proportions of each end product (liquid, char or gas). This means that specific pyrolysis conditions can be tailored to each desired outcome. For example, the IEA report (2007) stated that fast pyrolysis was of particular interest as liquids can be stored and transported more easily and at lower cost than solid or gaseous biomass forms. However, with regard to the use of biochar as a soil amendment and for climate change mitigation it is clear that slow pyrolysis, would be preferable, as this maximises the yield of char, the most stable of the pyrolysis end products.

Table 1.1 The mean post-pyrolysis feedstock residues resulting from different temperatures and residence times (adapted from IEA, 2007)

Mode	Conditions	Liquid	Biochar	Syngas
Fast pyrolysis	Moderate temperature, ~500°C, short hot vapour residence time of ~ 1 s	75%	12%	13%
Intermediate Pyrolysis	Moderate temperature ~500°C, moderate hot vapour residence time of 10 – 20 s	50%	20%	30%
Slow Pyrolysis (Carbonisation)	Low temperature ~400°C, very long solids residence time	30%	35%	35%
Gasification	High temperature ~800°C, long vapour residence time	5%	10%	85%

Owing to the fact that end products such as flammable gas can be recycled into the pyrolysis unit and so provide energy for subsequent pyrolysis cycles, costs, both in terms of fuel costs, and of carbon emission costs, can be minimised. Furthermore, the pyrolysis reaction itself becomes exothermic after a threshold is passed, thereby reducing the required energy input to maintain the reaction. However, it is important to note that other external costs are associated with pyrolysis, most of which will be discussed in Section 2.4. For example, fast pyrolysis requires that the feedstock is dried to less than 10% water (w w⁻¹). This is done so that the bio-oil is not contaminated with water. The feedstock then needs to be ground to a particle size of *ca.* 2 mm to ensure that there is sufficient surface area to ensure rapid reaction under pyrolysis conditions (IEA, 2007). The grinding of the feedstock, and in some cases also the drying require energy input and will increase costs, as well as of the carbon footprint of biochar production if the required energy is not produced by carbon neutral sources.

As well as different pyrolysis conditions, the scale at which pyrolysis is undertaken can also vary greatly. The two different scales discussed throughout this report are that of 'Closed' vs 'Open' scenarios. Closed refers to the scenario in which relatively small, possibly even mobile, pyrolysis units are used on each farm site, with crop residues and other bio-wastes being pyrolysed on site and added back to the same farm's soils. Open refers to biowastes being accumulated and pyrolysed off-site at industrial scale pyrolysis plants, before the biochar is redistributed back to farms for application to soil. The scales at which these scenarios function are very different, and each brings its own advantages and disadvantages.

1.7 Feedstocks

Feedstock is the term conventionally used for the type of biomass that is pyrolysed and turned into biochar. In principle, any organic feedstock can be pyrolysed, although the yield of solid residue (char) respective to liquid and gas yield varies greatly (see Section 1.6.2) along with physico-chemical properties of the resulting biochar (see Chapter 2).

Feedstock is, along with pyrolysis conditions, the most important factor controlling the properties of the resulting biochar. Firstly, the chemical and

structural composition of the biomass feedstock relates to the chemical and structural composition of the resulting biochar and, therefore, is reflected in its behaviour, function and fate in soils. Secondly, the extent of the physical and chemical alterations undergone by the biomass during pyrolysis (e.g. attrition, cracking, microstructural rearrangements) are dependent on the processing conditions (mainly temperature and residence times). Table 1.2 provides a summary of some of the key components in representative biochar feedstocks.

Table 1.2 Summary of key components (by weight) in biochar feedstocks (adapted from Brown et al., 2009)

	Ash	Lignin (w w ⁻¹)	Cellulose
Wheat straw	11.2	14	38
Maize residue	2.8-6.8	15	39
Switchgrass	6	18	32
Wood (poplar, willow, oak)	0.27 - 1	26 - 30	38 - 45

Cellulose and ligning undergo thermal degradation at temperatures ranging between 240-350°C and 280-500°C, respectively (Sjöström, 1993; Demirbas, 2004). The relative proportion of each component will, therefore, determine the extent to which the biomass structure is retained during pyrolysis, at any given temperature. For example, pyrolysis of wood-based feedstocks generates coarser and more resistant biochars with carbon contents of up to 80%, as the rigid ligninolytic nature of the source material is retained in the biochar residue (Winsley, 2007). Biomass with high lignin contents (e.g. olive husks) have shown to produce some of the highest biochar yields, given the stability of lignin to thermal degradation, as demonstrated by Demirbas (2004). Therefore, for comparable temperatures and residence times, lignin loss is tipically less than half of cellulose loss (Demirbas, 2004).

Whereas woody feedstock generally contains low proportions (< 1% by weight) of ash, biomass with high mineral contents such as grass, grain husks and straw residues generally produce ash-rich biochar (Demirbas 2004). These latter feedstocks may contain ash up to 24% or even 41% by weight, such as rice husk (Amonette and Joseph, 2009) and rice hulls (Antal and Grønly, 2003), respectively. The mineral content of the feedstock is largely retained in the resulting biochar, where it concentrates due to the gradual loss of C, hydrogen (H) and oxygen (O) during processing (Demirbas 2004). The mineral ash content of the feedstock can vary widely and evidence seems to suggest a relationship between that and biochar yield (Amonette and Joseph, 2009). Table 1.3 provides an example of the elemental composition of representative feedstocks.

Table 1.3 Examples of the proportions of nutrients (g kg⁻¹) in feedstocks (adapted from Chan and Xu, 2009)

	Ca	Mg	K	Р
		(g kg ⁻¹)		
Wheat straw	7.70	4.30	2.90	0.21
Maize cob	0.18	1.70	9.40	0.45
Maize stalk	4.70	5.90	0.03	2.10
Olive kernel	97.0	20.0	-	-
Forest residue	130	19.0	-	-

In the plant, Ca occurs mainly within cell walls, where it is bound to organic acids, while Mg and P are bound to complex organic compounds within the cell (Marschner, 1995). Potassium is the most abundant cation in higher plants and is involved in plant nutrition, growth and osmoregulation (Schachtman and Schroeder, 1994). Nitrogen, Mn and Fe also occur associated to a number of organic and inorganic forms. During thermal degradation of the biomass, potassium (K), chlorine (Cl) and N vaporize at relatively low temperatures, while calcium (Ca), magnesium (Mg), phosphorus (P) and sulphur (S), due to increased stability, vaporise at temperatures that are considerably higher (Amonette and Joseph, 2009). Other relevant minerals can occur in the biomass, such as silicon (Si), which occurs in the cell walls, mostly in the form of silica (SiO₂).

Many different materials have been proposed as biomass feedstocks for biochar, including wood, grain husks, nut shells, manure and crop residues, while those with the highest carbon contents (e.g. wood, nut shells), abundancy and lower associated costs are currently used for the production of activated carbon (e.g. Lua et al., 2004; Martinez et al., 2006; Gonzaléz et al., 2009;). Other feedstocks are potentially available for biochar production, among which biowaste (e.g. sewage sludge, municipal waste, chicken litter) and compost. Nevertheless, a risk is associated to the use of such source materials, mostly linked to the occurrence of hazardous components (e.g. organic pollutants, heavy metals). Crystalline silica has also been found to occur in some biochars. Rice husk and rice straw contain unusually high levels of silica (220 and 170 g kg⁻¹) compared to that in other major crops. High concentrations of calcium carbonate (CaCO₃) can be found in pulp and paper sludge (van Zwieten et al., 2007) and are retained in the ash fraction of some biochars.

Regarding the characteristics of some plant feedstocks, Collison et al. (2009) go further, suggesting that even within a biomass feedstock type, different composition may arise from distinct growing environmental conditions (e.g. soil type, temperature and moisture content) and those relating to the time of harvest. In corroboration, Wingate et al. (2009) have shown that the adsorbing properties of a charcoal for copper ions can be improved 3-fold by carefully selecting the growth conditions of the plant biomass (in this case, stinging nettles). Even within the same plant material, compositional heterogeneity has

also been found to occur among different parts of the same plant (e.g. maize cob and maize stalk, Table 1.3).

Lignocellulosic biomass is an obvious feedstock choice because it is one of the most abundant naturally occurring available materials (Amonette and Joseph, 2009). The spatio-temporal occurrence of biomass feedstock will influence the availability of specific biochars and its economic value (e.g. distance from source to field). For example, in an area with predominantly root crops on calcareous sandy arable soils and a dry climate, biochars that provide more water retention and are mechanically strong (e.g. woody feedstocks) are likely to be substantially more valuable than in an area of predominantly combinable crops on acidic sandy soils and a 'year round' wet climate. In the latter case, biochars with a greater CEC, liming capacity and possibly a lower mechanical strength (e.g. crop residue feedstock) may be more in demand.

In Terra Pretas potential feedstocks were limited to wood from the trees and organic matter from other vegetation. Nowadays any biomass material, including waste, is considered as a feedstock for biochar production. Considering that historical sites contain either biochar (Terra Preta) or BC (from wildfires), chronosequence studies can only give us information about the long term consequences and dynamics of those limited natural feedstocks. This implies an important methodological challenge for the study of the long term dynamics of soils with biochar produced from feedstocks other than natural vegetation. Even for trees and plants, careful consideration needs to be given to specific species that bioaccumulate certain metals, or, in the case of crop residues, that may contain relevant concentrations of herbicides, pesticides, fungicides, and in the case of animal manures that may contain antibiotics or their secondary metabolites. See Section 5.1.5 for a more detailed discussion on the (potential) occurrence of contaminants within biochar.

In addition, chronosequence studies using historic sites are often poor predictors of structural disintegration and concomitant chemical reactivity and mobility of biochars, because they are either not in arable land use, or have not been subject to the intense physical disturbance of modern arable tillage and cultivation (e.g. the power harrow).

A detailed description of all biochar feedstocks is beyond the scope of this report and feedstocks have been reviewed in other works (Collison et al., 2009; Lehmann and Joseph, 2009). The key point is that the suitability of each biomass type as a potential source for biochar, is dependent on a number of chemical, physical, environmental, as well as economic and logistical factors (Collison et al., 2009), as discussed, where appropriate, throughout this report. It is important to stress, however, that for any material to be considered as a feedstock for biochar production, and therefore also for application to soil, a rigorous procedure needs to be developed in order to assess the biochar characteristics and long term dynamics in the range of soil, other environmental conditions, and land use and management factors that are considered for its application.

1.8 Application Strategies

Biochar application strategies have been studied very little, although the way biochar is applied to soils can have a substantial impact on soil processes and functioning, including aspects of the behaviour and fate of biochar particles in soil and the wider environment (Chapter 3) as well as on 'threats to soil' (Chapter 4), occupational health and safety (5.2), and economic considerations (Section 5.4). Broadly speaking there are three main approaches: i) topsoil incorporation, ii) depth application, and iii) top-dressing.

For topsoil incorporation biochar can be applied on its own or combined with composts or manures. The degree of mixing will depend on the cultivation techniques used. In conventional tillage systems the biochar (and compost/manure/slurry) will generally be mixed more or less homogeneously throughout the topsoil (in most arable soils from 0-15/30 cm depth). Water and wind erosion will remove biochar along with other soil material, i.e. that would erode without biochar additions as well, and possibly more biochar will be eroded from the surface because of its low density. Potentially, the application of biochar combined with compost or manure would reduce this risk, but studies evidencing this are lacking. In conservation tillage systems the incorporation depth will be reduced (leading to greater biochar concentrations at equal application rates) and possibly a concentration gradient decreasing with depth. In no-till systems any incorporation would be through natural processes (see top-dressing below). Deep mouldboard ploughing effectively results in (temporary) 'depth application' (see below), with more topsoil homogenisation occurring during subsequent ploughing.

Depth application of biochar has been described mostly as 'deep-banded' application (e.g. Blackwell et al., 2007). The placement of the biochar directly into the rhizosphere is thought to be more beneficial for crop growth and less susceptible to erosion. The application can be either by pneumatic systems, which can operate at high rates, or by applying the biochar in furrows or trenches and subsequently levelling the soil surface. Deep mouldboard ploughing essentially results in temporary 'depth application', although horizontally continuous (unlike the 'deep-banded' application). Subsequent mouldboard ploughing and cultivation will then further homogenise the biochar distribution through the topsoil.

Top-dressing of biochar is the spreading of biochar (dust fraction mostly) to the soil surface and relying on natural processes for the incorporation of the biochar into the topsoil. This form of application is being considered mainly for those situations where mechanical incorporation is not possible, e.g. no-till systems, forests, and pastures. An obvious drawback is the risk of erosion by water and wind, as well as human health (inhalation) and impacts on other ecosystem components (e.g. surface water, leaf surfaces, etc.). It is also largely unknown what the rates of incorporation would be for different soil-climate-land use combinations.

The dust fraction of biochar is an issue for all application strategies during the storaging, handling, and applying phases of the biochar (see Sections 2.2.1 and 5.2 for more detailed information about the properties and implications of

biochar's dust fraction). This aspects needs to be investigated thoroughly before implementation. Like any trafficking on soil, there is a risk of (sub)soil compaction during biochar application. This may be particularly the case for the relatively heavy machinery involved in 'depth application'.

Both topsoil incorporation and top-dressing can be applied with a range of frequencies, i.e. a 'one-off' application', every few years, or every year. For specific effects on soil, e.g. nutrient availability (from a feedstock like poultry manure) or liming effect, a more frequent application may be more beneficial to the soil and/or less detrimental to the environment (nitrate leaching).

1.9 Summary

As a concept biochar is defined as 'charcoal (biomass that has been pyrolysed in a zero or low oxygen environment) for which, owing to its inherent properties, scientific consensus exists that application to soil at a specific site is expected to sustainably sequester carbon and concurrently improve soil functions (under current and future management), while avoiding short- and long-term detrimental effects to the wider environment as well as human and animal health'. Inspiration is derived from the anthropogenically created Terra Preta soils (Hortic Anthrosols) in Amazonia where charred organic material plus other (organic and mineral) materials appear to have been added purposefully to soil to increase its agronomic quality. Ancient Anthrosols have been found in Europe as well, where organic matter (peat, manure, 'plaggen') was added to soil, but where charcoal additions appear to have been limited or non-existent. Furthermore, charcoal from wildfires (pyrogenic black carbon - BC) has been found in many soils around the world, including European soils where pyrogenic BC can make up a large proportion of total soil organic carbon.

Biochar can be produced from a wide range of organic feedstocks under different pyrolysis conditions and at a range of scales. Many different materials have been proposed as biomass feedstocks for biochar. The suitability of each biomass type for such an application is dependent on a number of chemical, physical, environmental, as well as economic and logistical factors. The original feedstock used, combined with the pyrolysis conditions will determine the properties, both physical and chemical, of the biochar product. It is these differences in physicochemical properties that govern the specific interactions which will occur with the endemic soil biota upon addition of biochar to soil, and hence how soil dependent ecosystem functions and services are affected. The application strategy used to apply biochar to soils is an important factor to consider when evaluating the effects of biochar on soil properties and processes. Furthermore, the biochar loading capacity of soils has not been fully quantified, or even developed conceptually.

2. PHYSICOCHEMICAL PROPERTIES OF BIOCHAR

This chapter provides an overview of the physical and chemical properties of biochar, as determined mainly by feedstock and the pyrolysis operational conditions. The combined heterogeneity of the feedstock and the wide range of chemical reactions which occur during processing, give rise to a biochar product with a unique set of structural and chemical characteristics (Antal and Gronli, 2003; Demirbas, 2004). A primary focus was given to those characteristics that are more likely to impact on soil properties and processes when biochar is incorporated into soil. The implications of such characteristics in the context of the biochar-soil mixture are discussed in Chapter 3. More detailed information on a wider range of biochar properties can be found in the relevant scientific literature (e.g. Lehmann and Joseph, 2009; and others).

2.1 Structural and Chemical Composition

2.1.1 Structural composition

Thermal degradation of cellulose between 250 and 350°C results in considerable mass loss in the form of volatiles, leaving behind a rigid amorphous C matrix. As the pyrolysis temperature increases, so thus the proportion of aromatic carbon in the biochar, due to the relative increase in the loss of volatile matter (initially water, followed by hydrocarbons, tarry vapours, H₂, CO and CO₂), and the conversion of alkyl and O-alkyl C to aryl C (Baldock and Smernik, 2002; Demirbas 2004). Around 330°C, polyaromatic graphene sheets begin to grow laterally, at the expense of the amorphous C phase, and eventually coalesce. Above 600°C, carbonization becomes the dominant process. Carbonization is marked by the removal of most remaining non-C atoms and consequent relative increase of the C content, which can be up to 90% (by weight) in biochars from woody feedstocks (Antal and Gronli, 2003; Demirbas, 2004).

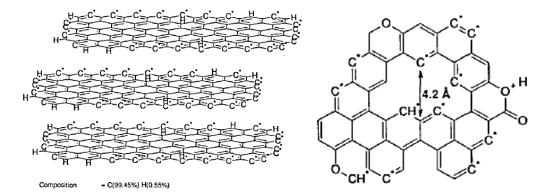


Figure 2.1 Putative structure of charcoal (adopted from Bourke et al., 2007). A model of a microcristalline graphitic structure is shown on on the left and an aromatic structure containing oxygen and carbon free radicals on the right

It is commonly accepted that each biochar particle comprises of two main structural fractions: stacked crystalline graphene sheets and randomly ordered amorphous aromatic structures (Figure 2.1). Hydrogen, O, N, P and S are found predominantly incorporated within the aromatic rings as heteroatoms (Bourke et al., 2007). The presence of heteroatoms is thought to be a great contribution to the highly heterogenous surface chemistry and reactivity of biochar (see the next section).

2.1.2 Chemical composition and surface chemistry

Biochar composition is highly heterogeneous, containing both stable and labile components (Sohi et al., 2009). Carbon, volatile matter, mineral matter (ash) and moisture are generally regarded as its major constituents (Antal and Gronli, 2003). Table 2.1 summarizes their relative proportion ranges in biochar as commonly found for a variety of source materials and pyrolysis conditions (Antal and Gronli, 2003; Brown, 2009).

Table 2.1 Relative proportion range of the four main components of biochar (weight percentage) as commonly found for a variety of source materials and pyrolysis conditions (adapted from Brown, 2009; Antal and Gronli, 2003)

Component	Proportion (w w ⁻¹)	
Fixed carbon	50-90	
Volatile matter (e.g. tars)	0-40	
Moisture	1-15	
Ash (mineral matter)	0.5-5	

The relative proportion of biochar components determines the chemical and physical behaviour and function of biochar as a whole (Brown, 2009), which in turn determines its suitability for a site specific application, as well as transport and fate in the environment (Downie, 2009). For example, coarser and more resistant biochars are generated by pyrolysis of wood-based feedstocks (Winsley, 2007). In contrast, biochars produced from crop residues (e.g. rye, maize), manures and seaweed are generally finer and less robust (lower mechanical strength). The latter are also nutrient-rich, and therefore, more readily degradable by microbial communities in the environment (Sohi et al., 2009). The ash content of biochar is dependent on the ash content of the biomass feedstock. Grass, grain husks, straw residues and manures generally produce biochar with high ash contents, in contrast to that from woody feedstocks (Demirbas 2004). For instance, manure (e.g. chicken litter) biochars can contain 45% (by weight) as ash (Amonette and Joseph, 2009). Moisture is another critical component of biochar (Antal and Gronli, 2003), as higher moisture contents increase the costs of biochar production and transportation for unit of biochar produced. Keeping the moisture content up to 10% (by weight) appears to be desirable (Collison et al., 2009). In order for this to be achieved, pre-drying the biomass feedstock may be a necessity, which can be a challange in biochar production.

Despite the feasibility of biochar being produced from a wide range of feedstocks under different pyrolysis conditions, its high carbon content and strongly aromatic structure are constant features (Sohi et al., 2009). According to Sohi et al. (2009), these features largely account for its chemical stability. Similarly, pH shows little variability between biochars, and is tipically

>7. Table 2.2 summarizes total elemental composition (C, N, C:N, P, K, available P-Pa - and mineral N) and pH ranges of biochars from a variety of feedstocks (wood, green wastes, crop residues, sewage sludge, litter, nut shells) and pyrolysis conditions (350-500°C) used in various studies (adapted from Brown, 2009).

Table 2.2 Summary of total elemental composition (C, N, C:N, P, K, available P and mineral N) and pH ranges and means of biochars from a variety of feedstocks (wood, green wastes, crop residues, sewage sludge, litter, nut shells) and pyrolysis conditions (350-500°C) used in various studies (adapted from Chan and Xu, 2009)

		рН	C (g kg ⁻¹)	N (g kg ⁻¹)	<i>N (NO₃</i> + <i>NH₄</i> +) (mg kg - 1)	C:N	P (g kg ⁻¹)	<i>Pa</i> (g kg ⁻¹)	K (g kg ⁻¹)
Range	From	6.2	172	1.7	0.0	7	0.2	0.015	1.0
	To	9.6	905	78.2	2.0	500	73.0	11.6	58
Mean		8.1	543	22.3	-	61	23.7	-	24.3

Total carbon content in biochar was found to range between 172 to 905 g kg⁻¹, although OC often accounts for < 500 g kg⁻¹, as reviewed by Chan and Xu (2009) for a variety of source materials. Total N varied between 1.8 and 56.4 g kg⁻¹, depending on the feedstock (Chan and Xu, 2009). Despite seemingly high, biochar total N content may not be necessarily beneficial to crops, since N is mostly present in an unavailable form (mineral N contents < 2 mg k⁻¹; Chan and Xu, 2009). Nuclear magnetic resonance (NMR) spectroscopy has shown that aromatic and heterocyclic N-containing structures in biochar occur as a result of biomass heating, converting labile structures into more recalcitrant forms (Almendros et al., 2003). C:N (carbon to nitrogen) ratio in biochar has been found to vary widely between 7 and 500 Chan and Xu, 2009), with implications for nutrient retention in soils (see Sections 3.2.3). C:N ratio has been commonly used as an indicator of the capacity of organic substrates to release inorganic N when incorporated into soils.

Total P and total K in biochar were found to range broadly according to feedstock, with values between 2.7 - 480 and 1.0 - 58.0 g kg⁻¹, respectively (Chan and Xu, 2009). Interestingly, total ranges of N, P and K in biochar are wider than those reported in the literature for typical organic fertilizers. Most minerals within the ash fraction of biochar are thought to occur as discrete associations independent of the carbon matrix, with the exception of K and Ca (Amonette and Joseph, 2009). Typically, each mineral association comprises more than one type of mineral. Joseph et al. (2009) emphasize that our current understanding of the role of high-mineral ash biochars is yet limited, as we face the lack of available data on their long-term effect on soil properties.

The complex and heterogeneous chemical composition of biochars is extended to its surface chemistry, which in turn explains the way biochar interacts with a wide range of organic and inorganic compounds in the environment. Breaking and rearrangement of the chemical bounds in the biomass during processing results in the formation of numerous functional groups (e.g. hydroxyl -OH, amino-NH₂, ketone -OR, ester -(C=O)OR, nitro -

NO₂, aldehyde -(C=O)H, carboxyl -(C=O)OH) occurring predominantly on the outer surface of the graphene sheets (e.g. Harris, 1997; Harris and Tsang, 1997) and surfaces of pores (van Zwieten et al., 2009). Some of these groups act as electron donors, while others as electron acceptors, resulting on coexisting areas which properties can range from acidic to basic and from hydrophilic to hydrophobic (Amonette and Joseph 2009). Some functional groups also contain other elements, such as N and S, particularly in biochars from manures, sewage sludge and rendering wastes.

There is experimental evidence that demonstrates that the composition, distribution, relative proportion and reactivity of functional groups within biochar are dependent on a variety factors, including the source material and the pyrolysis methodology used (Antal and Gronli, 2003). Different processing conditions (temperature of 700°C or 450°C) explained differences in N contents between three biochars from poultry litter (Lima and Marshall, 2005; Chan et al., 2007). As the pyrolysis temperature rises, so does the proportion of aromatic carbon in the biochar, while N contents peak at around 300°C (Baldock and Smernik, 2002). In contrast, low processing temperatures (<500°C) favour the relative accumulation of a large proportion of available K, CI (Yu et al., 2005), Si, Mg, P and S (Bourke et al., 2007; Schnitzer et al., 2007). Therefore, processing temperatures < 500°C favour nutrient retention in biochar (Chan and Xu, 2009), while being equally advantageous in respect to yield (Gaskin et al., 2008). Nevertheless, it is important to stress that different permutations of those processing conditions, including temperature, may affect differently each source material.

This emphasises the need for a case-by-case assessment of the chemical and physical properties of biochar prior to its application into soil. Relating the adverse effect of a particular constituent (or its concentration) of biochar to a desirable biochar application rate (biochar loading capacity concept; Section 1.5.1) is difficult, as the exact biochar composition is often not provided in the literature. The review of relevant literature has indicated that the full knowledge on the composition of biochar as a soil amendment, and the way it is influenced by those parameters, as well as the implications for soil functioning, is still scarce. Partially, this can be explained by the fact that most characterisation work has involved charcoals with high carbon and low ash content, as required by the increasingly demanding market for activated carbon. Another factor is the wide variety of processing conditions and feedstocks available. The Black Carbon Steering Committee has developed reference charcoal materials (from chestnut wood and rice grass) under standardised pyrolysis conditions, representative of natural samples created by forest fires, for comparison of quantification methods for BCs in soils and sediments. Nevertherless, the current sparsity of biochar standards is largely reflected on the poor understanding of the link between biochar composition and its behaviour and function in soil.

2.2 Particle size distribution

Initially, particle size distribution in biochar is influenced mainly by the nature of the biomass feedstock and the pyrolysis conditions (Cetin et al., 2004).

Shrinkage and attrition of the organic material occur during processing, thereby generating a range of particle sizes of the final product. The intensity of such processes is dependent on the pyrolysis technology (Cetin et al., 2004). The implications of biochar particle size distribution on soils will be discussed further throughout Chapter 3.

Particle size distribution in biochar also has implications for determining the suitability of each biochar product for a specific application (Downie et al., 2009), as well as for the choice of the most adequate application method (see Section 1.8). In addition, health and safety issues relating to handling, storage and transport of biochar are also largely determined by its particle size distribution, as discussed in this report in regard to its dust fraction (see Sections 2.2.1 and 5.2).

The influence of the type of feedstock on particle size distribution was discussed by Sohi et al. (2009), among others. Wood-based feedstocks generate biochars that are coarser and predominantly xylemic in nature, whereas biochars from crop residues (e.g. rye, or maize) and manures offer a finer and more brittle structure (Sohi et al., 2009). Downie et al. (2009) have further provided evidence of the influence of feedstock and processing conditions on particle size distribution in biochar. Sawdust and woodchips under different pre-treatments were pyrolised using continuous slow pyrolysis (heating rate of 5-10°C min⁻¹), after which particle size distribution in the resulting biochar was assessed through dry sieving. Generally, particle size was found to decrease as the pyrolysis heat treatment temperature increased (450°C-700°C range) for both feedstocks, due to a reduction of the biomass material resistance to attrition during processing (Downie et al., 2009).

The operating conditions during pyrolysis (e.g. heating rate, high treatment temperature -HTT, residence time, pressure, flow rate of the inert gas, reactor type and shape) and pre- (e.g. drying, chemical activation) and post- (e.g. sieving, activation) treatments can greatly affect biochar physical structure (Gonzalez et al., 1997; Antal and Grønli, 2003; Cetin et al., 2004; Lua et al., 2004; Zhang et al., 2004; Brown et al., 2006). Such observations were derived mainly from studies involving activated carbon produced from a variety of feedstocks, including maize hulls (Zhang et al., 2004), nut shells (Lua et al., 2004; Gonzaléz et al., 2009) and olive stones (Gonzaléz et al., 2009). Similarly, heating rate, residence time and pressure during processing were shown to be determinant factors for the generation of finer biochar particles, independently of the original material (Cetin et al., 2004). For instance, for higher heating rates (e.g. up to 105-500°C sec⁻¹) and shorter residence times, finer feedstock particles (50-2000 µm) are required in order to facilitate heat and mass transfer reactions, resulting in finer biochar material (Cetin et al., 2004). In contrast, slow pyrolysis (heating rates of 5-30°C min⁻¹) can use larger feedstock particles, thereby producing coarser biochars (Downie et al., 2009). Increasing the proportion of larger biochar particles can also be obtained by increasing the pressure (from atmospheric to 5, 10 and 20 bars) during processing, which was explained by both particle swelling and clustering, as a result of melting (i.e. plastic deformation) followed by fusion (Cetin et al., 2004).

2.2.1 Biochar dust

The term 'dust' is described in this report as referring to the fine and ultrafine fraction of biochar, comprising various organic and inorganic compounds of distinct particle sizes within the micro- and nano-size range (Harris and Tsang, 1997; Cornelissen et al., 2005). Harris and Tsang (1997) researched the micro- and nano-sized fraction of chars, although so far, this issue remains poorly understood. Biomass precursor (feedstock) and the pyrolysis conditions (Donaldson et al., 2005; Hays and van der Wal, 2007) are likely to be primary factors influencing the properties of biochar dust (Downie et al., 2009), including the type and size of its particles, as well as the proportion of micro- and nanoparticles, as discussed previously

Harris and Tsang (1997) used high resolution electron microscopy (HREM) for studying the smaller fraction of charcoal resulting from the pyrolysis (700°C) of sucrose and concluded that charcoal dust consists of round fullerene-like nanoparticles (Harris and Tsang, 1997). Brodowski et al. (2005) corroborates the finding of porous spherical-shaped particles (with surface texture ranging from smooth to rough) within the <2 µm fraction of charcoals in a field-plot topsoil (0-10 cm), although no reference to the word "fullerene" was found. What is important in this context is that, considering the small size of such particles and their reactivity, the proportion of dust within the biochar (which may also apply to biochars with high ash contents) has relevant practical, as well as health and safety implications (see Section 5.2).

The proportion of dust in biochar is also key in determining the suitability of a given application strategy (Blackwell et al., 2009). For example, Holownicki (2000) suggested that this fine fraction could be successfully employed in precision agriculture for spraying fungicide preparations in orchards and vineyards. When injection is appropriate, Blackwell et al. (2009) pointed out that the application of biochar dust may in fact be preferred when used in combination with liquid manure in selected crops.

On the other hand, biochar dust has been identified in the literature as a better sorbent for a wide range of trace hydrophobic contaminants (e.g. PAHs, polychlorinated biphenyls - PCBs, pesticides, polychlorinated dibenzeno-p-dioxins and –furans - PCDD/PCDFs), when compared to larger biochar particles or to particulate organic matter (Hiller et al., 2007; Bucheli and Gustafsson, 2001, 2003). As such, the addition of biochar dust to soils may increase the sorption affinity of the soil for common environmental pollutants (see Section 3.2.2 for a more detailed discussion on the sorption of hydrophobic compounds to biochar), as demonstrated for dioxin sorption in a marine system (Persson et al., 2002).

2.3 Pore size distribution and connectivity

Biomass feedstock and the processing conditions are the main factors determining pore size distribution in biochar, and therefore its total surface area (Downie et al., 2009). During thermal decomposition of biomass, mass loss occurs mostly in the form of organic volatiles, leaving behind voids, which form an extensive pore network. This section focuses on pore size distribution

in biochar, while biochar density is discussed in the context of the biochar-soil mixture in Section 3.1.1.

Biochar pores are classified in this review into three categories (Downie et al., 2009), according to their internal diameters (ID): macropores (ID >50 nm), mesopores (2 nm< ID <50 nm) and micropores (ID <2 nm). These categories are orders of magnitude different to the standard categories for pore sizes in soil science (see Table 3.1). The elementary porosity and structure of the biomass feedstock is retained in the biochar product formed (Downie et al., 2009). The vascular structure of the original plant material, for example, is likely to contribute for the occurrence of macropores in biochar, as demonstrated for activated carbon from coal and wood precursors (Wildman and Derbyshire, 1991). In contrast, micropores are mainly formed during processing of the parent material. While macropores have been were identified as a 'feeder' to smaller pores (Martinez et al., 2006), micropores effectively account for the characteristically large surface area in charcoals (Brown, 2009).

Among those operating parameters, HTT is thought to be the most significant factor for the resulting pore distribution in charcoals (Lua et al., 2004), as the physical changes undergone by the biomass feedstock during processing are often temperature-dependent (Antal and Grønli, 2003).

The development of microporosity in biochar, which is linked to an increase in structural and organisational order, has been showed to be favoured by higher HTT and retention times, as previously demonstrated for activated carbon (e.g. Lua et al., 2004). For example, increasing pyrolysis temperature from 250 to 500°C enhanced the development of micropores in chars derived from pistachio-nut shells, due to increased evolution of volatiles. For subsequent increases in temperature (>800°C), a reduction of the overall surface area of the char was observed and was attributed to partial melting of the char structure (Lua et al., 2004). Similarly, heating rate and pressure during processing have also been found to influence the mass transfer of volatiles produced at any given temperature range, and are therefore regarded as key contributing parameters influencing pore size distribution (Antal and Grønli, 2003). For instance, Lua et al. (2004) observed a peak in surface area of pistachio-nut shell char at low heating rates (10°C), whereas higher heating rates resulted in a decrease in surface area.

It is important to stress, however, that the relative influence of each processing parameter on the final microporosity in biochar is determined by the type of feedstock, as noted from the above studies (e.g. Cetin et al., 2004; Lua et al., 2004; Pastor-Villegas et al., 2006; Gonzaléz et al., 2009). In particular, the lignocellulosic composition of the parent material largely determines the rate of its thermal decomposition, and therefore, the development of porosity (Gonzaléz et al., 2009). In the case of charcoals from almond tree pruning, a greater volume of meso and macropores was obtained, which was accounted for by the slow decomposition rate of such precursor during the initial stages of pyrolysis (Gonzaléz et al., 2009). The

opposite was found for almond shell, probably due to its inherently high initial thermal decomposition rate (Gonzaléz et al., 2009).

2.4 Thermodynamic stability

The thermodynamic equilibrium concerning carbonised residues, such as biochar, favours the production of CO₂.

$$C(graphite) + O_2(g) \rightarrow CO_2$$

 $\Delta H^o{}_f = -393.51(kJ.mol^{-1})$ Equation 1

The standard enthalpy of formation is represented as ΔH°_{f} and the degree sign denotes the standard conditions (P = 1 bar and T = 25°C)

Equation 1 shows that the oxidation of graphite, being the most thermodynamically stable form of carbon, will occur spontaneously as shown by the negative energy value (meaning that 393.51 kJ of energy is emitted for every mole of CO_2 'produced'). Since the oxidation of graphite to carbon dioxide will occur, allbeit very slowly under normal conditions (Shneour, 1966), all other forms of carbon which are less thermodynamically stable than graphite, will also undergo oxidation to CO_2 in the presence of oxygen. The speed at which this oxidation occurs depends on a number of factors, such as the precise chemical composition, as well as the temperature and moisture regime to which the compound is exposed. Furthermore, residence time of biochar in soils will also be affected by microbial processes. The recalcitrance of biochar in soil is discussed in more depth in Sections 3.2.1 and 3.2.5.1.

2.5 CEC and pH

CEC variation in biochars ranges from negligible to around 40 cmol $_{\rm c}$ g $^{-1}$ and has been reported to change following incorporation into soils (Lehmann, 2007). This may occur by a process of leaching of hydrophobic compounds from the biochar (Briggs et al., 2005) or by increasing carboxylation of C via abiotic oxidation (Cheng et al. 2006; Liang et al. 2006). Glaser et al. (2001) discussed the importance of ageing to obtain the increases in CEC of black BC found in the Terra Preta soils of the Amazon.

Considering the very large heterogeneity of its properties, biochar pH values are relatively homogeneous, that is to say they are largely neutral to basic. Chan and Xu (2009) reviewed biochar pH values from a wide variety of feedstocks and found a mean of pH 8.1 in a total range of pH 6.2-9.6. The lower end of this range seems to be from green waste and tree bark feedstocks, with the higher end from poultry litter feedstocks.

2.6 Summary

Biochar is comprised of stable carbon compounds created when biomass is heated to temperatures between 300 to 1000°C under low (preferably zero) oxygen concentrations. The structural and chemical composition of biochar is highly heterogeneous, with the exception of pH, which is tipically > 7. Some properties are pervasive throughout all biochars, including the high C content

and degree of aromaticity, partially explining the high levels of biochar's inherent recalcitrance. Neverthless, the exact structural and chemical composition, including surface chemistry, is dependent on a combination of the feedstock type and the pyrolysis conditions (mainly temperature) used. These same parameters are key in determining particle size and pore size (macro, meso and micropore; distribution in biochar. Biochar's physical and chemical characteristics may significantly alter key soil physical properties and processes and are, therefore, important to consider prior to its application to soil. Furthermore, these will determine the suitability of each biochar for a given application, as well as define its behaviour, transport and fate in the environment. Dissimilarities in properties between different biochar products emphasises the need for a case-by-case evaluation of each biochar product prior to its incorporation into soil at a specific site. Further research aiming to fully evaluate the extent and implications of biochar particle and pore size distribution on soil processes and functioning is essential, as well as its influence on biochar mobility and fate (see Section 3.2.1).

3. EFFECTS ON SOIL PROPERTIES, PROCESSES AND FUNCTIONS

This chapter discusses the effects of biochars with different characteristics (Chapter 2) on soil properties and processes. First, effects on the soil properties are discussed, followed by effects on soil physical, chemical and biological processes. The agricultural aspect of the production function of soil is reviewed in detail (including meta-analyses)

3.1 Properties

3.1.1 Soil Structure

The incorporation of biochar into soil can alter soil physical properties such as texture, structure, pore size distribution and density with implications for soil aeration, water holding capacity, plant growth and soil workability (Downie et al., 2009). Particularly in relation to soil water retention, Sohi et al. (2009) propose an analogy between the impact of biochar addition and the observed increase in soil water repellency as a result of fire. Rearrangement of amphiphilic molecules by heat from a fire, as proposed by Doerr et al. (2000), would not affect the soil, but could affect the biochar itself during pyrolysis. In addition, the soil hydrology may be affected by partial or total blockage of soil pores by the smallest particle size fraction of biochar, thereby decreasing water infiltration rates (see Sections 3.1.1 and 3.2.3). In that sense, further research aiming to fully evaluate the extent and implications of biochar particle size distribution on soil processes and functioning is essential, as well as its influence on biochar mobility and fate (see Section 3.2.1).

3.1.1.1 Soil Density

Biochar has a bulk density much lower than that of mineral soils and, therefore, application of biochar can reduce the overall bulk density of the soil, although increases in bulk density are also possible. If 100 t ha⁻¹ of biochar with a bulk density of 0.4 g cm⁻³ is applied to the top 20 cm of a soil with a bulk density of 1.3 g cm⁻³, and the biochar particles do not fill up existing soil pore space, then the soil surface in that field will be raised by *ca.* 2.5 cm with an overall bulk density reduction (assuming homogeneous mixing) of 0.1 g cm⁻³ to 1.2 g cm⁻³. However, if the biochar that is applied has a low mechanical strength and disintegrates relatively quickly into small particles that fill up existing pore spaces in the soil, then the dry bulk density of the soil will increase.

In agronomy, relatively small differences in soil bulk density can be associated with agronomic benefits. Conventionally, i.e. without biochar additions, lower bulk density is associated with higher SOM content leading to nutrient release and retention (fertiliser saving) and/or lower soil compaction due to better soil management (potentially leading to improved seed germination and cost savings for tillage and cultivation). Biochar application to soil by itself may improve nutrient retention directly (see Section 3.2.2), but nutrient release is mostly very small (except for some biochars in the first years, especially in ash-rich biochars) and the application of biochar with heavy machinery may compact the subsoil, depending on the application method and timing

Soil compactibility is closely related to soil bulk density. Soane (1990) reviewed the effect of SOM, i.e. not including biochar, on compactibility and proposed several mechanisms by which SOM may influence the ability of the soil to resist compactive loads:

- Binding forces between particles and within aggregates. Many of the long-chain molecules present in SOM are very effective in binding mineral particles. This is of great importance within aggregates which "...are bound by a matrix of humic material and mucilages" (Oades in Soane, 1990).
- 2) Elasticity. Organic materials show a higher degree of elasticity under compression than do mineral particles. The relaxation ratio – R – is defined as the ratio of the bulk density of the test material under specified stress to the bulk density after the stress has been removed. Relaxation effects of materials such as straw are therefore much greater than material like slurry or biochar.
- 3) Dilution effect. The bulk density of SOM is usually appreciably lower than mineral soil. It can however differ greatly, from 0.02 t m⁻³ for some types of peat to 1.4 t m⁻³ for peat moss, compared to 2.65 t m⁻³ for mineral particles (Ohu et al. in Soane, 1990).
- 4) Filament effect. Roots, fungal hyphae and other biological filaments have the capacity to bind the soil matrix.
- 5) Effect on electrical charge. Solutions/suspensions of organic compounds may increase the hydraulic conductivity of clays by changing the electrical charge on the clay particles causing them to move closer together, flocculate and shrink, resulting in cracks and increased secondary macro porosity (Soane, 1990). Biochar's ash fraction could cause similar effects.
- 6) Effect on friction. An organic coating on particles and organic material between particles is likely to increase the friction between particles (Beekman in: Soane, 1990). The direct effect of biochar on soil friction has not been studied.

The effect of biochar application on soil compactibility has not been tested experimentally yet. From the above mechanisms, however, direct effects of biochar are probably mostly related to bullet points 3, 5 and 6 above. The very low elasticity of biochar suggests that resilience to compaction, i.e. how quickly the soil 'bounces back', is unlikely to be increased directly by biochar. The resistance to compaction of soil with biochar could potentially be enhanced via direct or indirect effects (interaction with SOM dynamics and soil hydrology). For example, some studies have shown an increase in mycchorizal growth after additions of biochar to soil (see Section 3.2.6) while under specific conditions plant productivity has also been shown to increase (see Section 3.3). The enhanced development of hyphae and roots will have an effect on soil compaction However, experimental research into the mechanisms and subsequent modeling work is required before any conclusions can be drawn regarding the overall effect of biochar on soil compaction.

3.1.1.2 Soil pore size distribution

The incorporation of biochar into soil can alter soil physical properties such as texture, structure, pore size distribution and density with implications for soil aeration, water holding capacity, plant growth and soil workability. The soil pore network can be affected by biochar's inherent porosity as well as its other characteristics, in several ways. Biochar particle size and pore size distribution and connectivity, the mechanical strength of the biochar particles, and the translocation and interaction of biochar particles in the soil are all determining factors that will lead to different outcomes in different soil-climate-management combinations. As described in the above section, these factors can cause the overall porosity of the soil to increase or decrease following biochar incorporation into soils.

There is evidence that suggests that biochar application into soil may increase the overall net soil surface area (Chan et al., 2007) and consequently, may improve soil water retention (Downie et al., 2009; see Section 3.1.2) and soil aeration (particularly in fine-textured soils; Kolb, 2007). An increased soil-specific surface area may also benefit native microbial communities (Section 3.2.6) and the overall sorption capacity of soils (Section 3.2.2). In addition, soil hydrology may be affected by partial or total blockage of soil pores by the smallest particle size fraction of biochar, thereby decreasing water infiltration rates (see Sections 3.1.1, 3.1.2 and 3.2.3). Nevertheless, experimental evidence of such mechanisms is scarce and, therefore, any effects of the pore size distribution of biochar on soil properties and functions is still uncertain at this stage. Further research aiming to fully evaluate the extent and implications of biochar particle size distribution on soil processes and functioning is essential, as well as its influence on biochar mobility and fate in the environment (see Section 3.2.1).

Table 3.1 shows the classifications of pore sizes in material science and soil science. Fundamental differences, i.e. orders of magnitude difference for classes with the same names, are obstacles in communicating to any audience outside of biochar research and also hinder the communication efficiency within interdisciplinary research groups that work on biochar in soils. Therefore, it is recommended that existing classifications are modified to resolve this confusion. However, in this review we will use the existing terminology and the relevant classification will need to be retrieved from the context.

Table 3.1 Pore size classes in material science vs. soil science

	Material science	Soil science
	Po	re size (µm)
Cryptospores	na	<0.1
Ultramicropores	na	0.1-5
Micropores	<0.002	5-30
Mesopores	0.002-0.05	30-75
Macropores	>0.05	>75

3.1.2 Water and Nutrient Retention

The addition of biochar to soil will alter both the soil's chemical and physical properties. The net effect on the soil physical properties will depend on the interaction of the biochar with the physicochemical characteristics of the soil, and other determinant factors such as the climatic conditions prevalent at the site, and the management of biochar application.

Adding biochar affects the regulation and production function of the agricultural soil. To what extent biochar is beneficial to agriculture, and the dominant mechanisms that determine this, is still under scientific scrutiny. Agronomic benefits of biochar are often attributed to improved water and/or nutrient retention. However, many of the scientific studies are limited to site-specific soil conditions, and performed with biochar derived from specific feedstocks. Of more concern, and as of yet underexposed, is the stability of the structural integrity of the biochar. Especially when biochar is used in today's intensive agriculture with the use of heavy machinery, opposed to the smallholder system that led to the formation of Terra Preta. Another concern relates to the potential externalities of bringing large quantifies of biochar in the environment (see Chapter 5).

The mechanisms that lead to biochar-provided potential improvements in water retention are relatively straightforward. Adding biochar to soil can have direct and indirect effects on soil water retention, which can be short or long lived. Water retention of soil is determined by the distribution and connectivity of pores in the soil-medium, which is largely regulated by soil particle size (texture), combined with structural characteristics (aggregation) and SOM content.

The direct effect of biochar application is related to the large inner surface area of biochar. Biochars with a range in porous structures will result from feedstocks as variable as straw, wood and manure (see Sections 1.7, 2.1 and 2.3). Kishimoto and Sugiura (1985) estimated the inner surface area of charcoal formed between 400 and 1000°C to range from 200 to 400 m² g⁻¹. Van Zwieten et al. (2009) measured the surface area of biochar derived from papermill waste with slow pyrolysis at 115 m² g⁻¹.

The hypothesised indirect effects of biochar application on water retention of soil relate to improved aggregation or structure. Biochar can affect soil aggregation due to interactions with SOM, minerals and microorganisms. The surface charge characteristics, and their development over time, will determine the long term effect on soil aggregation. Aged biochar generally has a high CEC, increasing its potential to act as a binding agent of organic matter and minerals. Macro-aggregate stability was reported to increase with 20 to 130% with application rates of coal derived humic acids between 1.5 Mg ha⁻¹ and 200 t ha⁻¹ (Mbagwu and Piccolo, 1997). Brodowski et al (2006) found indications that BC acted as a binding agent in microaggregates in soils under forest, grassland and arable land use in Germany. In-situ enhancement of soil aggregation by biochar requires further analysis.

The mechanical stability and recalcitrance of biochar once incorporated in the soil will determine long term effects on water retention and soil structure. This is determined by feedstock type and operating conditions as well as the prevalent physical-chemical conditions that determine its weathering and the

compaction and compression of the biochar material in time. The effect of the use of heavy agricultural machinery on compaction of the soil-biochar matrix has yet to be studied in detail. Another factor contributing to the uncertainty in long-term beneficial effects of biochar application to soil is the potential clogging or cementation of soil pores with disintegrated biochar material.

Glaser et al. (2002b) reported that Anthrosols rich in charcoal with surface areas three times higher than those of surrounding soils had an increased field capacity of 18%. Tryon (1948) studied the effect of charcoal on the percentage of available moisture in soils of different textures. In sandy soil the addition of charcoal increased the available moisture by 18% after adding 45% of biochar by volume, while no changes were observed in loamy soil, and in clayey soil the available soil moisture decreased with increasing coal additions. This was attributed to hydrophobicity of the charcoal, although another factor could simply be that the biochar was replacing clay with a higher water retention capacity. Biochar's high surface area can thus lead to increased water retention, although the effect seems to depend on the initial texture of the soil. Therefore, improvements of soil water retention by charcoal additions may only be expected in coarse-textured soils or soils with large amounts of macropores. A draw-back is the large volume of biochar that needs to be added to the soil before it leads to increased water retention.

The capacity of the agricultural soil to store water regulates the time and amount water is kept available for crop transpiration. Tseng and Tseng (2006) found that activated biochar contained over 95% of micropores with a diameter <2 nm. Since the porosity of biochar largely consists of micropores, the actual amount of additional plant available water will depend on the biochar feedstock and the texture of the soil it is applied to. The agronomic water-storage benefit of biochar application will thus dependent on the relative modification of the proportion of micro, meso and macro pores in the root zone. In sandy soils, the additional volume of water and soluble nutrients stored in the biochar micropores may become available as the soil dries and the matric potential increases. This may lead to increased plant water availability during dry periods.

The potential co-benefits or negative externalities of the use of biochar in irrigated agricultural systems have not been explored in detail. If the water holding capacity of the soil increases this may hypothetically reduce the irrigation frequency or irrigation volume. However, the potential susceptibility of disintegrated biochar particles to cement or clog the soil may also result in increased runoff and lower infiltration rates.

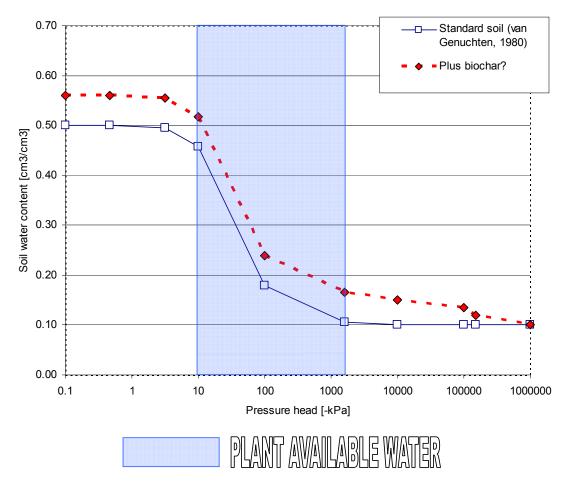


Figure 3.1 Typical representation of the soil water retention curve as provided by van Genuchten (1980) and the hypothesized effect of the addition of biochar to this soil

Figure 3.1 shows a typical representation of the soil water retention curve (van Genuchten, 1980) and the hypothesised effect of the addition of biochar to this soil. Notice that in this conceptual example most of the water that is stored additionally in the soil will not be available for plant water uptake since it occurs at tensions superior to the range wherein plant roots are able to take up water. In this hypothetical representation this is mainly due to the pore size distribution of the biochar which largely consists of very small pores and only very little pores in the range relevant for plant water uptake. Although this is a hypothetical consideration; it highlights the need for a further understanding of the direct and indirect effects of biochar addition on soil water retention, and its longevity.

3.1.2.1 Soil water repellency

Soil water repellency (SWR), or hydrophobicity, is defined functionally as "the reduction of the affinity of soils to water such that they resist wetting for periods ranging from a few seconds to hours, days or weeks" (King, 1981). SWR is a widespread phenomenon associated with decreased infiltration rates, fingered flow infiltration, and increased runoff. In the case of agricultural land, fertiliser and biocide (herbicide, pesticide) leaching to the groundwater via bypass flow (secondary porosity) can be costly to the farmer and the

environment. Most of the literature on soil water repellency focuses the effect of the heat wave from a (wild)fire on the hydrophobic properties of the SOM. Reorientation of amphiphilic molecules is one of the hypothesised mechanisms (Doerr et al., 2000) explaining the water repellent effect, although other mechanisms are also hypothesised. In relation to soil water retention, Sohi et al. (2009) propose an analogy between the impact of biochar addition and the observed increase in soil water repellency as a result of fire. Rearrangement of amphiphilic molecules by heat from a fire, as proposed by Doerr et al. (2000), would not affect the soil, but could affect the biochar itself during pyrolysis.

Field studies on water repellent properties of biochar or charcoal are absent from the scientific literature and very limited even for charcoal produced by wildfires. Briggs et al. (2005) measured WR of charcoal particles after a wildfire in a pine forest and found very large differences in WR between charcoal particles on the surface and in the mineral soil vs. those on the border of the litter layer and mineral soil. The water drop penetration time, that is the time it takes a droplet of water to infiltrate, was >2 h for the former and <10 s for the latter. The authors proposed leaching by organic acids as a mechanism explaining the reduction of water repellent properties underneath the litter layer. How biochar may influence soil water repellency, directly or indirectly, is a topic that still requires a substantial research effort before the mechanisms are understood and predictions can be made. A trade off appears to exist between the capacity to bind HOCs, like PAHs (see Section 3.2.2), and the capacity to bind water molecules.

3.1.3 Soil colour, albedo and warming

From the Anthrosol profile pictures (Figure 1.5) it is obvious that high concentrations of biochar in soil darken its colour. Briggs et al. (2005) measured changes in dry soil colour from charcoal additions and found the Munsell value to decrease from 5.5 to 4.8 at charcoal concentrations of 10 g kg⁻¹, and down to 3.6 at 50 g kg⁻¹. Oguntunde et al. (2008) compared the soil colour of charcoal sites (i.e. where charcoal used to be produced) with that of adjacent soil and found the Munsell value to decrease from 3.1 (± 0.6) to 2.5 (± 0.4). The degree of darkening is dependent on i) the colour of the soil prior to biochar additions (Munsell value 1-9), ii) the colour of the biochar (probably Munsell value 0-2), iii) the biochar concentration in the soil, iv) the degree of mixing (related to particle size of both the biochar and the soil), v) the surface roughness, and vi) the change in water retention at the soil surface that accompanies the addition of biochar (moist soil is darker in colour). Wang et al. (2005) conducted three years of continuous measurement in a semi-desert area in Tibet and showed an exponential relationship between soil moisture content (v v⁻¹) and surface albedo. The combined effects of the changes in these factors subsequently determine the albedo effect of the soil.

Land surface albedo is an important component of global and regional climate change models. However, almost exclusively, the albedo of the vegetation is used, not that of soil. Levis et al. (2004) introduced a modification to soil albedo into their community climate system model and found this change to

be the key for the model output to resemble the botanic evidence for climate-vegetation interactions in mid-Holocene North Africa. Model simulations with a darker soil colour led to an intensified monsoon which brought precipitation further north; testifying the importance of changes in soil albedo on climate feedbacks.

The principle that biochar application to soils decreases the albedo of bare soil and thereby contributes to further warming of the planet is accepted, however, if, and where, that would lead to an effect of relevant magnitude is much less certain. Bare soil is limited to the winter months on fields growing spring crops, or in orchards without ground cover (e.g. olive orchards, vineyards). In the former case, the warming effect may be relatively small because solar radiation reaching the surface is low in winter months, however, many orchards and vineyards are in more southern parts that receive a greater solar input and the bare soil conditions persist throughout the year. Post et al. (2000) investigated the influence of soil colour and moisture content on the albedo of 26 different soils ranging widely in colour and texture. They found that wet samples had their albedo reduced by a mean of 48% (ranging between 32-58%), and that Munsell colour value is linearly related to soil albedo.

The amount of solar radiation that reaches the soil surface (as affected by sun angle and slope and vegetation cover) and the specific heat of soils, largely control the rate at which soils warm up in the spring, and thus influence the emergence of seedlings. Soil colour and soil moisture content are the main factors determining the specific heat of soil. For pure water the specific heat is about 4.18 J g⁻¹ K⁻¹; that of dry soil is about 0.8 J g⁻¹ K⁻¹. Therefore, although soils high in biochar content are usually dark in colour, if the biochar increases the water retention of the soil concomitantly (see Section 3.1.2) then the associated extra energy absorption is countered by a high water content, which causes the soil to warm up much more slowly (Brady, 1990). This implies that biochar with low water retention capacity (e.g. because of water repellent properties, see Section 3.1.2.1) will cause the greatest increase in soil warming, and that this impact will be greatest where biochar is applied to light-coloured soils (high Munsell value) with spring crops (i.e. bare soil in spring) or orchards/vineyards.

3.1.4 CEC and pH

The cation exchange capacity (CEC) of soils is a measure for how well some nutrients (cations) are bound to the soil, and, therefore, available for plants uptake and 'prevented' from leaching to ground and surface waters. It is at negatively charged sites on the reactive surface area of biochar (and clay and organic matter) where cations can be electro-statically bound and exchanged. Cations compete with each other as well as with water molecules and can be excluded when the pore size at the charged site is smaller than their size. Cheng et al. (2006) assessed the effects of climatic factors on biochar oxidation in natural systems. The CEC of biochar was correlated to the mean temperature and the extent of biochar oxidation was related to its external surface area, being seven times higher on the external surfaces than in its interior (Cheng et al., 2008). It is not known at present how the CEC of

biochar will change as the biochar disintegrates by weathering and tillage operations, 'ages' and moves through the soil.

Anions are bound very poorly by soils under neutral or basic pH conditions. This is one of the reasons why crops need fertilising, as anionic nutrients (e.g. phosphates) are leached or flushed from the soil into ground/surface waters (eutrophication). Cheng et al. (2007) found biochar to exhibit an anion exchange capacity (at pH 3.5) which decreased to zero as it aged in soil (over 70 years). If biochar can play a role in anion exchange capacity of soils remains an unanswered question and a research effort is required into the mechanisms to establish under what conditions (e.g. more neutral pH) anions may be retained.

As previously discussed, biochar pH is mostly neutral to basic (see Table 2.2). The liming effect has been discussed in the literature as one of the most likely mechanisms behind increases in plant productivity after biochar applications, and the meta-analysis in this report (Section 3.3) provides supporting evidence for that mechanism. Lower pH values in soils (greater acidity) often reduce the CEC and thereby the nutrient availability. In addition, for many of the tropical soils studied, reduced aluminium toxicity by reducing the acidity is proposed as the most likely chemical mechanism behind plant productivity increases.

For the experimental studies used in the meta-analysis on plant productivity (see Section 3.3.1) the average pre-amendment soil pH was 5.3 and post-amendment 6.2, although for poultry litter biochar on acidic soils the change was as large as from pH 4.8 to 7.8. Therefore, a scientific consensus on a short term liming effect of biochar applied to soil is apparent. This implies that biochars with greater liming capacity can provide greater benefit to arable soils that require liming, by being applied more frequently at lower application rates. Thereby reducing, or potentially cutting, a conventional liming operation, and hence providing a clear cost saving.

3.2 Soil Processes

3.2.1 Environmental behaviour, mobility and fate

An effective evaluation of biochar stability in the environment is paramount, particularly when considering its feasibility as a carbon sequestration tool. A sound understanding of the contribution that biochar can make to improve soil processes and functioning relies on knowing the extent and implications of the changes biochar undergoes in soil over time. Such knowledge remains, however, sparse and most experimental evidence has been gathered for other forms of black carbon. Energy-dispersive X-ray spectrometry looks promising as a tool for providing evidence of such changes in soil (Glaser et al., 2000; Brodowski et al., 2005a).

Current evaluations of the age of black carbon particles from both wildfires and anthropogenic activity indicate great stability of (at least) a significant component of biochar, ranging from several millennia to hundreds of years (e.g. Skjemstad et al., 2001; Lehmann et al., 2009). Such stability has been employed as a tool for evaluating, dating and modelling of ancient cropping

and management practices (Scott et al., 2000; Ferrio et al., 2006). Yet, establishing the mean residence time of biochars in natural systems remains a challenge, partly due to their inherent heterogeneity, and partly due to different interactions with both the biotic (e.g. microbial communities, flora) and abiotic (e.g. clays, humic substances) components of soil (Brodowski et al., 2005a, 2006).

Analysis of biochar-enriched agricultural soil using X-ray spectrometry and scanning electron microscopy showed that biochar particles in soil occur either as discrete particles or as particles embedded and bound to minerals (mainly clay and silt; Brodowski et al., 2005). This corroborates earlier studies reporting that most biochar in Amazonian Terra Preta was found in the light (<0.2 g cm⁻³) fraction of soil (Gu et al., 1995), which Hammes and Schmidt (2009) refer to as "intrinsically refractory", while a minor amount occurred adsorbed to the surface of mineral particles (Gu et al., 1995). It is also likely that a significant portion of biochar occurs in aggregate-occluded organic matter in soil (see Section 3.2.5.3).

Biochar is no longer considered inert, although mechanisms involved in biochar degradation in soil not being fully understood (Hammes and Schmidt, 2009). It has been demonstrated that exposure to strong chemical oxidants (e.g. Skjemstad et. al., 1996), including ozone (Kawamoto et al., 2005), and to high temperatures (Morterra et al., 1984; Cheng et al., 2006) can cause oxidation in charcoal over short periods of time. In natural environments, photochemical and microbial breakdown appear to be the primary degradation mechanisms (Goldberg, 1985), which can result in alteration of the charcoal's surface chemistry and functional properties (e.g. CEC, nutrient retention; Glaser et al., 2002). Such mechanisms have been assessed by a relatively small number of short-term experiments involving biochar-enriched soils in the presence and absence of added substrates (e.g. Hamer et al., 2004; Cheng et al., 2006). Incubation studies appear to indicate that biological decomposition is very slow (see Section 3.2.5.1) and might be of minor relevance compared to abiotic degradation (see Section 3.2.5.1), particularly when fresh biochars are concerned (Cheng et al., 2006).

Surfaces of fresh biochars are generally hydrophobic and have relatively low surface charges (Lehmann et al., 2005). However, over time, biochar oxidation in the soil environment due to aging, may reflect in accumulation of carboxylic functionalities at the surfaces of biochar particles (Brodowski et al., 2005), promoting, perhaps, further interactions between biochar and other soil components (Cheng et al., 2006), including organic and mineral matter (Brodowski et al., 2005), as well as contaminants (Smernik et al., 2006). It is reasonable to hypothesize that solubilisation, leaching and translocation of biochar within the soil profile and into water systems is also expected to be gradually enhanced for longer exposure periods in soil (Cheng et al., 2006). Whether the relative importance of microbial decomposition increases over time (as biochar particle size decreases) remains largely unknown and attempts to determine actual mineralisation rates are still scarce.

Although biochar characteristics (e.g. particle and pore size distribution, surface chemistry, relative proportion of readily available components), as well as physical and chemical stabilisation mechanisms may contribute to the

long mean residence times of biochar in soil, the relative contribution of each factor to short- and long-term biochar loss has been poorly assessed, influenced by environmental conditions. when characteristics are largely determined by the feedstock and pyrolysis conditions, as previously discussed. For instance, particle size is likely to influence the rate of both abiotic and biotic degradation in soil, as demonstrated for biochar particles >50 µm in a Kenyan Oxisol (Nguyen et al., 2008 in Lehmann et al., 2009). Therefore, processes which favour biochar fragmentation into smaller particles (e.g. freeze-thaw cycles, rain and wind erosion, bioturbation) may not only enhance its degradation rate, but also render it more susceptible to transport (reviewed by Hammes and Schmidt, 2009).

Processes which may influence biochar fate in soil might be the same as those for other natural organic matter (NOM), although little experimental evidence on this is still available. If that is the case, a lower clay content and an increase in soil temperature and water availability will probably enhance biochar degradation and loss, as previously suggested by Sohi et al. (2009). For example, mean annual temperature of the site that biochar is applied to has shown to be a contributing factor in accelerating biochar oxidation in soil (Cheng et al., 2008). One could hypothesize that the same might apply to tillage (Sohi et al., 2009) through altering soil aggregate distribution. Interestingly, Brodowski et al. (2006) did not find evidence that different management practices have an effect on BC contents in Haplic Luvisol topsoil (0-30 cm; 13.4±0.2 g kg⁻¹ organic C) from continuous wheat and maize plots. Adjacent grassland (0-10 cm; 10.3 g Kg⁻¹ organic C; since 1961) and spruce forest (0-7 cm; 41.0 g kg⁻¹ OC; since ca. 1920) topsoil were also sampled (Brodowski et al., 2006).

Sohi et al. (2009) and Collision et al. (2009) proposed that feedstock material (including its degree of aromaticity) and cropping patterns (which influences nutrient composition in the rhizosphere) are contributing factors in determining biochar degradation rates in soil. These authors provided the following example: Pyrolysis of wood-based feedstocks generate coarser and more resistant biochars explained by the rigid xylemic structure of the parent material, whereas biochars produced from crop residues (e.g. rye, maize) and manures are generally finer and nutrient-rich, therefore more readily degradable by microbial communities (Collison et al., 2009).

Cheng et al. (2008) have recently assessed the effects of climatic factors (mainly temperature) on biochar oxidation in natural systems. The cation exchange capacity of biochar was correlated to the mean temperature and the extent of biochar oxidation was related to its external surface area, being seven times higher on the external surfaces than in its interior (Cheng et al., 2008). In addition, X-ray photoelectron spectroscopy (Cheng et al., 2006) and later, near-edge X-ray absorption fine structure spectroscopy (Lehmann et al., 2005) have shown that abiotic oxidation occurs mainly in the porous interior of biochar, while biotic oxidation is the predominant process on external surfaces. This probably means that biotic oxidation may become more relevant as particle size decrease as a consequence of biochar weathering, although there are doubts on the relative importance of such a process (Cheng et al., 2006). Nevertheless, the influence of increasingly warmer

climates on biochar degradation rates in natural systems has not been resolved yet.

Translocation of biochar within the soil profile and into water systems may also be a relevant process contributing to explain biochar loss in soil (Hockaday et al., 2006). Such a translocation via aeolian (e.g. Penner et al., 1993) and mostly fluvial (e.g. Mannino and Harvey, 2004) long-range transport has been previously proposed for other forms of BC, in order to explain its occurrence in deep-sea sediments (Masiello and Druffel, 1998), as well as in natural riverine (Kim et al., 2004) and estuarine (Mannino and Harvey, 2004) water.

Soil erosion (in a global context) might result in greater amounts of BC being redistributed onto neighbouring hill slopes and valley beds (Chaplot et al., 2005), or enriching marine and river sediments through long-range transport, as recently suggested by Rumpel et al. (2006a;b) for tropical sloping land under slash and burn agriculture. Partially, this can be explained by the light nature (low mass) of biochar (Rumpel et al., 2006a;b), and may be particularly relevant for finer biochars or those with higher dust contents. Similarly, this might apply predominantly to soils and sites which are more prone to erosion (Hammes and Schmidt, 2009).

Up to now, biochar loss and mobility through the soil profile and into the water resources, has been scarcely quantified and translocation mechanisms are poorly understood. This is further complicated by the limited amount of long-term studies and the lack of standardized methods for simulating biochar aging and for long-term environmental monitoring (Sohi et al., 2009). Sound knowledge at this level will not only enable for a more robust estimate of global BC budget to be put forward (through an improved understanding of the role of BC as a global environmental carbon sink) but also attenuate uncertainties in relation to current estimates of BC environmental fluxes.

The finest biochar dust fraction, comprising condensed aromatic carbon in the form of fullerene-like structures (Harris, 1997), is thought to be the most recalcitrant portion of the BC continuum in natural systems (Buzea et al., 2006). Interactions between this ultrafine fraction and soil organic and mineral surfaces has been suggested to contribute to biochar's inherent recalcitrance (Lehmann et al., 2009), although quantifying its relative importance by experimental evidence, may render difficult. Free sub-micron BC particles are primarily transported to the oceans, where the majority is deposited on coastal shelves, while smaller amounts continue on to deep-ocean sediments (Masiello and Druffel, 1998; Mannino and Harvey, 2004) with expected residence times of thousands of years (Masiello and Druffel, 1998). The remaining fraction remains suspended in the atmosphere in the form of aerosols (Preston and Schmidt, 2006) and can be transported over long distances, eventually reaching the water courses and sediments (Buzea et al., 2006).

3.2.2 Sorption of Hydrophobic Organic Compounds (HOCs)

The sorption of anthropogenic hydrophobic organic compounds (HOC) (e.g. PAHs, polychlorinated biphenyl - PCBs, pesticides and herbicides) in soils and sediments, is generally described based on two coexisting and

simultaneous processes: absorption into natural (amorphous) organic matter (NOM) and adsorption onto occurring charcoal materials (Cornelissen et al., 2005; Koelmans et al., 2006). Comparatively to that of NOM, charcoals (including soot) generally hold up to 10-1000 times higher sorption affinities towards such compounds (Chiou and Kile, 1998; Bucheli and Gustafsson, 2000, 2003). It has been estimated that BC can account for as much as 80-90% of total uptake of trace HOC in soils and sediments (Cornelissen et al., 2005), and that it applies to a much broader range of chemical species than previously thought (Bucheli and Gustafsson, 2003; Cornelissen et al., 2004).

Biochar application is, therefore, expected to improve the overall sorption capacity of soils (Chiou 1998), and consequently, influence toxicity, transport and fate of trace contaminants, which may be already present or are to be added to soils. Enhanced sorption capacity of a silt loam for diuron (Yang and Sheng, 2003) and other anionic (Hiller et al., 2007) and cationic (Sheng et al., 2005) herbicides has previously been reported following the incorporation of biochar ash from crop (wheat and rice) residues. The relative importance of these latter studies is justified by the fact that charring of crop residues is a widespread agricultural practice (Hiller et al., 2007). Nevertheless, while the feasibility for reducing mobility of trace contaminants in soil might be beneficial (see Section 4.3), it might also result in their localised accumulation, with potentially detrimental effects on local flora and fauna if at some point in time the sorbed compounds become available to organisms. Experimental evidence is required to verify this.

Despite that little is still known on the micro-scale processes controlling sorption to biochar (Sander and Pignatello, 2005) in soils and sediments, it has been suggested that it is mechanistically different from the traditional sorption models for NOM, and that it is also a less reversible process (Gustafsson et al., 1997; Chiou and Kile, 1998; Jonker et al., 2005). While absorption to NOM has little or no concentration dependence, adsorption to biochars has been shown to be strongly concentration dependent (e.g. Gustafsson et al., 1997; Sander and Pignatello, 2005; Pastor-Villegas et al., 2006; Wang et al., 2006; Chen et al., 2007), with affinity decreasing for increasing solute concentrations (Cornelissen et al., 2004; Wang et al., 2006). Several equations have been employed to describe such a behaviour, including that of Freundlich (e.g. Cornelissen et al., 2004) and Langmuir (e.g. van Noort et al., 2004), although more recent equations based on pore-filling models have shown better fits (e.g. Kleineidam et al., 2002).

Previous studies have convincingly demonstrated that adsorption to charcoals is mainly influenced by the structural and chemical properties of the contaminant (i.e. molecular weight, hydrophobicity, planarity) (Cornelissen et al., 2004, 2005; Zhu and Pignatello, 2005; Zhu et al., 2005; Wang et al., 2006), as well as pore size distribution, surface area and functionality of the charcoal (e.g. Wang et al., 2006; Chen et al., 2007). For example, sorption of tri- and tetra-substituted-benzenes (such as trichlorobenzene, trinitrotoluene and tetramethilbenzene) to maple wood charcoal (400°C) was sterically restricted, when comparing to that of the lower size benzene and toluene (Zhu and Pignatello, 2005). Among most classes of common organic compounds, biochar has been shown to adsorb PAHs particularly strongly, with desorption having been regarded as 'very slow' (rate constants for desorption in water of

 10^{-7} - 10^{-1} h⁻¹, and even lower in sediments) (Jonker et al., 2005). This can be explained both by the planarity of the PAH molecule, allowing unrestricted access to small pores (Bucheli and Gustafsson, 2003; van Noort et al., 2004), and the strong π - π interactions between biochar's surface and the aromatic molecule (e.g. Sander and Pignatello, 2005).). In fact, experimental evidence has recently demonstrated that organic structures in the form of BC (including biochar) or NOM, which are equipped with strong aromatic π -donor and -acceptor components, are capable of strongly adsorbing to other aromatic moieties through specific sorptive forces other than hydrophobic interactions (Keiluweit and Kleber, 2009).

Although a large body of evidence is available on the way the characteristics of HOC influence sorption to biochars, the contribution of the char's properties to that process has been far less evaluated. It is generally accepted that mechanisms leading to an increase in surface area and/or hydrophobicity of the char, reflected in an enhanced sorption affinity and capacity towards trace contaminants, as demonstrated for other forms of BC (Jonker and Koelmans, 2002; Noort et al., 2004; Tsui and Roy, 2008). The influence of pyrolysis temperatures mostly in the 340-400°C range (James et al., 2005; Zhu et al., 2005; Tsui and Roy, 2008) and feedstock type (Pastor-Villegas et al., 2006) on such a phenomena has been recently evaluated for various wood chars by a number of authors. Interestingly, sorption to high-temperature chars appear to be exclusively by surface adsorption, while that to low-temperature chars derive from both surface adsorption and (at a smaller scale) absorption to residual organic matter (Chun et al., 2004).

The influence of micropore distribution on sorption to biochars has been clearly demonstrated by Wang et al. (2006). Diminished O functionality on the edges of biochar's graphene sheets due to heat treatment (e.g. further charring), resulted in enhanced hydrophobicity and affinity for both polar and apolar compounds, by reducing competitive adsorption by water molecules (Zhu et al., 2005; Wang et al., 2006). The treated char also revealed a consistent increase in micropore volume and pore surface area, resulting in better accessibility of solute molecules and an increase in sorption sites (Wang et al., 2006).

Once released in the environment, the original adsorption properties of biochar may be affected by 'aging' due to environmental factors, such as the impact of coexisting substances. The presence of organic compounds with higher hydrophobicity and/or molecular sizes have shown reduce adsorption of lower molecular weight compounds to biochars (e.g. Sander and Pignatello, 2005; Wang et al., 2006). In the same way, some metallic ions (e.g. Cu²⁺, Ag⁺) present at environmental relevant concentrations (50 mg L⁻¹) may significantly alter surface chemistry and/or pore network structure of the char through complexation (Chen et al., 2007).

Perhaps a more important mechanism to consider, is the influence of dissolved NOM, including the humic, fulvic (Pignatello et al., 2006) and lipid (Salloum et al., 2002) fractions, on the physical-chemical properties and adsorption affinity and capacity of biochars (Kwon and Pignatello, 2005). Similar evidence has long been reported for activated carbon (Kilduff and Wigton, 1999). "Aging" of maple wood charcoal (400°C) particles in a

suspension of Amherst peat soil (18.9% OC)-water has demonstrated that NOM reduced affinity of the char for benzene (Kwon and Pignatello, 2005), corroborating other research (Cornelissen and Gustafsson, 2005; Pignatello et al., 2006). Similar observation over a period of 100 years has been reported for pyrene in forest soil enriched with charcoal (Hockaday, 2006). In both cases, such a behaviour was explained by mechanisms of pore blockage (Kwon and Pignatello, 2005; Pignatello et al., 2006), and by the capacity of NOM to compete with (e.g. Cornelissen and Gustafsson, 2005) and displace the organic compound from the sorption sites (Hockaday, 2006). A wider range of soil characteristics remain to be tested.

Frequently, contaminated soils contain a mix of organic solvents, PAHs, heavy metals and pesticides, adding to the naturally occurring mineral and organic matter (Chen et al., 2007). Nevertheless, most studies on organic sorption to charred materials have relied on single-solute experiments, whereas those using multiple solutes hold more practical relevance (Sander and Pignatello, 2006). Competitive sorption can be a significant environmental process in enhancing the mobility as well as leaching potential of HOC in biochar-enriched soil.

Most of the evidence of increased sorption to HOC by biochar incorporation into soil is indirect (i.e., bulk and biochar or soot sorption is determined separately and biochar's contribution is then proved comparatively to a treatment without biochar) and earlier attempts for its direct assessment overestimated it (Cornelissen and Gustafsson, 2004). Yet, the potential of biochar amendment of soils for enhancing soil sorption capacity and, therefore mitigating the toxicity and transport of relevant environmental contaminants in soils and sediments appears undeniable. One can suggest that such an enhancement of soil sorption capacity may result in long mean residence times and accumulation of organic contaminants with potentially hazardous health and environmental consequences. At this stage, very little is known about the short- and long-term distribution, mobility and bioavailability of such contaminants in biochar-enriched soils.

It is worth underlining that although such a strong adsorptive behaviour appears to imply a reduced environmental risk of some chemical species (e.g. PAHs), very little data is, in fact, currently available which confirms this. The underlying sorption mechanism, including the way it is influenced by a wide range of factors inherent to the contaminant, to the char material and to the environment, remains far from being fully understood (Fernandes and Brooks, 2003), and thus it is identified in this report as a priority for research. In this context, it is vital to comprehensively assess the environmental risk associated to these species in biochar-enriched soils, while re-evaluating both the use of generic OC-water distribution coefficients (Jonker et al., 2005) and of remediation endpoints (Cornelissen et al., 2005). For instance, remediation (undetectable. endpoints non-toxic or environmentally concentrations, as set by regulatory agencies) for common environmental contaminants in biochar-enriched soils would need to be assessed based on dissolved (bioavailable) concentrations rather than on total concentrations (Pointing, 2001; Cornelissen et al., 2005). In order to achieve that, prior careful experimental evaluation of the contaminant distribution, mobility and availability in the presence of biochar is paramount.

3.2.3 Nutrient retention/availability/leaching

Reduction of nutrient leaching from agriculture is an objective in line with the Water Framework Direct (WFD). The WFD promotes an integrated management approach to improve the water quality of European water bodies. Application of fertilisers has led to increased concentrations of nitrates and phosphates in European surface and ground waters. Specific water quality targets have been set by the Water Framework Directive with respect to nitrates, which are very susceptible to leaching (European Parliament and the Council of the European Union, 2000). Improved agricultural management practices are increasingly stimulated by the Common Agricultural Policy (cf. CAP Health Check).

Evidence from several laboratory and field studies suggests that the application of biochar may lead to decreased nutrient leaching (studies particularly focussed on nitrates) and contaminant transport below the root zone. Several mechanisms contribute to the decrease in nutrient leaching which are related to increased nutrient use efficiency by increased water and nutrient retention (residence time in the root zone) and availability, related to an increased internal reactive surface area of the soil-biochar matrix, decreased water percolation below the root zone related to increased plant water use (increased evaporative surface), and increased plant nutrient use through enhanced crop growth. Higher retention times also permit a better decomposition of organic material and promote the breakdown of agrichemicals. Nevertheless, mechanisms such as colloid-facilitated transport of contaminants by biochar particles, or preferential flow induced by biochar applications, and long term stability of biochar in soil, are potential factors that my increase the leaching of nutrients and/or contaminants.

The magnitude and dynamics resulting from biochar application are time, space and process specific. The myriad of interactions within the soil-plant-atmosphere, and the range of potential feedstock specific effects of biochar on these interactions, makes it inherently difficult to formulate generic qualities of "biochar". It also has to be kept in mind that other factors, such as rainfall patterns and agricultural management practices, will be more strongly determining the loss of nutrients from the root zone.

The mobility of the water percolating beyond the root zone depends on the infiltration capacity, hydraulic conductivity and water retention of the root zone, the amount of crop transpiration dependent on the density and capability of the root network to extract water, and the prevalent meteorological conditions at the site. These factors are largely dependent on the proportion and connections between micro, meso and macro pores.

The partitioning of groundwater recharge, surface-water runoff and evapotranspiration is affected by changes in the soil's water retention capacity. In those situations where biochar application improves retention (of plant available water) and increases plant transpiration (Lehmann et al., 2003), percolation below the root zone can be reduced, leading to the retention of mobile nutrients susceptible to leaching such as nitrates, or base cations at low pH.

Biochar directly contributes to nutrient adsorption through charge or covalent interactions on a high surface area. Major et al. (2002) showed that biochar

must be produced at temperatures above 500°C or be activated to results in increased surface area of the biochar and thus increased direct sorption of nutrients. Glaser et al. (2002) conclude that 'charcoal may contribute to an increase in ion retention of soil and to a decrease in leaching of dissolved OM and organic nutrients' as they found higher nutrient retention and nutrient availability after charcoal additions to tropical soil. A possible contributing mechanism to increased N retention in soils amended with biochar is the stimulation of microbial immobilisation of N and increased nitrates recycling due to higher availability of carbon (see Section 3.2.3). Biological N fixation by common beans was reported to increase with biochar additions of 50 g kg⁻¹ soil (Rondon et al., 2007), although soil N uptake decreased by 50%, whereas the C:N ratios increased with a factor of two.

Lehmann et al. (2003) reported on lysimeter experiments which indicated that the ratio of uptake to leaching for all nutrients increases with charcoal application to the soil. However they also concluded that it could not clearly be demonstrated which role charcoal played in the increased retention, although, in these experiments, water percolation was not decreased. Therefore, nutrients must have been retained on electrostatic adsorption complexes created by the charcoal. Similarly, Steiner et al. (2004) attributed decreased leaching rates of applied mineral fertiliser N in soils amended with charcoal to increased nutrient use efficiency. Nevertheless, the interaction between mineral fertiliser and biochar seems critical. Lehmann et al. (2003) found that while cumulative leaching of mineral N, K, Ca and Mg in an Amazonian Dark Earth was lower compared to a Ferralsol in unfertilised experiments, leaching from the ADE exceed that from the Ferralsol in fertiliser experiments.

If biochar applications lead to improved soil aggregation, this may lead to an increase in the soil's water infiltration capacity. Using measured properties such as saturated hydraulic conductivity and total porosity in a modelling assessment of the impact of charcoal production, Ayodele et al. (2009) showed that infiltration was enhanced and runoff volume reduced. The increase in infiltration may be accompanied by improved water retention in the root zone in coarse soils. On the other hand, however, since a large percentage of the pores in biochar are very small (<2 x 10^{-3} µm, following Tseng and Tseng, 2006), it may also reduce the mobility of water through the soil. If the increased infiltration is not off-set by increased retention and transpiration, due to factors related to the native soil, and/or if crop nutrient uptake is not increased, the net results may be an increased percolation below the root zone, especially of soluble and mobile nutrients such as nitrates.

Fine biochar particles resulting from transportation, application, and further weathering in the field, may facilitate the colloidal transport of nutrients and contaminants (Major et al., 2002).

Hydrophobicity (see Section 3.2.2) induced by biochar is thought to be most significant in the first years after application since 'fresh' biochar contains a large fraction of hydrophobic groups. The implications of biochar hydrophobicity on runoff and unwanted export of nutrients from the field has not been investigated in detail. Another potential concern in certain soils is preferential flow induced by the incorporation of biochar in the soil matrix, it

has been suggested that biochar can alter percolation patterns, residence times of soil solution, and affect flow paths (Major et al., 2002).

3.2.4 Contamination

Given that the widespread interest in biochar applications to soils continues to rise, so does the concern regarding the potential for soil contamination associated to some of its components. It is crucial to ensure that soil functions and processes as well as water quality are not put at risk as a consequence of biochar application to soils, which would carry severe health, environmental and socio-economic implications (Collison et al., 2009). Mineral contaminants like salts that are often present in some biochars and may be detrimental to soil functioning rather than to human and animal health, and have been discussed previously. This section is dedicated to contaminants such as heavy metals, PAHs and dioxins, which remain major issues of concern with regard to potential for soil contamination and health hazards, and yet have surprisingly received very little attention.

The occurrence of these compounds in biochar may derive either from contaminated feedstocks or from pyrolysis conditions which favour their production. For example, slow pyrolysis at temperatures below 500°C is known to favour the accumulation of readily available micronutrients (e.g Sulphur) in biochar (Hossain et al., 2007). However, heavy metals, PAHs and other species with disinfectant and antibiotic properties (e.g. formaldehydes, creosols, xylenols, acroleyn) may also accumulate under such operating conditions (Painter, 2001). Full and careful risk assessment for such contaminants is urgently required, in order to relate contaminant toxicity to biochar type, safe application rates and operating pyrolysis conditions.

Organic wastes (e.g. biosolids, sewage sludge, tannery wastes) are known to generally contain high levels of light and heavy metals, which remain in the final biochar product following pyrolysis (Hospido et al., 2005; Chan and Xu, 2009). Bridle and Pritchard (2004) reported high concentrations of Copper (Cu), zinc (Zn), chromium (Cr) and nickel (Ni) in biochar produced from sewage sludge. Muralidhar (1982) has long found that Cr, which accounts for up to 2% (total dry weight) of tannery wastes, is commonly found in biochar produced from this material. On the other hand, relatively low concentrations of aluminium (AI), Cr, Ni and molybdenum (Mo) have been recently detected in poultry litter, peanut hull and pine chip biochars produced between 400-500°C, while poultry litter biochar generally contained the highest levels of these metals (Gaskin et al., 2008). In contrast, Zn, Cu, Al and Fe were lower in the poultry litter biochar compared to that in pine chip and peanut hulls biochars, which pattern seem to be reverse to that observed in the feedstock materials. Although one could suggest pyrolysis as means of reducing metal availability in some feedstocks (such as poultry litter), and be encouraged to use biochar (instead of poultry litter) for mitigating some of the concerns relating to soil contamination, there is no clear evidence to confirm this (Gaskin et al., 2008).

Metal concentration in the biomass feedstock often determines biochar's safe application rate (McHenry, 2009). Preliminary data seems to suggest that, at current ordinary biochar application rates, there is little environmental risk by metal species within biochar, which McHenry (2009) describes as similar to

that associated to the use of conventional fertilisers. In fact, for contaminants such as Zn, mercury (Hg), arsenic (Ar), lead (Pb) and Ni, it is likely that significant risk can only be expected from exceedingly high biochar application rates (>250 t ha⁻¹) (McHenry, 2009). A wider range of biochars and soil types remains to be tested, which would undoubtedly shed more light onto the potential for soil and water contamination by metals.

Secondary chemical reactions during thermal degradation of organic material at temperatures exceeding 700°C, is generally associated to the generation of heavily condensed and highly carcinogenic and mutagenic PAHs (Ledesma et al., 2002; Garcia-Perez, 2008). Nevertheless, little evidence exists that PAHs can also be formed within the temperature range of pyrolysis (350-600°C), although these appear to carry lower toxicological and environmental implications (Garcia-Perez, 2008). Nevertheless, their potential occurrence in the soil and water environments via biochar may constitute a serious public health issue. Evidence seems to show that biomass feedstock and operation conditions are influencing factors determining the amount and type of PAHs generated (Pakdel and Roy, 1991), and therefore, there is great need to assess the mechanisms, as well as identify specific operational and feedstock conditions, which lead to their formation and retention in the final biochar product.

Very little data is available on the occurrence of PAHs in pyrolysis products, compared to that from combustion or incineration. Among such studies, Fernandes and Brooks (2003), Brown et al. (2006) and Jones (2008) do stand out. Pea straw and eucalyptus wood charcoal produced at 450°C for 1 h, exhibited low PAHs concentrations (<0.2 µg g⁻¹), although their levels in straw (0. 12 µg g⁻¹) were slightly higher than that from the denser feedstock material (0.07 µg g⁻¹) (Fernandes et al., 2003). Similarly, Brown et al. (2006) reported that PAHs concentrations in several chars produced at temperatures exceeding 500°C, ranged between 3-16 µg g⁻¹ (depending on peak treatment temperature), compared to that (28 µg g⁻¹) in char from prescribed burn in pine forest. The range of producing conditions and feedstock materials employed in the latter studies was narrow. In contrast, Jones (2008) studied twelve biochar products from a variety of biomass sources and producers. with evidence that PAHs levels in biochar were often comparable or even lower than those found in some rural urban and urban soils. This finding corroborates previous studies (reviewed by Wilcke, 2000), in which topsoil concentration ranges of several PAHs were found to increase in the order of arable < grassland < forest < urban. For example, at the lower end (arable soil), concentration ranges for naphthalene, fluorene, phenanthrene, anthracene and pyrene were up to 0.02, 0.05, 0.067, 0.134 $\mu g g^{-1}$ (respectively). At the top end of the concentration range (urban soil), levels of those compounds (respectively) were up to 0.269, 0.55, 2.809, 1.40 and 11.90 µg g⁻¹ (reviewed by Wilcke, 2000). It is important to note, however, that the latter data refers to initial concentrations in soil, not taking into account interactions with organic and mineral fractions, and most importantly, not providing information on the bio-available fraction.

Recently, however, the mild (supercritical fluid) extraction of pyrogenic PAHs from charcoal, coal and different types of soot, including coal soot, showed promising results (Jonker et al., 2005). To the best of our knowledge, this

study was pioneer in reporting desorption kinetics of pyrogenic PAHs from their 'natural' carrier under conditions which mimic those in natural environments. Such "soot and charcoal-associated PAHs" were found to be strongly sorbed to their carrier matrix (e.g. charcoal, soot) by means of physical entrapment within the matrix nanopores (so called "occlusion sites") in charcoal and sequestration within the particulate matter. Consequently, it is anticipated "very slow desorption" (rate constants of up to 10⁻⁷ to 10⁻⁶ h⁻¹) of these compounds from the carrier in natural environments, which can range from several decades to several millennia (Jonker et al., 2005). PAHs sorption to charcoals has been reviewed extensively in Section 3.2.2 of this report, including the mechanisms leading to increases in their accessibility, such as interactions with NOM and coexisting chemical species.

To the best of our knowledge, there are no toxicological reports involving PAHs incorporated in soil due to biochar application, nor have biochar application rates have been defined in terms of PAHs accumulation and bioavailability, both in soil and water systems. Further research is paramount on the behaviour of such contaminants in biochar-enriched natural systems. In this context, a re-evaluation of risk assessment procedures for these compounds needs to be put in place, which takes into account the influence of NOM on their desorption from biochar, transport and bioavailability.

Dioxins and furans are planar chlorinated aromatic compounds, which are predominantly formed at temperatures exceeding 1000°C (Garcia-Perez, 2008). Although data exists confirming their presence in products from combustion reactions, such as incineration of landfill and municipal solid wastes (as cited by Garcia-Perez, 2008), no reports were found on their content in biochar derived from traditional biomass feedstocks. In contrast, char from automobile shredder residues was shown to contain up to 0.542 mg kg⁻¹ of dioxins, while their generation and accumulation in the char was dependent on the operational conditions (Joung et al., 2007). Scarce experimental evidence on dioxin levels in pyrolysis products (biochar in particular) in the range of temperatures between 350-600°C, is largely limiting towards our knowledge on potential dioxin contamination of soil via biochar. More research on this matter is urgently needed. It appears that pyrolysis of strongly oxygenated feedstocks under low temperatures (400 and 600°C) do not favour the generation of dioxins and dioxin-related compounds. Based on the current knowledge, it is likely that such a risk is low for the aforementioned biochar production factors, particularly when using low-chlorine and low-metal containing feedstocks (Garcia-Perez, 2008).

At this stage, extrapolating a link between the presence of contaminants on biochar and a detrimental effect on human and animal health, particularly in regard to bioaccumulation and bioamplification in the food chain, can only be hypothesised. One can suggest that potential uptake and toxicity of such contaminants is perhaps more prominent in the case of microbial communities, sediment-dwelling organisms and filter feeders. In note of the application of biochar into soil being an irreversible process, Blackwell et al. (2009) emphasised the need for full case-by-case characterisation and risk assessment of each biochar product previous to its application to soil, accounting not only for heterogeneity among biochars, but also for soil type and environmental conditions. There are no current standards for biochar or

processing conditions which can provide sound basis for biochar quality regulations with regard to the presence of contaminants, thus ensuring soil and water protection. Also lacking is a clearly defined set of conditions under which biochar and related materials can be applied to soil without licensing (Sohi et al., 2009).

As Collison et al. (2009) noted, the natural occurrence of BC in soils is widespread and detrimental effects on environmental quality are generally not apparent. However, it is the perspective of an extensive and indiscriminate incorporation of biochars into soils, derived from some feedstock materials under specific operation conditions, without previous full risk assessment, which constitutes the main issue of concern. This is particularly the case for small-scale and on-farm pyrolysis units using local biomass resources (e.g. forestry and agricultural wastes), which may not hold the necessary technological and economic infrastructures to tackle this matter. Also, it is likely that these small landholders in rural areas might prefer using low-temperature pyrolysis, thereby reducing operation costs. Farmers should be made aware that sub-optimal pyrolysis operating conditions and certain feedstocks may not only reduce the benefits associated to biochar application, but also enhance the risk of land and water contamination.

3.2.5 Soil Organic Matter (SOM) Dynamics

SOM stabilisation mechanisms for temperate soils have been researched comprehensively and reviewed recently (Von Lützow et al., 2006; 2008 2008; Kögel-Knabner et al., 2008; Marschner et al., 2008).

Primary recalcitrance refers to the recalcitrance of the original plant matter, while secondary recalcitrance refers to that of its charred product, i.e. pyrogenic BC. For biochars from feedstocks that have already undergone selective preservation, i.e. any process leading to the relative accumulation of recalcitrant molecules, it may be appropriate to consider tertiary recalcitrance. Stability of SOM is the result of recalcitrance, organo-mineral interactions, and accessibility. Because biochar is OM but also has many properties functionally similar to mineral matter, it is necessary to consider the stability of biochar in soils as well as the stability of native SOM, or OM that is added with, or after, the biochar.

3.2.5.1 Recalcitrance of biochar in soils

Studies of charcoal produced by wildfires have shown that abiotic processes generally have more impact on the decomposition of charcoal than biotic processes, in the short term (Cheng et al 2006; Bruun and Luxhøi. 2008). However, abiotic oxidation can only occur on the surface and as such once the surface of biochar has been oxidised biotic process are thought to become more important. The fact that the soil microbiota is capable of oxidising graphitic carbon, which is thermodynamically stable and recalcitrant carbon, was first demonstrated by Shneour (1966). This author found that a 'substantially higher' oxidation rate, being at least a 3-fold increase, was found in non-sterile soils than in sterilised soils.

More work regarding recalcitrance has been conducted on BC, specifically pyrogenic BC, rather than on biochar *per se*. Nevertheless, owing to its relatively similar physical and chemical composition BC is an acceptable

analogue and it is likely that the recalcitrance of biochars will function according to similar mechanisms.

As graphite has been shown to be oxidised by microbial activity, albeit very slowly (Shneour 1966), a degree of decomposition of biochars can be expected. Contradictory experimental results exist, with both rapid (Bird et al. 1999) and slow (Shindo 1991) decomposition of biomass-derived BC being reported. This difference is likely to be an artefact of the different microbial communities to which the BC was exposed. Although precise details regarding the turnover of BC in soils remain unknown, and due to the complexity of its interaction within the soil system and its biota exact details are unlikely to be found, BC has been found to be the oldest fraction of C in soil, being older than the most protected C in soil aggregates and organomineral complexes (Pessenda et al., 2001), which are commonly the most stable forms of C in soil. This demonstrates that even without knowing the precise details of turnover of BC in soil, it at least has highly stable components with "decomposition leading to subtle, and possibly important, changes in the bio-chemical form of the material rather than to significant mass loss" (Lehmann et al 2006).

It has been noted that the recalcitrance of BC in soils cannot be characterised by a single number (Hedges et al., 2000; Von Lützow et al., 2006). This is because pyrogenic BC is an amalgamation of heterogeneous compounds and, as such, different fractions of it will decompose at different rates under different conditions (Hedges et al., 2000). According to Preston & Schmidt (2006) the more recalcitrant compounds in pyrogenic BC, created by wildfire and therefore of a woody feedstock, can be expected to have a half life in the region of thousands of years (possibly between 5 and 7 thousand years) in cold and wet environments. However, some fractions of pyrogenic BC which may have undergone less thermal alteration (being more analogous to biochars which have also undergone less thermal alteration due to low heat pyrolysis, a half life in the region of hundreds of years as opposed to thousands may be expected (Bird et al., 1999). This agrees with work reported by Brunn et al. (2008) who found that the rate of microbial mineralisation of charcoal decreases with increasing mineralisation temperature (see also Section 1.6).

Besides physical and chemical stabilization mechanisms, another important factor that may affect the residence time of biochar in soils is the phenomenon of co-metabolism. This is where biochar decomposition is increased due to microbial metabolism of other substrates, which is often increased when SOM is 'unlocked' from the soil structure due to disturbance (e.g. incorporating biochar into the soil via tillage).

3.2.5.2 Organomineral interactions

The interactions between SOM and soil minerals have received considerable attention in the literature. Von Lützow et al. (2006) concluded that some evidence exists for interactions between biochar and soil minerals, leading to accumulation in soil, but that the mechanisms responsible are still unknown. One potential mechanism is the oxidation of the functional groups at the surface of the charcoal, which favours interactions with soil organic and

mineral fractions (Lehmann et al., 2005; Glaser et al., 2002). Section 3.2.1 explores further the interaction between biochar and other soil components.

3.2.5.3 Accessibility

Biochar can both increase and decrease the accessibility of SOM to microorganisms and enzymes. Brodowski et al. (2006) provided evidence that a significant portion of BC occurs in the aggregate-occluded OM in soil. Interestingly, the largest BC concentrations occurred in microaggregates (<250 μ m) and it has been suggested that it may be actively involved in the formation and stabilisation of microaggregates, comparatively to other forms of organic matter (Brodowski et al., 2006). At the present, one can only speculate on such a role of biochar in soil. Most importantly, organo-mineral interactions may be relevant in determining the environmental behaviour and fate of biochar (Hammes and Schmidt, 2009; Section 3.2.1) and can contribute to physically protecting it from degradation, while promoting its long mean-residence times in soil (Glaser et al., 2002; Lehmann et al., 2005; Brodowski et al., 2006).

3.2.5.4 Priming effect

The priming effect has been defined as being "the acceleration of soil C decomposition by fresh C input to soil" (Fontaine et al., 2004) and are generally considered to be short-term changes in the turnover of SOM (Kuzyakov et al., 2000). The priming effect is thought to be a function of changes in microbial community composition upon fresh C input into soil (e.g. cellulose, Fontaine et al., 2004). This means that addition of a 'new' source of carbon into the soil system can potentially lead to a priming effect whereby SOC is reduced. Several mechanisms may be involved: changes in pH, changes in water-filled pore space, changes in habitat structure, or changes in nutrient availability.

Following cellulose addition, Fontaine et al. (2004) found that decomposition rate of soil humus stock in savannah soil increased by 55%. Kuzyakov et al. (2009) demonstrated that BC in soil underwent increased decomposition upon the addition of glucose to soil. They concluded that while soil microorganisms were not dependant on BC as an energy source, the extracellular enzymes produced by the microbial community for the decomposition of the glucose (and its metabolites) also decomposed the BC, albeit at a vastly decreased rate when compared to the added glucose. They estimated the mean decomposition time of black carbon to be in the range of 0.5% per year and concluded that the mean residence time of back carbon in soil is likely to be in the range of about 2000 years. This provides some further evidence of priming effects occurring with regard to mineralisation of C in soils, in this case BC, upon addition of a substance, in this case glucose. As to whether the addition of biochar to soil can lead to a priming effect leading to accelerated mineralisation of SOM is still a matter of debate.

This then leads to the question as to whether biochar addition to soils can cause a priming effect. Kuzyakov et al. (2000) stated that the most important mechanisms concerning priming effects are due to increased activity or quantity of the microbial biomass. Biochar has been shown to increase both of these factors (Section 3.2.6.1), and as such there is the clear potential for

biochar to cause a priming effect on SOM. There is a paucity of data on the possible priming effect of biochar on SOM, but some initial data is available. Steinbeiss (2009) found that the addition of homogeneous biochars, made from glucose and yeast to produce N-free biochar and biochar with a N content of ~5%, respectively. When these biochars were mixed with arable soils and forest soils in controlled microcosm experiments a clear priming effect could be observed with between 8% and 12% of carbon from the SOC pool being lost in 4 months after addition of either type of biochar to either type of soil. The addition of nitrogen containing biochar to forest soil had the largest effect (13% loss) with addition of the nitrogen free biochar to arable soil having the smallest effect (8%). That said, it is important to note that the controls of both the arable soil and the forest soil which had no biochar addition but were subject to the same disturbance (sieved to 2 mm and mixed) also showed a loss of carbon from the SOC pool of 4% and 6% respectively. This demonstrates that disturbance to the soil which is sufficient to break up soil aggregates and expose previously protected soil organic matter to microbial decomposition and mineralisation itself has a strong priming effect on SOC.

Biochars made from these specific feedstocks are unlikely to be used in reality particularly as they were almost certainly lacking in micronutrients such as P and K which would be introduced into the soil with most biochar types. Also, they were produced by hydrothermal pyrolysis, which is not the most commonly used or posited method of pyrolysis. This, combined with large amount of variance seen within each treatment group means that the results must be extrapolated with caution. However, it appears to be preliminary evidence that biochars can instigate, or at least increase the priming effect and accelerate the decomposition of SOC. There is some evidence that the availability of N in a soil is the main factor affecting the priming effect, with more available N leading to a reduced priming effect (Neff et al., 2002; Fontaine, 2007). This suggests that the priming effect could perhaps be reduced or eliminated though the co-addition of N fertiliser along with biochar.

If biochar components are highly recalcitrant in soil, as evidence suggests, and its addition, in some scenarios at least, speeds up the decomposition. and thereby depletion of SOC, soil fertility and the ecosystem services which it provides may be negatively affected. It is conceivable that, through biochar addition to soil, it may be possible to increase the level of C in soils beyond what is found in most given soils on average at the moment. However, if this is C in the form of a highly recalcitrant substance that does not take part in the cycling of C in the soil (i.e. biochar) and not the highly chemically complex and dynamic substance (i.e. humus) and other SOM fractionations, then ecosystem functioning of soils may well be compromised. This is because it is well recognised that it is not the presence of C within the soil which is important for functioning, but rather it is the decomposition of SOC which drives the soil biota and leads to the provision of ecosystem services. This was recognised even before Russell (1926) who stated that SOM must be decomposed before it has 'served its proper purpose in the soil'. This is clearly an area that warrents further research.

3.2.5.5 Residue Removal

One of the often proposed methods of obtaining biomass for use as a feedstock to make biochar is the removal of crop residues for pyrolysis. The removal of residues, and the possible associated impacts has already been discussed extensively from the point of view of biofuels (Wilhelm et al., 2004; Lal, 2007; Blanco-Canqui and Lal, 2008; Lal, 2009). Removal of crop residues is associated with increased risk of soil loss by both water and wind erosion with associated off-site effects, depletion of SOM, degradation of soil quality leading to decrease in agronomic productivity and a reduction in crop yields per unit input of fertiliserand water, thereby compromising the sustainability of agriculture (Lal, 2007).

Removal of crop residues for biochar production, therefore, has the potential to have multiple negative effects on the soil, which may only be partially outweighed, if at all, by the positive effects of biochar addition. While it is possible that the inclusion of biochar into the soil system may aid the reduction of atmospheric CO₂, it is also feasible that more CO₂ will be required to be produced as a by-product of processes undertaken to remediate the damage done by crop residue removal, such as increased production of fertiliser which may need to be undertaken to keep yields stable.

Furthermore, as discussed above, the soil biota relies on the breakdown of SOM to provide energy for it to perform the multitude ecosystem services which it provides. It is the SOM *dynamics* that helps drive the system, not just the presence of SOM. If the potential new inputs of SOM, being crop residues in many agricultural situations, are removed, and converted into a substantially more recalcitrant form which does not function as an energy source for the edaphic microflora and fauna, then ecosystem services may well be compromised and reduced.

3.2.6 Soil Biology

The soil biota is vital to the functioning of soils and provides many essential ecosystem services. Understanding the interactions between biochar, when it is used as a soil amendment, and the soil biota is therefore vital. It is largely through interactions with the soil biota, such as promoting arbuscular mycchorizal fungi (AMF) as well as influences on water holding capacity, which leads to the reported effects of biochar on yields (see Section 3.3).

Soil is a highly complex and dynamic habitat for organisms, containing many different niches due to its incredibly high levels of heterogeneity at all scales. On the microscale, soil is often an aquatic habitat, as micropores in soil are full of water at all times, apart from very extreme drought, due to the high water tension which exists there. This is vital for the survival of many microbial species which require the presence of water for mobility as well as to function. Indeed, many soil organisms, specifically nematodes and microorganisms such as protozoa enter a state of cryptobiosis, whereby they enter a protective cyst form and all metabolism stops in the absence of water. When biochar application leads to an increased water retention of soils (see Section 3.1.2), it seems likely, therefore, that this will have a positive effect on soil organism activity, which may well lead to concurrent increases in soil functioning and the ecosystem services which it provides.

Organisms in the soil form complex communities and food webs and engage in many different techniques for survival and to avoid becoming prey, ranging from hiding in safe refuges, through to conducting forms of chemical 'warfare'. Biochar, due to its highly porous nature, has been shown to provide increased levels of refugia where smaller organisms can live in small spaces which larger organisms cannot enter to prey on them. Microorganisms within these micropores are likely to be restriced in growth rate due to relying on diffusion to bring necessary nutrients and gases, but as this occurs in micropores within the soil, this demonstrates that microorganisms utilising these refugia almost certainly would not be reliant of decomposition of the biochar for an energy source. This is likely to be one of the mechanisms for the demonstrated increases in microbial biomass (Steiner et al., 2008; Kolb et al., 2009), and combined with the increased water holding potentials of soil is a possible mechanisms for the increased observed basal microbial activity (Steiner et al., 2008; Kolb et al., 2009). However, due to the complexities of the soil system and its biota, it is probable that many more mechanisms are at work. For example Kolb et al. (2009) demonstrated that while charcoal additions affected microbial biomass and microbial activity, as well as nutrient availability, differences in the magnitude of the microbial response was dependent on the differences in base nutrient availability in the soils studied. However, they noted that the influences of biochar on the soil microbiota acted in a relatively similar way in the soils they studied, albeit at different levels of magnitude, and so suggested that there is considerable predictability in the response of the soil biota to biochar application.

As with all interactions between the soil biota and biochar, there is a scarcity of data regarding the interaction of biochar with fungi. However, considering the diverse saprophytic abilities of fungi it is probable that the interaction between fungi and biochar is most likely to affect the stability and longevity of biochar within the soil. While there is evidence of long residence times of biochar in soils from Terra Pretas, biochar from different sources and exposed to different fungal communities may well have differing levels of recalcitrance and hence residence times in soils. This is therefore a highly pertinent area for further research.

There is some evidence that the positive effects of biochar on plant production may be attributable to increased mycorrhizal associations (Nisho and Okano, 1991). The majority of studies concerning biochar effects on mycorrhiza show that there is a strong positive effect on mycorrhizal abundance associated with biochar in soil (Harvey et al., 1976; Ishii and Kadoya, 1994; Vaario et al., 1999). The possible mechanisms were hypothesised by Warnock et al. (2007) to include (in decreasing order of currently available experimental evidence)

- a) alteration of soil physico-chemical properties
- b) indirect effects on mycorrhizae through effects on other soil microbes
- c) plant–fungus signalling interference and detoxification of allelochemicals on biochar
- d) provision of refugia from fungal grazers

Biochar, immediately after pyrolysis, can have a wide range of compounds on its surface. These can include ones that are easily metabolised by microbes, such as sugars and aldehydes which are turned over quickly, but may also include compounds which have bactericidal and fungicidal properties such as formaldehyde and cresols (Painter, 2001). However, residence times of these substrates has been shown to be in the range of one to two seasons and, therefore, long term effects of these chemicals on the soil biota are unlikely (Zackrisson et al., 1996).

The structure of biochar provides a refuge for small beneficial soil organisms, such as symbiotic mycorrhyzal fungi which can penetrate deeply into the pore space of biochar and extraradical fungal hyphae (fungal hyphae which are found outside of roots) which sporulate in the micropores of biochar where there is lower competition from saprophytes (Saito and Marumoto, 2002). Nishio (1996) stated that "the idea that the application of charcoal stimulates indigenous arbuscular mycorrhiza fungi in soil and thus promotes plant growth is relatively well-known in Japan, although the actual application of charcoal is limited due to its high cost". The specifics of the cost-benefit relationship of biochar application to soil and its associated effects on yield have not yet been covered in depth by the scientific community and is subject of discussion in Section 5.4.

The relationship between mycorrhizal fungi and biochar may be important in realising the potential of charcoal to improve fertility. Nishio (1996) also reported that charcoal was found to be ineffective at stimulating alfalfa growth when added to sterilised soil, but that alfalfa growth was increased by a factor of approximately 1.8 when unsterilised soil containing native mycorrizal fungi was also added. This demonstrates that it is the interaction between the biochar and the soil biota which leads to positive effects on yield, and not just the biochar itself (See Section 3.3).

3.2.6.1 Soil microbiota

It has long been assumed that soil biodiversity and SOM are positively correlated although experimental evidence for this is scarce. Even if this assumption is proven to be true, it is unclear as to what role biochar will play in this interaction. This is because, for the majority of the soil biota at least, biochar appears to function more as the mineral constituent of the soil, than the OM *per se.* Nevertheless, there is experimental evidence that microbial communities are directly affected by the addition of biochar to soils (Ogawa, 1994; Rondon et al., 2007; Warnock et al., 2007; Steiner et al., 2008).

Due to the fact that experiments involving the addition of biochar to soils are relatively new, with only relatively few experiments being more than a decade old, quantifying the long term effects of biochar addition to soil is problematic. While not perfect analogies to the addition of biochar to temperate soils, investigation of Terra Preta soils in the Amazon Basin does have the potential to lead to insights regarding the long term effects of biochar addition to soil.

O'Neill et al. (2009) performed 16s rRNA analysis on Terra Pretas and their surrounding soils. Although their experiment was limited by the fact that they isolated microorganisms through culturing techniques, they did find numerous differences between Terra Pretas and their surrounding soils. Firstly, higher

numbers of culturable bacteria, by over two orders of magnitude were found in the Terra Pretas consisting of five possible new bacterial families. They also reported greater diversity being isolated from the Terra Preta soils. This increase in culturable bacterial populations and a greater culturable diversity were found in all of the Anthrosols, to a depth of up to 1 m, when compared to adjacent soils located within 50-500 m of terra preta. Although using culturing of the microorganisms as a form of isolation is undoubtedly a weakness in this experiment design owing to the fact that the vast majority of soil microorganisms are not culturable in the laboratory (Torsvik et al., 1990; Ritz, 2007), soil extract media was used which when compared to standard culture media revealed an increased diversity in the soil microbial populations of the Terra Pretas

As well as affecting the inherent recalcitrance of biochar, the pyrolysis temperature range also affects how the biochar will interact with the soil community. This is particularly true of woody charcoal which, at lower pyrolysis temperatures retains an interior layer of bio-oil which is equal to glucose in its effect on microbial growth (Steiner, 2004). When pyrolysed at higher temperatures, this internal layer of bio-oil is lost and so it is likely that the biochar will have less impact with regard to promoting soil fertility when compared to biochar which does have the internal layer of bio-oil.

When added to soil, biochar has been shown to cause a significant increase in microbial efficiency as a measure of units of CO_2 released per microbial biomass carbon in the soil as well as a significant increase in basal respiration (Steiner et al., 2008). Steiner et al. (2008) also found that the addition of organic fertiliser amendments along with biochar lead to further increases in microbial biomass, efficiency in terms of CO_2 release per unit microbial carbon, as well as population growth and concluded that biochar can function as valuable component of the soil system, especially in fertilised agricultural systems.

As well as increasing basal respiration and microbial efficiency, there is experimental evidence that biochar addition to soil increases N₂ fixation by both free living and symbiotic diazotrophs (Ogawa, 1994; Rondon et al., 2007). Rondon et al. (2007) reported that the positive effects of biochar, including increased N₂ fixation, lead to a between 30 and 40% increase in bean (Phaseolus vulgaris L.) yield at biochar additions of upto 50 g kg-1. However, they found that at an application rate of 90 g kg⁻¹ a negative effect with regard to yield occurred. It should be noted that this appears contrary to data shown in Figure 3.1 which shows a general trend for positive crop productivity effects upon biochar addition to soil. This may be due to the Rondon et al. (2007) study being excluded from the meta-analysis owing to the study not reporting the variance of within their treatments meaning that the data could not be included. This means that a possible negative weighting was not included in the meta-analysis which could have caused a slight scew of the results. However, as n was low in the Rondon study when compared to the combined data used in the meta-analysis, the effects of this omission are likely to be minimal and this highlights the need of accurate reporting of variances in experimental data to both allow effective interpretation of the results, and to allow further analyses such as statistical meta-analyses to be undertaken. Furthermore, many more studies which are reported in the metaanalysis showed a positive effect on crop productivity at similar or higher application rates. However, this highlights the fact that while biochar addition to soil is potentially positive with regard to crop yield, situations also exist where negative effects can occur regarding yield. There is currently no clear mechanism which may lead to positive effects on yield can become negative once a threshold has been crossed regarding the amount of biochar which is added to soil. While it is possible to hypothesise mechanisms responsible for this effect, there is, as yet, no experimental evidence to confirm or refute any hypothesis and this highlights the need for further research.

3.2.6.2 Soil meso and macrofauna

There is a current paucity of research with regard to the interaction of biochar with the soil meso and macrofauna, with the exception of earthworms.

Both the application rate of biochar and the original feedstock used have been shown to affect the soil biota. Weyers et al. (2009) reported that application rates higher than 67 t ha⁻¹ of biochar made from poultry litter had a negative impact on earthworm survival rates. They hypothesised that increased soil pH or salt levels may have been the reason for the observed reduced survival rates. They noted that earthworm activity was greater in soil amended with pine chip biochar than with poultry litter biochar and so concluded that different types of biochar can have different effects on the soil biota. This confirmed work reported by Chan et al. (2008) who found that earthworms had different preferences for different types of biochar, but noted that the underlying mechanisms driving these preferences required further work.

Recent work by Van Zwieten et al. (2009) has shown that earthworms preferred biochar-amended Ferrosols over control soils, although they found no significant difference for Calcarosols. This shows that it is not just the application rate or feedstock of the biochar which is important to consider when predicting possible effects, but the soil to which it is added must also be taken into account. This highlights the complex dynamic interactions which can vary greatly with soil type, application rate and feedstock used and shows that predicting the effects of biochar application on the soil biota of a given soil, whilst very important, is inherently very difficult.

Some work has been undertaken looking at the effects of charcoal ingestion on earthworms (Hayes, 1983). When charcoal is ingested by an earthworm, along with other soil particles, the two are mixed with mucus secreted in the oesophagus and finely ground in the muscular gizzard. When excreted, the charcoal/soil paste is stabilised by Van der Waals forces after drying and forms a dark-coloured humus (Hayes, 1983). Ponge et al. (2006) reported that in laboratory experiments the earthworm *Pontoscolex corethrurus* was found to prefer to ingest a mixture of charcoal and soil compared to either pure soil or pure charcoal. Because of this, Ponge et al (2006) concluded that *Pontoscolex corethrurus* was the organisms most responsible for the incorporation of charcoal into the topsoil in the form of silt size particles which aids the formation of stable humus in Terra Pretas.

In further laboratory experiments on the effects of charcoal on populations of earthworms, Topoliantz and Ponge (2003) found differences in the way in which different populations of the earthworm species *P. corethrurus*, taken

from either forest soil or fallow soil, were adapted to the presence of charcoal, implying that the addition of charcoal to soil is exerting a selective influence on the worms although what the specific effects of this selective pressure may eventually be is unclear. They also reported that the observed transport of charcoal within the soil demonstrated the importance of *P. corethrurus* in the incorporation of charcoal particles into the soil.

No research has yet been undertaken investigating the effects of biochar addition to soil on soil microarthropods such as collembola or acari, or on other soil dwelling organisms such as rotifers and tardigrades. Any negative effect on these organisms seems likely to only occur as a result of any contamination which exists in the biochar, if that contaminant is bioavailable (Section 3.2.4). Stimulation of the microbial community may or may not have concurrent effects on soil invertebrates depending on whether the increase in microbial biomass is exposed for predation. If the majority of the increase in microbial biomass occurs within biochar particles in the soil, then the microorganisms may not be available as a food source for soil invertebrates. However, if the stimulated growth in microbial biomass also occurs outside of biochar particles within the soil, then it is possible that an increase in the soil invertebrate community may also occur. This could have implications for nutrient cycling, crop yield and other ecosystem services which are hard to predict owing to a paucity of experimental data and the high intrinsic complexity and dynamic nature of the edaphic community.

3.2.6.3 Soil megafauna

There is no research reported in the literature on the effects of charcoal or biochar addition to soil on soil megafauna such as badgers, moles or other vertebrates. As these organisms are not generally found in the arable environment it is likely that any effects may be minimal if biochar addition is limited to agricultural land. However, should biochar addition be planned for other soils, including forest soils, then an impact assessment may well need to be carried out to investigate any possible impacts.

Off-site effects of biochar addition to arable soils are possible, and are likely to include any contaminants such as heavy metals moving up through the food chain. This is likely to be particularly true of moles that have a diet high in earthworms. As it has been shown that earthworms ingest charcoal which exists within the soil profile, it is probable that moles will in turn ingest charcoal particles when they ingest worms. It is still currently unclear what quantity of heavy metals, if any, will be able to pass from the biochar, if present, into the tissues of other organisms and this is an area which requires significant further work to ensure the safety of heavy metal containing biochars in soils (see also Section 3.2.4).

The main point of contact between biochar in the soil and other megafauna such as rabbits, badgers and foxes is likely to be through skin contact when the animals are building and resting in their burrows, sets and 'earths'. Heavy metal absorption is extremely limited through skin, with the exception of mercury which is likely to exist in biochars in extremely minute amounts, if at all. It is possible that some small amount of biochar may enter these organisms' digestive tracts and airways if it is in the form of very small particles, as well as through ingestion of earthworms in the case of some

organisms such as moles, as earthworms have been shown to ingests charcoal in soil (Topoliantz and Ponge, 2005).

Concerning possible ingestion of biochar fragments from the soil by soil megafauna there is no published data in the primary literature. However, Van et al. (2006) found that incorporation of bamboo charcoal (0.5 to 1.0 mg kg⁻¹ of body weight) into the feed of growing goats resulted in enhanced growth and no adverse effects were observed at the study concentrations. Clearly care must be taken when extrapolating data to other animals and to biochars made from alternative feedstocks and this area warrents further research.

Ingestion is not the only mode of possible uptake of biochar fragments by the soil megafauna. Biochar dust particles may possibly be inhaled by the soil megafauna. However, there is currently no research reported in the primary literature concerning the effect of charcoals on the respiratory systems of soil megafauna and as such robust predictions concerning the possible effects is currently not possible and requires further research.

3.3 Production Function

Increased yields are the most commonly reported benefits of adding biochar to soils. Nearly all experiments have been conducted in the tropics, while field trials in temperate regions have been set up only recently. Taking a step back, SOM is generally believed to be correlated positively with crop yields in modern arable agriculture, although there is still poor scientific understanding of the strength of this relationship, the influence of environmental conditions (sandy or clayey soil, wet, dry, etc.), crop types (combinable vs. root crops) and the underlying mechanisms. Loveland and Webb (2003) reviewed 1200 papers in the scientific literature on the relationship between SOC and crop yield in temperate regions and concluded that a consensus does not exist.

Diaz-Zorita et al. (1999) performed stepwise regression analysis between wheat yields and soil properties and found different relationships in different years. In a year without a water deficit, N and P influenced yield, in drought years however, yields were correlated to water availability and OM. Pan and Smith (2009) investigated the relationship between SOM and yield by using statistical data for China (1949-1998) and found a particularly strong relationship between yield stability and SOM.

Considering the poor understanding of the relationship between SOM and crop yield or plant production, it may be expected that similar challenges exist regarding the scientific understanding of the relationship between biochar and plant productivity. However, to investigate the relationship between biochar additions to soils and crop productivity in more detail, new tools can be used. Therefore, a meta-analysis on this relationship was performed (see next sections).

3.3.1 Meta-analysis methods

Objectivity of systematic reviews on biochar is paramount. In the medical sciences this has been resolved by the founding of an independent organisation (the Cochrane Collaboration) that provides regularly updated systematic reviews on specific healthcare issues using a global network of volunteers and a central database/library. The methodologies used in medical

science can be transferred to ensure objectivity when compiling literature reviews in other research areas such as those related to biochar, even though the amount of literature and information available on biochar is currently limited. One such methodology which was developed for objective analysis of a range of different medical studies testing the same (or similar) hypothesis was that of meta-analysis which is being increasingly used across a range of scientific disciplines.

Here, meta-analysis techniques (Rosenberg et al., 1997) were used to quantify the effect of biochar addition to soil on plant productivity. For each study the control mean and experimental means were recorded, or calculated where necessary. Standard deviation was used as a measure of variance and this was reported where given or calculated from the published measure of variance from each study. To maximise the number of studies used in the analysis, both pot and field experiments were recorded, providing the results were quantitative.

Standardisation of the results from the studies was undertaken through calculation of the "effect size" which allows quantitative statistical information to be pooled from and robust comparisons of effects from studies with different variables to be made. Data was square root transformed to normalise the distribution. Effect size was calculated using the transformed data taken as the natural logarithm of the response ratio by using the following equation:

$$\ln R = \ln \left(\frac{\overline{x}^E}{\overline{x}^C} \right)$$

Where $\overline{\chi}^E$ = mean of experimental group; and $\overline{\chi}^C$ = mean of control group

For the meta-analysis, the following nine studies concerning the effects of biochar addition to soil on crop production were used: Van Zwieten et al. (2008); Yamato (2006); Chan (2007); Chan (2008); Lehmann (2003); Ishii and Kadoya (1994); Nehls (2002); Kimetu et al. (2008) and Blackwell (2007). These studies combined produced 86 different 'treatments' for use in the meta-analysis.

In order to use change in pH as a grouping category, changes were grouped by 'no change' (0 – representing no change from soil starting pH upon addition of biochar) and in consecutive changes in pH of 0.5 for both increasing and decreasing pH values upon biochar addition. For calculation of grouped effect sizes a categorical random effects model was used. Groups with fewer than two variables were excluded from each analysis. Resampling tests were generated from 999 iterations. For each of the analyses, grouped by different categorical predictors, the data was analysed using a fixed effects model if the estimate of the pooled variance was less than or equal to zero. When plotting figures, the effect size was unlogged (exponentially transformed) and the result multiplied by 100 to obtain the percentage change in effect size upon biochar addition in each category. Analysis was undertaken using MetaWin Version 2 statistical software (Rosenberg et al., 2000). While more than the nine reported studies looking at the effect of

biochar addition to soil on crop productivity, studies were excluded from the analysis when no quantitative results or measures or variance were available, leaving the nine studies reported above.

3.3.2 Meta-analysis results

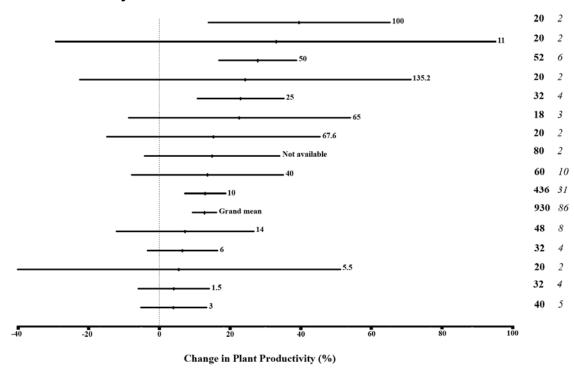


Figure 3.2 The percentage change in crop productivity upon application of biochar at different rates, from a range of feedstocks along with varying fertiliserco-amendments. Points represent mean and bars represent 95% confidence intervals. Numbers next to bars denote biochar application rates (t ha⁻¹). Numbers in the two columns on the right show number of total 'replicates' upon which the statistical analysis is based (bold) and the number of 'experimental treatments' which have been grouped for each analysis (italics)

Figure 3.2 shows the effect of biochar addition to soil on crop productivity, grouped by application rate and vertically partitioned by effect size. The sample means seem to indicate a small but positive effect on crop productivity with a grand mean (being the mean of all effect sizes combined) of about 10%. There appears to be a general trend, when looking at the sample means, for increased biochar application rate to be correlated with increased crop productivity (Figure 3.2). However, there was no statistically significant difference (at P = 0.05) between any of the application rates as is evident from the overlapping error bars which represent the 95% confidence intervals. Application rates of 10, 25, 50 and 100 t ha⁻¹ were all found to significantly increase crop productivity when compared to controls which received no biochar addition. However, other application rates which fall within the range of these statistically significant application rates, such as 40 and 65 t ha⁻¹ showed no statistically significant effect of biochar addition to soil on crop yield, demonstrating that while biochar addition to soil may increase crop productivity it is not linearly correlated.

It can be seen from Figure 3.2 that even with the same application rate of biochar, a large variation in effect size occurs. This is particularly true of the

lower application rates of 5.5 and 11 t ha⁻¹ and also for the large application rate of 135.2 t ha⁻¹. Other application rates also have a large variance in their effect size, but to a lesser extent. The reason for this large variation is likely to be due to the different biochar feedstocks used, the different crops assessed and differences in soil type to which the biochar was added. It is interesting to note that while there was often large variation in the data for a given application rate, the means for each application rate all fall on the positive productivity effect side, and no single biochar application rate was found to have a statistically significant negative effect on the crops from the range of soils, feedstocks and application rates studied. It should be noted that while no negative effects have been detected by this meta-analysis with regard to the effect of application rate on crop productivity, the studies used in the meta-analysis do not cover a wide range of latitudes and the data used was heavily scewed towards (sub)tropical conditions. This means that while this analysis provides good evidence of the generally positive effects of biochar addition to soil on crop productivity, care needs to be taken when extrapolating these results to European latitudes, crops and soil types.

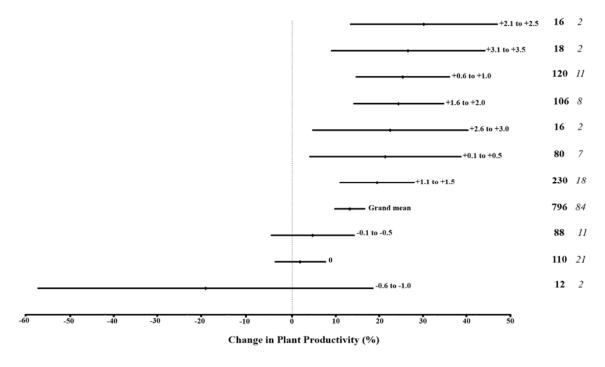


Figure 3.3 Percentage change in crop productivity upon application of biochar at different rates along with varying fertiliserco-amendments grouped by change in pH caused by biochar addition to soil. Points represent mean and bars represent 95% confidence intervals. Values next to bars denote change in pH value. Numbers in the two columns on the right show number of total 'replicates' upon which the statistical analysis is based (bold) and the number of 'experimental treatments' which have been grouped for each analysis (italics)

Figure 3.3 shows the effect of biochar addition to soil on crop productivity, grouped by liming effect. It should be noted that where the biochar addition to soil lead to a liming effect (i.e. the pH of the soil was increased), there was a significant increase in crop productivity compared to controls, although there were no significant differences between treatments which lead to a positive liming effect.

Regarding those treatments that showed no change, or a reduction in pH upon biochar addition to soil, biochar addition to soil showed no statistically significant effect. All other groupings where biochar addition to soil led to an increase in soil pH, a concurrent increase in crop productivity was seen. This effect was not strictly linear, with the mean increase in crop productivity where biochar caused a liming effect (with an increase in pH units ranging from 1.1-1.5), was lower when compared to those treatments where the liming effect resulted in an increase ranging from 0.6 to 1.0 pH units. This may be due to differences in initial pH, before biochar addition to soil, meaning that a lesser increase was still sufficient to pass a tipping point with regard to metal ion availability for example, meaning a slightly increased crop productivity effect even with a decreased liming effect.

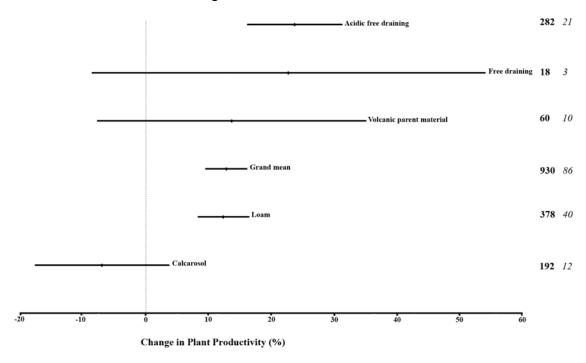


Figure 3.4 The percentage change in crop productivity o upon application of biochar at different rates along with varying fertiliserco-amendments to a range of different soils. Points shows mean and bars so 95% confidence intervals. Numbers in the two columns on the right show number of total 'replicates' upon which the statistical analysis is based (bold) and the number of 'experimental treatments' which have been grouped for each analysis (italics)

Figure 3.4 shows the effect of biochar addition to soil on crop productivity, grouped by soil type. As with the previous meta-analysis figures, the error bars are again very large. Again, there were found to be no statistically significant negative effects of biochar to soil on crop productivity when grouped by soil type. The trend of the effect in Calcarosols was towards the negative, but this effect was not statistically significant when compared to control soils, although it was significantly less than then positive effects seen upon biochar addition to both loam soils and acidic free draining soils. The effect of biochar addition to these soils ('loam' and 'acidic free draining') was also found to show a statistically significant increase when compared to control soils with no biochar addition. For the other soil types investigated by this analysis ('volcanic parent material' and 'free draining'), there was a general trend towards a positive effect as evidenced by the means being on

the positive effect side of 0. However, the effect for these soils was not found to be statistically significant owing to the large variation from the samples.

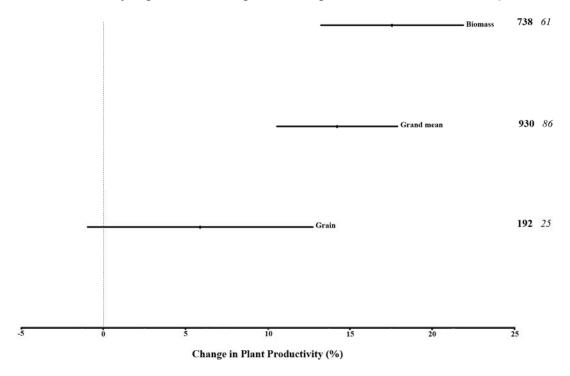


Figure 3.5 The percentage change in crop productivity of either the biomass or the grain upon application of biochar at different rates along with varying fertiliserco-amendments. Points shows mean and bars so 95% confidence intervals. Numbers in the two columns on the right show number of total 'replicates' upon which the statistical analysis is based (bold) and the number of 'experimental treatments' which have been grouped for each analysis (italics)

Figure 3.5 shows the effect of biochar addition to soil on crop productivity, grouped by overall biomass productivity *vs.* grain yield. There was no significant difference in grain yield for those crops grown in biochar amended soils compared to non-biochar amended soils. There was a significant increase in overall crop biomass production in biochar amended soils compared to non-biochar amended soils, although this difference was not significant when compared to the impact of growth on biochar amended soils on grain production.

The fact that biomass was positively affected by growth on biochar amended soils whereas grain was not is possibly due to grain being a relatively small part of the biomass and so any slight change would be more difficult to detect. Again, the error bars show that there was considerable variation within treatments, as would be expected due to the data being amalgamated from several different studies, and each treatment in the above figure includes data obtained from different crops, soils and biochar feedstocks.

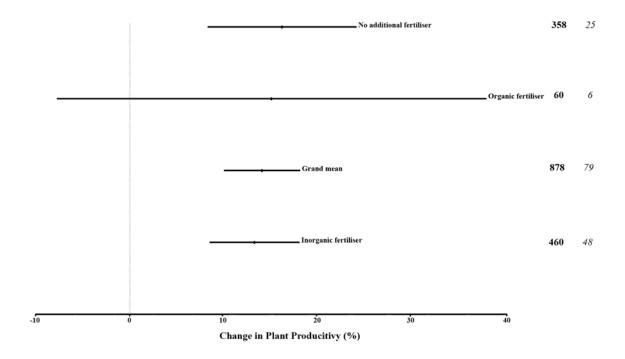


Figure 3.6 The percentage change in crop productivity upon application of biochar along with a co-amendment of organic fertiliser(o), inorganic fertiliser(I) or no fertiliser(none). Points shows mean and bars so 95% confidence intervals. Numbers in the two columns on the right show number of total 'replicates' upon which the statistical analysis is based (bold) and the number of 'experimental treatments' which have been grouped for each analysis (italics)

There was no statistically significant difference between biochar application to soil whether no concurrent fertiliser addition was used, or whether organic or inorganic fertiliser was used (Figure 3.6). This is contrary to what is often reported in the literature where specific recommendations often state that fertiliser addition is necessary to maximise crop yields.

Care must be taken when interpreting Figure 3.6, as it appears at first glance to show no difference in effect size between addition of biochar alone, or with fertiliser. It is important to remember that the effect sizes are between 'controls without biochar' vs 'treatments with biochar'. This means that the no fertiliser application treatment shows the effect of biochar addition to soil alone. In the other treatments, the control includes the addition of fertiliser, but without the addition of biochar, compared to the experimental treatments which include both fertiliser and biochar. Figure 3.6 shows, therefore, that the impact of biochar addition to soil was not significantly different whether fertiliser, either organic or inorganic was used. This does not show, as appears at first glance, that there was no significant effect of co-addition of fertiliser with biochar, over addition of biochar to soil alone.

While there was found to be no significant difference between the effects of inorganic fertiliser with biochar compared to no fertiliser with biochar, both of these treatments showed increased crop productivity when compared to control non-biochar amended soils. Chan et al. (2007) reported a lack of response upon addition of biochar without the co-addition of N and as such it seems likely that in those studies available N in the soil was not a limiting factor, possibly due to previous cropping with legumes, or owing to the quantity and quality of SOM meaning that available N levels were not limiting.

The addition of organic fertiliser along with biochar to soils was found to have no statistically significant effect when compared to application of organic fertiliser to non-biochar amended soils. This is due to extreme levels of variance in results of the biochar plus organic fertiliser treatments, as shown by the large error bars.

3.3.3 Meta-analysis recommendations

As was shown in this report, soils are very heterogeneous systems, in both time and space and at a multitude of scales, and biochar is a very heterogeneous material. Meta-analysis is a valuable tool for amalgamating, summarising and reviewing studies on biochar. It can elucidate trends in a quantitative way that in conventional reviews might be perceived as being biased by personal judgement. A combination of meta-analysis with a qualitative review of the literature will provide the most comprehensive discussion of both the status of scientific knowledge on a specific 'effect' and the possible underlying mechanisms and exceptional or marginal conditions. As new studies are published, the meta-analyses on the effect of biochar application to soil on productivity can be updated (and refined) periodically. In addition, many other effects of biochar (see Chapter 3) can be analysed by meta-analyses once a large enough body of research has been established.

From this work it is strongly recommended that scientists publishing results on effects of biochar describe the data, and the variance of those data, consistently and completely. This means including the Z or F statistic for regression data and clear measures of variance for comparative analysis data, such as standard deviations or standard errors for each treatment, including the control, rather than an LSD (least significant difference) which has been pooled for several treatments. In all cases, it should be absolutely clear what the sample number is for every treatment (including control). Clearly this should be normal scientific conduce, but unfortunately does not seem to occur in all cases. To enable meta-analyses on effects of a factor that is not the dependent variable of a study, it is also recommended to include all sample numbers, standard deviations or standard errors of other parameters measured in the study, e.g. CEC, pH, bulk density, microbial activity, etc. Finally, it is recommended to report all the data in tabular format, possibly as an annex.

3.3.4 Other components of crop production function

Crop production is, however, only one possible agronomic effect of on-farm benefit from biochar. Many other effects still need to be investigated, for example i) direct impacts on yields (seed rate); ii) crop-related impacts (crop establishment, fertiliser, disease and weeds); and iii) non-crop-related impacts (workability, soil hydrology, soil degradation).

3.4 Summary

This section has highlighted the relative paucity of knowledge concerning the specific mechanisms behind the reported interactions of biochar within the soil environment. However, while there is still much that is unknown, large steps have been taken towards increasing our understanding of the effects of biochar on soil properties and processed. Biochar interacts with the soil

system on a number of levels. Sub-molecular interactions with clay and silt particles and SOM occur through Van der Waals forces and hydrophobic interactions. It is the interactions at this scale which will determine the influence of biochar on soil water repellency and also the interactions with cations and anions and other organic compounds in soil. These interactions are very char specific, with the exact properties being influenced by both the feedstock and the pyrolysis conditions used.

There has been some evidence to suggest that biochar addition to soil may lead to loss of SOM via a priming effect in the short term. However, there is only very little research reported in the literature on this subject, and as such it is a highly pertinent area for further research. The fact that Terra Pretas contain SOM as well as char fragments seems to demonstrate that the priming effect either does not exist in all situations or if it does, perhaps it only lasts a few seasons and it appear not to be sufficient to drive the loss of all native SOM from the soil. Biochar has the potential to be highly persistent in the soil environment, as evidenced both by its presence in Terra Pretas, even after millennia, and also as evidenced by studies discussed in this section. While biochars are highly heterogeneous across scales, it seems likely that properties such as recalcitrance and effects on water holding capacity are likely to persist across a range of biochar types. It also seems probable, that while difference may occur within biochars on a microscale, biochars produced from the same feedstocks, under the same pyrolysis conditions are likely to be broadly similar, with predictable effects upon application to soil. What remains to be done are controlled experiments with different biochars added to a range of soils under different environmental conditions and the precise properties and effects identified. This may lead towards biochars possibly being engineered for specific soils and climate where specific effects are required.

After its initial application to soil, biochar can function to stimulate the edaphic microflora and fauna due to various substrates, such as sugars, which can be present on the biochar's surface. Once these are metabolised, biochar functions more as a mineral component of the soil rather than an organic component, as evidenced by its high levels of recalcitrance meaning that it is not used as a carbon source for respiration. Rather, the biochar functions as a highly porous network the edaphic biota can colonise. Due to the large inherent porosity, biochar particles in soil can provide refugia for microorganisms whereby they may often be protected from grazing by other soil organisms which may be too large to enter the pores. This is likely to be one of the main mechanisms by which biochar-amended soils are able to harbour a larger microbial biomass when compared to non-biochar amended soils. Biochar incorporation into soil is also expected to enhance overall sorption capacity of soils towards trace anthropogenic organic contaminants (e.g. PAHs, pesticides, herbicides), in a stronger way, and mechanistically different, from that of native organic matter. Whereas this behaviour may greatly contribute to mitigating toxicity and transport of common pollutants in soil, biochar aging over time may result in leaching and increased bioavailability of such compounds. On the other hand, while the feasibility for reducing mobility of trace contaminants in soil might be beneficial, it might also result in their localised accumulation, although the extent and implications of this have not been experimentally assessed.

Soil quality may not be necessarily improved by adding biochar to soil. Soil quality can be considered to be relatively high for supporting plant production and provision of ecosystem services if it contains carbon in the form of complex and dynamic substances such as humus and SOM. If crop residues are used for biochar, the proportion of carbon going into the dynamic SOM pool is likely to be reduced, with the carbon being returned to the soil in a relatively passive biochar form. The proportion of residues which are removed for pyrolysis versus the proportion which is allowed to remain in the soil will determine the balance between the dynamic SOM and the passive biochar and so is likely to affect soil quality for providing the desired roles, be it provision of good use as crop or timber, or functioning as a carbon pool. Biochar also has the potential to introduce a wide range of hazardous organic compounds (e.g. heavy metals, PAHs) into the soil system, which can be present as contaminants in biochar that has been produced either from contaminated fedstocks or under processing conditions which favour their production. While a tight control over the feedstock type and processing conditions used can reduce the potential risk for soil contamination, experimental evidence of the occurrence and bioavailability and toxicity of such contaminants in biochar and biochar-enriched soil (over time) remain scarce. A comprehensive risk assessment of each biochar product prior to its incoporation into soil, taking into account the soil type and environmental conditions, is therefore paramount.

Increased crop yields are the most commonly reported benefits of adding biochar to soils. A full search of the scientific literature led to a compilation of studies used for a meta-analysis of the effects of biochar application to soils and plant productivity. Meta-analysis techniques (Rosenberg et al., 1997) were used to quantify the effect of biochar addition to soil on plant productivity from a range of experiments. Our results showed a small overall, but statistically significant, positive effect of biochar application to soils on plant productivity in the majority of cases, covering a range of both soil and crop types. The greatest positive effects were seen on acidic free-draining soils with other soil types, specifically Calcarosols showing no significant effect. No statistically significant negative effects were found. There was also a general trend for concurrent increases in crop productivity with increases in pH up on biochar addition to soils. This suggests that one of the main mechanisms behind the reported positive effects of biochar application to soils on plant productivity may be a liming effect. These results underline the importance of testing each biochar material under representative conditions (i.e. soilenvironment-climate-management factors).

The degree and possible consequences of the changes biochar undergo in soil over time remain largely unknown. Biochar loss and mobility through the soil profile and into water resources has so far been scarcely quantified and the underlying transport mechanisms are poorly understood. This is further complicated by the limited amount of long-term studies and the lack of standardized methods for simulating biochar aging and for long-term environmental monitoring.

4. BIOCHAR AND 'THREATS TO SOIL'

This chapter summarises the findings and gaps in the biochar literature relevant to the threats to soil, as identified by the Thematic Strategy for Soil Protection (COM(2006) 231). For a more in-depth discussion of patterns, effects, processes and mechanisms, please refer to the relevant Sections in this report. For the threats to soil of 'soil sealing' and 'landslides', biochar holds no relevance at present.

4.1 Soil loss by erosion

In the context of threats to soil, soil loss by erosion is specified by being "as a result of anthropogenic activity, in excess of natural soil formation rates causing a deterioration or loss of one or more soil functions" (Jones et al., 2008). Experimental studies on the effects of biochar application on soil erosion have not been found. Even erosion of charcoal particles from the soil surface after wildfires is a topic that has only started being researched relatively recently. However, an obvious potential effect is the wind erosion of biochar particles during application to soils. For application strategies where the biochar is incorporated into the soil, further erosion by either wind is likely to be reduced to the 'normal' erosion rates of the site. For application strategies where the biochar is applied to the soil surface only, the risk of erosion increases strongly because biochar generally has a relatively low density and, therefore, a greater erodibility by wind for smaller particles and by water for also the larger biochar particles. Surface application has been discussed for grassland and forest land uses mostly (and no-till systems). The greater risk may be expected for grasslands since these are open systems with generally greater wind velocities than forests.

Biochar application to soils can also be considered from a soil formation perspective. Verheijen et al. (2009) reviewed soil formation rates in Europe to be in the range of 0.3-1.4 t ha⁻¹ yr⁻¹. Considering the human life span, these very low formation rates (measurable only in geological terms) mean that soil is a non-renewable resource. Even low application rates of biochar are likely to outstrip natural soil formation rates by physicochemical weathering and dust deposition (i.e. mineral dust mainly from the Sahara). However, great care must be taken when considering biochar application to soils as constituting towards soil formation rates, and thereby tolerable soil erosion rates. Most notably, the residence time of biochar particles in soils needs to be considered, which depends on i) decomposition rates of biochar components (physicochemical and biological degradation), and ii) mobility and fate of biochar particles (movement through the soil matrix and into ground/surface waters). Both these factors are likely to be influenced strongly by variation in soil properties, climatic conditions, biochar properties, and land use and soil management. A substantial body of experimental scientific research into the mechanisms affecting the residence time of biochar particles in soils is required before biochar application to soils might be considered in the context of tolerable soil erosion rates. Conventionally, SOM build up is not considered for soil formation rates of mineral soils. Under what conditions those components of biochar that are very recalcitrant (e.g. residence time >1,000 yr) will reside in the soil matrix during their 'life span', is unknown at present. The interaction between biochar particles, mineral soil particles and

native organic matter (NOM), or OM that is applied with (or after) the biochar, is likely to play a major role (see Section 3.2.1 and 3.2.5).

Wind erosion is caused by the simultaneous occurrence of three conditions: high wind velocity; susceptible surface of loose particles; and insufficient surface protection. Theoretically, if biochar particles are produced with water retention properties greater than the water retention capacity of the soil surface at a site, and if the biochar particles become a structural component of that surface soil (e.g. not residing on top of the soil surface), and possibly interacting with OM and mineral particles, then wind erosion rates at that site may be reduced, all other factors remaining equal. The application of biochar dust to the soil surface (i.e. not incorporated) can pose risks via wind erosion of the dust particles and subsequent inhalation by people. Strict guidelines on biochar application strategies under specific environmental and land use conditions could prove sufficient to prevent this risk.

Water erosion takes place through rill and/or inter-rill (sheet) erosion, and gullies, as a result of excess surface runoff, notably when flow shear stresses exceed the shear strength of the soil (Kirkby et al., 2000, 2004; Jones et al., 2004). This form of erosion is generally estimated to be the most extensive form of erosion occurring in Europe. If biochar reduces surface runoff, then, logically, it will reduce soil loss by water erosion, all other factors remaining equal. Surface runoff can be reduced by increased water holding capacity (decreasing saturation overland flow) or increased infiltration capacity (decreasing infiltration excess – or Hortonian - overland flow) of the topsoil. Under specific environmental conditions, it seems that biochar with large water retention properties could diminish the occurrence of saturation overland flow. This effect could be enhanced when biochar addition leads to stabilisation of NOM, or OM that is added with, or after, the biochar. Infiltration excess overland flow depends more on soil structure and related drainage properties. In particular the soil surface properties are important for this mechanism. It is not inconceivable that specific biochar particles can play a role in increasing infiltration rates, however, other biochar particles could also lead to reduced infiltration rates when fine biochar particles fill in small pore spaces in topsoils, or increased hydrophobicity (Section 3.1). In addition, and this could be an overriding factors at least in the short term, the biochar application strategy and timing is a potential source of topsoil and/or subsoil compaction (Section 1.8) and, thereby, reduced infiltration rates.

It stands to reason that under those conditions where surface runoff is reduced by biochar application, possibly as part of a wider package of soil conservation measures, a concomitant reduction in flooding occurrence and severity may be expected, all other factors remaining equal. However, as stated at the beginning of this section, experimental evidence of biochar application on erosion was not encountered in the scientific literature, nor was it for flooding. On the other hand, under conditions where biochar application leads to soil compaction (see Section 1.8) runoff may be increased leading to more erosion. Research is needed into all aspects of effects from biochar addition to soil loss by erosion described here, and in particular into the mechanisms behind the effects. Even a small effect may be worthwhile considering estimates of the cost to society from erosion. For example annual costs have been estimated to be £205 million in England and Wales alone

and \$44 billion in the U.S.A. (Pimentel et al., 1995). In addition, active and targeted modification of the water retention function of specific soils could be considered in the context of scenarios of adapting to changing rainfall patterns (seasonal distribution, intensity) with climate change. In the future, climate change looks likely to increase rainfall intensity over large areas of Europe, if not annual totals, thereby increasing soil erosion by water, although there is much uncertainty about the spatio-temporal structure of this change as well as the socio-economic and agronomic changes that may accompany them (e.g. Boardman and Favismortlock, 1993; Phillips et al., 1993; Nearing et al., 2004).

4.2 Decline in soil organic matter

Decline in SOM is defined as a negative imbalance between the build-up of SOM and rates of decomposition leading to an overall decline in SOM contents and/or quality, causing a deterioration or loss of one or more soil functions (Jones et al., 2008).

The interaction between biochar and NOM, or OM that is added with the biochar, or afterwards, is complex. Many mechanisms have been identified and are discussed in this report, i.e. priming effect, residue removal, liming effect, organomineral interactions, aggregation and accessibility.

Biochar replacing peat extraction

If biochar is engineered to have good plant-available water properties as well as nutrient retention, it could come to replace peat as a growing medium in horticulture (also agriculture), and as a gardening amendment sold in garden centres. Peatlands currently used ('mined') for peat extraction could then be restored with substantial benefits to their functioning and the ecosystem services which they provide, e.g. maintenance of biodiversity, C sequestration, water storage, etc. Janssens et al. (2005) reported that undisturbed European peatlands sequester C at a rate of 6 g m⁻² total land area, while peat extraction caused a C loss of 0-36 g m⁻² total land area. Janssens et al. (2003) estimated a net loss of 50 (±10) Mt yr⁻¹ for the European continent, which is equivalent to around 1/6 of the total yearly C loss from European croplands. However, this value is likely to be greater when also considering C emissions associated with continued decomposition at abandoned peat mines (Turetsky et al., 2002), transport to processing plant, transport to market, and decomposition of the applied peat (e.g. in a life cycle assessment; Cleary et al., 2005).

4.3 Soil contamination

Recently, increasing knowledge on the sorption capacity of biochar has had two environmentally important outcomes. Firstly, the realisation that biochar addition to a soil can be expected to improve its overall sorption capacity, and consequently influence the toxicity, transport and fate of any organic compounds, which may be already present or are to be added to that soil (see Section 3.2.2). Secondly, enhanced awareness that biochar from widely available biomass resources can be applied to soils and sediments as a low-

cost and low-environmental-impact mitigation/remediation strategy for common environmental pollutants.

The latter outcome appears to be even more attractive when considering the time and cost benefits associated to biochar production, relatively to that of activated carbon in various applications. Activated carbon results from activating (involving partial oxidation) a charcoal precursor by means of exposing it to CO₂, steam or acid at high temperatures, in order to further increase its surface area (per gram; McHenry, 2009). Overall, evidence suggests that biochar and activated carbon have comparable sorption affinities, as demonstrated by Tsui and Roy (2008), using compost biochar (pyrolysis temperatures ranging between 120-420°C) and corn stillage activated carbon for removal of the herbicide atrazine in solution (1.7 mg L⁻¹). In fact, the effectiveness of activated carbon over that of wood biochar has been questioned in some instances (Pulido et al., 1998; Wingate et al., 2009), but this aspect remains far from fully evaluated.

Wingate et al. (2009) have very recently patented the development and application of charcoal from various plant and crop tissues (leaves, bark and stems) of ammonium (NH₄⁺) and heavy metal-contaminated environments (soil, brown-field site, mine tailings, slurry, and aqueous solution). Heavy metal ions are strongly adsorbed onto specific active sites containing acidic carboxyl groups at the surface of the charcoal (e.g. Machida et al., 2005). Surprisingly, the mechanism of metal uptake by charcoals appears to involve replacing pre-existing ions contained in the charcoal (e.g. K, Ca, Mg, Mn, excluding Si), with the metal ion, suggesting a relationship between the mineral content of the charcoal and its remediation potential for heavy metals (Wingate et al., 2009).

In the soil environment, biochar has already been shown to be effective in mitigating mobility and toxicity of heavy metals (Wingate et al., 2009) and endocrine disruptors (Smernik, 2007; Winsley, 2007). However, very little work of this kind has been accomplished and data is still scarce. It is likely that soil heterogeneity and the lack of monitoring techniques for biochar in this environment may partly explain such a gap. The previous discussion on contaminant leaching over time as a consequence of biochar aging in the environment (see Section 3.2.1) does not necessary mean that its high remediating potential should be disregarded. For example, it could be employed as a 'first-instance' pollutant immobilisation from point sources. Also, biochar's highy porous matrix might be ideal as carrier for microrganisms as part of bioaugmentation programs for specific sites, where indigenous microbial populations are scarce or have been suppressed by the contaminant (Wingate et al., 2009). In this context, for instance, Wingate et al. (2009) have reported the successful application of charcoal carrying 10¹⁰ hydrocarbon degraders (per gram of charcoal) in diesel-polluted sites, resulting in 10 fold enhancement of hydrocarbon degradation in this environment. Clearly, it is likely that appropriate regulatory requirements for cleanup and closure would be needed before any remediation plan involving biochar could be implemented. Experimental evidence is required in order to verify this.

There is also evidence that it is possible to use biochar's sorptive capacity in water and wastewater treatments (Wingate et al., 2009), whereas the use of activated carbon for removal of chlorine and halogenated hydrocarbons, organic compounds (e.g. phenols, PCBs, pesticides) and heavy metals (Boateng, 2007) has long been established. Crop residue (mainly wheat) biochar produced at temperatures between 300°C and 700°C has already shown potential for removal of sulphate (Beaton, 1960), benzene and nitrobenzene from solution (Chun et al., 2004), while bamboo charcoal powder has been effective in uptake of nitrate from drinking water (Mizuta et al., 2004). Other studies in aqueous media have reported biochar's capacity to adsorb phosphate and ammonium (Lehmann et al., 2002; Lehmann et al., 2003, 2003b), with further applications having been reviewed by Radovic et al. (2001). In the context of water treatment, Sohi et al. (2009) have pointed out that a higher control over the remediation process would be achievable, comparatively to that in soil.

The possibility of using 'engineered' (or 'tailor-made') biochar (Pastor-Villegas et al., 2006) in order to meet the requirements for a specific remediation plan looks increasingly promising. As the mechanisms of biochar production, behaviour and fate, as well as its impact on ecosystem health and functioning become increasingly well understood, biochar can be optimised to deliver specific benefits (Sohi et al., 2009). Nevertheless, data on competitive sorption in soils and sediments emphasize the need for a full characterisation of the contaminated site and the coexisting chemical species before any remediation plan involving biochar is put in place.

4.4 Decline in soil biodiversity

Decline is soil biodiversity is defined as a 'reduction of forms of life living in the soil (both in terms of quantity and variety) and of related functions, causing a deterioration or loss of one or more soil functions' (Jones et al., 2008). There is evidence of decline in soil biodiversity in some specific cases. For example, the Swiss Federal Environment Office has published the first-ever "Red List" of mushrooms detailing 937 known species facing possible extinction in the country (Swissinfo 2007). In another instance, the New Zealand flatworm is increasing in numbers and extent and potentially poses a great threat to earthworm diversity in the UK with a 12% reduction in earthworm populations in some field sites in Scotland already reported (Boag et al. 1999). Changes in earthworm community structure have been also recorded (Jones et al., 2001).

The exact impacts of a decline in soil biodiversity are far from clear, due to complications by such phenomena as functional redundancy. However, it is clear that any decline in soil biodiversity has the potential to compromise ecosystem services, or at least reduce the resistance of the soil biota to further pertubations. Although evidence exists for declines in soil biodiversity in some specific cases, it is a highly depauperate area of research. However, no studies have been published to date looking at how biochar additions to soil can be used to restore soil biodiversity to previous levels in any given area.

Threats to soil biodiversity consist of those soil threats as described in the Thematic Strategy for Soil Protection (COM(2006) 231) and as such, in those

situations where biochar either helps the mitigation of, or increases the problem of, it is likely that knock on effects for the soil biota will occur.

4.6 Soil compaction

Soil compaction is defined as the densification and distortion of soil by which total and air-filled porosity are reduced, causing a deterioration or loss of one or more soil functions (Jones et al., 2008).

The effects of biochar on soil compaction have been studied very little. Both potential positive and negative effects may occur, for topsoil as well as subsoil compaction. Whereas topsoil compaction is 'instantaneous', subsoil compaction is a cumulative process leading to densification just below the topsoil over the years. A biochar application strategy, where application occurs every year, is, therefore, a greater risk of subsoil compaction than a 'single application' biochar strategy. An obvious risk of compaction is the actual application of biochar itself. When applied with heavy machinery and while the water-filled pore volume of soil is high, the risk of compaction increases. Biochar also has a low elasticity, measured by the relaxation ratio (R), which is defined as the ratio of the bulk density of the test material under specified stress to the bulk density after the stress has been removed. Straw has a very high elasticity ratio and, therefore, when straw is charred and applied as biochar instead of fresh straw, the resilience of the soil to compactive loads is reduced, all other factors remaining equal. The bulk density of biochar is low and, therefore, adding biochar to soil can lower the bulk density of the soil thereby reducing compaction. However, when biochar is applied as very fine particles, or when larger biochar particles disintegrate in arable soils under influence of tillage and cultivation operations, these can fill up small pores in the soil leading to compaction.

Compaction by machinery may be prevented relatively easily by promoting sound soil management. However, compaction by the behaviour of biochar particles in the soil has received very little attention in research so far and mechanisms are understood poorly.

4.7 Soil salinisation

Soil salinisation is defined as the accumulation of water soluble salts in the soil, causing a deterioration or loss of one or more soil functions. The accumulated salts include sodium-, potassium-, magnesium- and calcium-chlorides, sulphates, carbonates and bicarbonates (Jones et al., 2008). A distinction can be made between primary and secondary salinisation processes. Primary salinisation involves accumulation of salts through natural processes as physical or chemical weathering and transport processes from salty geological deposits or groundwater. Secondary salinisation is caused by human interventions such as inappropriate irrigation practices, use of salt-rich irrigation water and/or poor drainage conditions (Huber et al., 2009). Salts associated with biochar should be considered as a potential source for secondary salinisation.

Various salts can be found in the ash fraction of biochar, depending mostly on the mineral content of the feedstock. Indications are that the ash content of biochar varies from 0.5% - 55%. In classic charcoal manufacturing, 'good

quality' charcoal is referred to as having 0.5% – 5.0% ash (Antal and Gronli, 2003). However, biochar produced from feedstocks such as switchgrass and maize residue have been reported to have an ash content 26% - 54% much of which as silica, while hardwood ash contains mainly alkali metals (Brewer et al., 2009). A wide range of trace elements have been measured in biochar ash, e.g. boron, cupper, zinc, etc., however, the most common elements are potassium, calcium, silicon and in smaller amounts aluminium, iron, magnesium, phosphorus, sodium and manganese. These elements are all in oxidised form, e.g. Na₂O, CaO, K₂O, but can be reactive or soluble in water to varying degrees. It is the ash fraction that provides the liming effects of biochar that is discussed as a potential mechanism of some reported increases in plant productivity (see Section 3.3). However, for soils that are salinised or are sensitive to become salinised, that same ash fraction might pose an increased threat. Surprisingly little work has been found on biochar ash and under what conditions it may become soluble and contribute to salinisation.

4.8 Summary

This chapter has described the interactions between biochar and 'threats to soil'. For most of these interactions, the body of scientific evidence is currently insufficient to arrive at a consensus. However, what is clear is that biochar application to soils will effect soil properties and processes and thereby interact with threats to soil. Awareness of these interactions, and the mechanisms behind them, is required to lead to the research necessary for arriving at understanding mechanisms and effects on threats to soil, as well as the wider ecosystem.

5. WIDER ISSUES

5.1 Emissions and atmospheric pollution

The high load of aerosol and pollutant emissions generated by wildfires and the combustion of fossil fuels explain much of the concern on biochar production being associated to high levels of particulate matter and atmospheric pollutants. Nevertheless, the type and composition of such emissions, including the way these are influenced by pyrolysis conditions and factors associated to biomass feedstock, are considerably less well understood (Fernandes and Brooks, 2003).

Particulate matter emitted during pyrolysis is a main focus of human and environmental health concern based on what is known regarding the inherent toxicity associated to some types of fine and ultrafine particles, due to their small size and large surface area (Fernandes and Sicre, 1999). Whereas until recently, some cases of disease (e.g. respiratory and cardiac) associated to atmospheric pollution were thought to be caused by some particle types with dimensions up to 10 µm, recent progress has demonstrated that those responsible are mainly within the nano-size range. The U.S.A. Environment Protection Agency (EPA) has responded by putting forward new ambient standards on Air Quality for particulate matter <2.5 µm (PM2.5). Current annual mean limits are 40 µg m⁻³ and 20 µg m⁻³ for PM10 (<10 µm) and PM2.5 respectively (EPA, 2007), whereas ambient standards for sub-micron particles in the environment were not found. Besides the potential health risks associated to fine and ultrafine particle emissions, their direct and indirect role in climate change has also granted them wide attention. Further research involving characterisation of biochar-related particulate emissions during pyrolysis would be vital for assessing the true contribution of such emissions to ambient aerosols, as well as identifying processing conditions and technologies that may help reducing them.

Typically, large amounts of organic and inorganic volatile compounds are emitted during biomass pyrolysis, particularly at temperatures exceeding 500°C (Greenberg et al., 2005; Gaskin et al., 2008; Chan and Xu, 2009). Major volatile organic compounds emissions from pyrolysis (30 to 300°C) of leaf and woody plant tissue (pine, eucalyptus and oak wood, sugarcane and rice) included acetic acid, furylaldehyde, methyl acetate, pyrazine, terpenes, 2,3 butadione, phenol and methanol, as well as smaller quantities of furan, acetone, acetaldehyde, acetonitrile and benzaldehyde (Greenberg et al., 2005). At treatment temperatures between 300 and 600°C, heat- and masstransfer rates are high, resulting in a gas-forming pathway dominating the pyrolysis process, being linked to the production of heavy molecular weight (tarry) vapours of highly diverse composition (Amonette and Joseph, 2009). At temperatures around that lower limit, these tars remain trapped within micropores of the carbonaceous residue but become volatile for higher temperatures. While the majority of such vapours are commonly recovered from the gas stream as bio-oil using a condensation tower (Amonette and Joseph. 2009), a significant proportion is still emitted into the atmosphere. especially where simple charcoal kilns are used.

Emissions of PAHs resulting from both natural (e.g. forest fires, volcanic eruptions) and anthropogenic sources (e.g. burning of fossil fuels) are recognized as relevant environmental pollutants (Pakdel and Roy, 1991). Secondary chemical reactions during thermal degradation of organic material at high temperatures (>700°C), is generally associated to the generation and emission of heavily condensed and highly carcinogenic and mutagenic PAHs (Ledesma et al., 2002; Garcia-Perez, 2008). Nevertheless, some evidence also exists that PAHs can be formed within the temperature range of pyrolysis (350-600°C). These low-temperature generated PAHs are highly branched in nature and appear to carry lower toxicological and environmental implications (Garcia-Perez, 2008). Preliminary results from a recent study have shown that the amount of biochar-related PAH emissions from traditional feedstocks remain within environmental compliance (Jones, 2008).

Dioxins (PCDD) and furans (PCDF) are planar chlorinated aromatic compounds, which are predominantly formed by combustion of organic material in the presence of chlorine and metals, at temperatures exceeding 1000°C (Lavric et al., 2005; Garcia-Perez, 2008). Wood (accidental fires, wildfires and wood wastes) is an important air emission source for dioxins (Lavric et al., 2005). While combustion of firewood and pellets in residential stoves, as well as paper and plastic wastes, are well know for emitting high loads of dioxins (Hedman et al., 2006), actual emission factors and corresponding activity rates remain poorly assessed (Lavric et al., 2005). No experimental evidence was found confirming dioxin emissions from pyrolysis of traditional biomass feedstocks used in biochar production.

The emission of atmospheric pollutants during biochar production requires a full evaluation. This assessment is vital for establishing whether such emissions may cancel out benefits such as carbon sequestration potential. Such an evaluation should focus beyond a qualitative and quantitative characterisation of those pollutants, and should include the pyrolysis operational conditions and technologies required to reduce their emissions vto acceptable levels. Evidence in the literature suggests that a certain degree of control in respect to biochar-related emissions can be achieved through the use of traditional feedstock materials and lower (<500°C) temperature pyrolysis. Whereas this aspect looks promising in relation to Air Quality, current biochar-producing technologies remain largely inefficient. According to Brown (2009), there is still wide room for improvement in the context of both energy consumption and atmospheric emissions, particularly when traditional gasifiers are concerned. At this level, the author identifies specific goals for optimal biochar production, among which are the use of continuous feed pyrolisers and an effective recovery of co-products (Brown, 2009). A detailed analysis on current and future biochar technologies aiming for a more 'environmentally friendly' biochar production is also provided.

Collison et al. (2009) in a report to EEDA, reminded that generation and emission of environmental pollutants as well as the incidence of health and safety issues associated to biochar production, transport and storage, is probably of greater concern for small-scale pyrolysis units, particularly in developing countries. It is often the case, that such smaller units lack the knowledge and/or financial support, to comply to the environmental standards (Brown, 2006). A joint effort is necessary to overcome this gap, which

includes the use of clean pyrolysis technologies (Lehmann et al., 2006) and the establishment of tight policy and regulations in respect to biochar production and handling. Furthermore, adequate educating and training, and perhaps the granting of governmental financial support would allow putting in place equipment and measures, aiming to minimise environmental and human exposure to emissions linked to biochar production.

5.2 Occupational health and safety

Biochar production facilities, as well as those associated to transportation and storage may pose an Occupational Health hazard for the workers involved, particularly when exposure to biochar dust is concerned (Blackwell et al., 2009). In addition, health and fire hazards are related directly to the key physical properties of biochar determining the suitability for a given application method (Blackwell et al., 2009). However, any discussions and recommendations in the context of health and safety can only be addressed generally, given the heterogeneity among biochars. Further research on acute and chronic exposure to biochar dust, in particular to its nano-sized fraction, remains scarce and is thus identified as a priority.

'Nanoparticle' has been used broadly to refer to those particles within biochar dust (e.g. fullerenes or fullerene-like structures, crystalline forms of silica, cristobalite and tridymite), with at least one dimension smaller than 100 nm. Two major aspects distinguish them from the remaining larger-sized microparticles: large surface area and high particle number per unit of mass, which may signify a 1000-fold enhanced reactive surface (Buzea et al., 2007). Such reactivity and their small size widely explain their hazardous potential. Several reports have focused on their ability to enter, transit within and damage living cells and organisms. This capacity is partly consequence of their small size, enabling easy penetration through physical barriers, translocation trough the circulatory system of the host, and interaction with various cellular components (Buzea et al., 2007), including DNA (Zhao et al., 2005).

Most toxicological and epidemiological studies using fish, mice and mammalian cell lines (Andrade et al., 2006; Moore et al., 2006; Oberdorster et al., 2006; Nowack et al., 2007) demonstrate an inflammatory response in the cell or animal host (Donaldson et al., 2005). In biological systems, nanoparticles are known to generate disease mainly by mechanisms of oxidative stress, either by introducing oxidant species into the system or by acting as carriers for trace metals (Oberdorster, et al., 2004; Sayes et al., 2005). Those studies have also demonstrated that oxidative stress may result ultimately in irreversible disruption of basic cellular mechanisms such as proliferation, metabolism and death. However, extrapolating such effects to humans remains a challenge, and any outcomes are expected to be dependent on various factors relating to exposure conditions, residence time and inherent variability of the host (Buzea et al., 2007).

Exposure to nanoparticles within biochar dust (e.g. carbon-based NP, crystalline silica) appears to have associated health risks primarily for the respiratory system (e.g. Borm et al., 2004; Knaapen et al., 2004) and the gastrointestinal tract (e.g. Hussein et al., 2001). If inhalation of biochar dust should occur, measures which rapidly enhance airway clearance (e.g.

mucociliary rinsing with saline solution), and reduce inflammatory and allergic reactions (e.g. sodium cromoglycate) should be promptly carried out (Buzea et al., 2007). On the other hand, dermal uptake of combustion-derived nanoparticles was also found to occur, although this issue remains a controversial one. It has been suggested that nanoparticle incursion through the skin may occur at hair follicles (Toll et al., 2004), as well as broken (Oberdörster et al., 2005) or flexed (Tinkle et al., 2003) skin, depending mainly on particle size.

Besides unusually high levels (up to 220 g kg⁻¹) of silica, highly toxic crystalline forms of cristobalite and tridymite have also been found in rice husk biochars produced at temperatures above 550°C. Blackwell et al. (2009) did not hesitate in recommending careful handling, transport and storage of rice husk biochar as well as strict quality control measures for its production. Regarding those mineral forms, Stowell and Tubb (2003) have recommended maximum exposure limits of 0.1, 0.05 and 0.05 mg m⁻³ for crystalline silica, cristobalite and tridymite respectively. In comparison, those authors have suggested that current maximum exposure limits for crystalline silica (given as an example) assigned by the UK (0.3 mg m⁻³) and the US (10 mg m⁻³ divided by the percentage of SiO₂) may be too high.

In the context of Occupational Health, reducing biochar dust exposure requires tight health and safety measures to be put in place. For biochars containing a large proportion of dust, health risks associated to safe transport and storage, as well as application, may be reduced using dust control techniques (Blackwell et al., 2009). For example, covering or wrapping biochar heaps or spraying the surface with stabilising solutions can minimise the risk of exposure during transport and storage. In regard to reducing dust formation during application, especially with concern to uniform topsoil mixing and top-dressing, water can be used to support on-site spreading (when spreading is appropriate) (Blackwell et al., 2009).

It has been reported that generation of free-radicals during thermal (120°C<T<300°C) degradation of lignocellulosic materials, may be responsible for the propensity of fresh biochars to spontaneously combust (Amonette and Joseph, 2009), particularly at temperatures <100°C (Bourke et al., 2007). The free-radicals are primarily produced by thermal action on the O-functionalities and mineral impurities within the source material. Under certain conditions, an excessive accumulation of free-radicals at the biochar surface (Amonette and Joseph, 2009) and within its micropores (Bourke et al., 2007) might occur. The proportion of free-radicals in biochar is primarily dependent on the temperature of pyrolysis, and generally decrease with increasing operation temperatures (Bourke et al., 2007).

There is also evidence that an excessive accumulation of biochar dust in enclosed spaces may enhance its pyrophoric potential, as recently reported with coal dust in mines (Giby et al., 2007). To tackle this issue, increasing biochar density through pelleting may be advisable (Werther et al., 2000). In addition, the volatile (e.g. aldehydes, alcohols and carboxylic acids) content of biochar (as influenced by biomass feedstock and operation conditions; Brown 2009) may also constitute a fire hazard during transport, handling and storage (Werther et al., 2000), and should be taken into account.

Overall, increasing awareness of biochar flammability means that avoiding biochar storage with neighbouring residential buildings and goods is advisable. Nevertheless, successful attempts to reduce the risk of combustion of rice husk char by adding fire retardants (e.g. boric acid, ferrous sulphate; Maiti et al., 2006) and inert gases for removal of atmospheric O₂ (Naujokas, 1985) have been reported. There is also sound proof of the effective use of water in assisting cooling of a wide range of carbonaceous materials, including charcoals (Naujokas, 1985).

5.3 Monitoring biochar in soil

Research methodologies for comparing different biochars produced under laboratory conditions already have been put in place, based on work involving charcoal and other BCs. Currently, ¹³C nuclear magnetic resonance (NMR) and mid-infrared spectroscopy appear to be reliable methods for providing compositional characterisation (at the functional group level) of biochar, as well as differentiation between biochar products. Nevertheless, using such methods for routine purposes is expensive and time consuming, particularly when a large number of samples is involved. An efficient, rapid and economically feasible method for long-term routine assessment of biochar in soil has not yet been described. Furthermore, at the present, it is perhaps more important for research to focus on assessing and comparing between biochar produced under industrial and field conditions.

5.4 Economic Considerations

There is no established business model in the sense of industry-wide accepted set of standards of production, distribution and use of biochar. In fact, even the term "biochar industry" would be misplaced. What there is, is a multitude of start-up companies and other entities experimenting with alternative pyrolysis technologies operating at various scales.

An open and closed system can be distinguished in biochar operation design. These are not mutually exclusive and distinguish different modes of operation in relation to scale and feedstock choice. Biochar can be produced in a centralized, industrial fashion with an associated network for biochar distribution, or adopt a small-scale, local approach where biochar is derived from on-farm residues. A further distinction can be made between agricultural, forestry and waste residues, opposed to dedicated biomass growing for biochar production. Distinctions along these lines are important because of the different economic implications associated with the respective biochar systems and associated private and social costs and benefits.

5.4.1 Private costs and benefits

The private costs and benefits determine the commercial viability of any biochar operation and are a combination of biochar's value as a soil additive, as a source of carbon credits and as an energy source. Crudely, the cost-revenue structure of a biochar system could be broken down as follows (McCarl et al., 2009; Collison et al., 2009). On the revenue side, the following sources of value should be considered:

sale of pyrolysis-derived energy co-products;

- value of biochar as a soil amendment;
- value of biochar as a source of carbon credits.

Potential value to farmers, if any, could arise from increases in crop yield, although current evidence indicates a relatively small overall effect (see Section 3.3) and plant production is likely to vary considerably for combinations of environmental factors and crop types (see Sections 3.3).

Additional economic benefits, in the form of reduced production costs, may also come about from a reduction in fertilizer application or liming (both very dependent on biochar quality and quantity as well as frequency of application, see Section 1.8). Irrigation costs could also potentially be reduced if biochar application leads to enhanced water retention capacity, which evidence suggests may be possible at least for sandy soils (see Section 3.1.2). However, although the intention of biochar is to improve the soil it can also be envisaged that unforeseen effects on the soil, due to improper management, would actually lead to an increase in production costs.

For example, when (sub)soil compaction is caused during biochar application to the soil, subsequent subsoiling operations to alleviate the compaction would incur a cost. Due to the lack of a functioning biochar industry, it is not yet clear whether any payments for carbon credits will accrue to the land owners or the biochar producers. Either way, the economic viability of the carbon offsetting potential could be limited owing to the potentially high monitoring and verification costs (Gaunt and Cowie, 2009).

Regardless whom the proceeds from carbon credits accrue to, their value should reflect not only the carbon sequestration potential of biochar but also the reduced emissions due to lower fertiliser applications, as well as emissions from the transportation needs of biomass and biochar. Accounting for these indirect emissions might add to the costliness of certifying any carbon credits and, thus, further undermine its profitability.

The cost elements of the equation are the following:

- cost of growing the feedstock (in case of an open system);
- cost of collecting, transporting and storing the feedstock;
- cost of pyrolysis operation (purchase of equipment, maintenance, depreciation, labour);
- cost of transporting and applying the biochar

Despite the large uncertainties on biochar costs and benefits, the following factors ought to be taken into account. First, it is clear that the private costs and benefits of a biochar operation will vary depending on the scale of the operation. Biochar production at an industrial scale implies significantly higher costs of transporting the feedstock and the biochar produced from it than when produced at a small scale. System analysis studies will be of great help in understanding these issues. Higher transportation needs also lead to higher GHG emissions, as more fuel is needed for hauling the biomass and the biochar. The increased emissions need to be accounted for and included in the carbon offsetting potential of biochar, which would reduce the biochar's value as a source of carbon credits. On the other hand, industrial production

of biochar means that bigger pyrolysis plants could generate economies of scale, which would bring the average cost of producing biochar down.

Another factor that may influence the commercial appeal and the reliability in the supply of biochar is the fact that biochar is only one co-product of pyrolysis, the other ones being syngas and bio-oil. Different types of pyrolysis (fast vs. slow) will yield different proportions of these products (see Section 1.6), and biochar with varying properties, for a given amount of feedstock. This means that decisions pertaining to the quantity and quality of produced biochar will depend on the economic attractiveness of the other two products and not just on the cost elements of biochar production and the demand for biochar. For instance, if demand for bio-oil and syngas increases, the opportunity cost of biochar production will increase, thus shifting production away from it and rendering it relatively more expensive. Such flexibility in production is, of course, a welcome trait for pyrolysis operators, but adds an extra layer of unpredictability that might dampen demand for biochar as a soil amendment and as a potential source of carbon credits.

As biochar development and adoption are still at an early stage, there is currently very little quantitative information on these costs and benefits. McCarl et al. (2009) undertook a cost benefit analysis (CBA) of a pyrolysis operation in lowa that uses maize crop residues as feedstock. Assuming a 5 t ha⁻¹ biochar application and a 5% increase in yields, they conclude that both fast and slow operations are not profitable at current carbon and energy prices, with a net present value of about -\$44 and -\$70 (per tonne of feedstock) respectively.

In a somewhat less sophisticated attempt to estimate costs and benefits, Collison et al. use a hypothetical case study of biochar application in the East of England, without, however, taking into account the costs of biochar production, distribution and application. They estimate an increase in profitability of the order of £545 ha⁻¹ for potatoes and £143 ha⁻¹ for feed wheat.

Similarly, Blackwell et al. (2007) estimated the wheat income benefits for farmers in Western Australia by carrying out a series of trials of applying varying rates of mallee biochar and fertiliser. The trials produced benefits of up to \$96 ha⁻¹ of additional gross income at wheat prices of \$150 ha⁻¹. Again, no account was taken of the costs of biochar production.

The lesson to be taken home from such studies is that at this early stage, any CBA is an assumption-laden exercise that is prone to significant errors and revisions as more information becomes available on pyrolysis technologies and the agronomic effects of biochar.

5.4.2 Social costs and benefits

The social costs and benefits closely follow from the private ones but can be quite hard to monetize, or even model. Like the private ones, they also depend on the type of biochar system that is adopted. If an open system is adopted, the biggest concern is that the drive for larger volumes of biochar may lead to unsustainable land practices, causing significant areas of land to be converted into biomass plantations. Such competition for land could encourage the destruction of tropical forests directly or indirectly, via the

displacement of agricultural production. The latter possibility could also have negative consequences on the prices and the availability of food crops, much like in the case of the market for biofuels.

However, these social costs are not inevitable. Tropical deforestation could be avoided if, for instance, biomass is grown sustainably on land previously deforested. Moreover, any adverse effects of growing biochar feedstock on food security and availability could be mitigated by the biochar-induced gains in crop yields (see Section 3.3). Furthermore, wide, health-related social benefits can be ascribed to biochar's potential for land remediation and decontamination. Of course, the biggest source of social benefits would be biochar's climate change mitigation potential.

This section has briefly sketched the economic considerations that ought to be taken into account when planning for the development of a biochar system. For biochar to be successful it must not only deliver on its environmental promise but it should also be commercially viable.

The profitability of any biochar operation will depend mainly on its potential to attract revenue as a soil additive and carbon sink and will be affected by the type of production (open *vs.* closed, local *vs.* centralised), which can in turn result in environmental and economic spillovers. Moreover, the demand for biochar will be influenced by, and will indeed influence the demand for biofuels, as a byproduct of pyrolysis, the demand for products such as manure and compost and the price of carbon in the carbon markets.

Which shape and direction the biochar industry is likely to take is very much unknown at this stage. However, any outcomes will be greatly influenced by policy measures on energy, agriculture and climate change. The interplay and interdependence of such policies call for a holistic, systemic assessment of the opportunities and pitfalls presented by biochar.

5.5 Is biochar soft geo-engineering?

Geo-engineering is the artificial modification of Earth systems to counteract the consequences of anthropogenic effects, such as climate change. Large-scale (industrial) deployment of biochar thus qualifies as a geo-engineering scheme. Geo-engineering is very controversial and the primitive nature of geo-engineering schemes has been likened to a planetary version of 19th century medicine (Lovelock, 2007). Furthermore, panaceas often fail (Ostrom et al., 2007). However, biochar may be considered a 'softer' form of geo-engineering compared to more intrusive schemes. Especially if used with certain feedstocks under certain conditions and compared to those geo-engineering proposals that focus on lowering temperature rather than reducing GHG emissions or sequestering carbon. Indeed, biochar has been promoted as a lower-risk strategy compared to other sequestration methods (Lehmann, 2007). Nevertheless, deploying biochar on a scale with a mitigative effect entails a large construction of necessary infrastructure and a very intrusive impact on the way agriculture is performed.

The scalability of biochar is both a potential strength and a potential weakness. As noted by Woods et al. (2006) 'one is sometimes left the

impression that the biochar initiative is solely directed towards agribusiness applications'. However, several trials exist in collaboration with smallholder farmers, the closest approximation to the original Terra Preta formation. Small scale biochar systems that lead to a reduction of net GHG emissions have been suggested to be part of C offset mechanisms and so possibly contribute to soil C storage in Africa (Whitman and Lehmann, 2009). However, given the extensive use of biomass burning for energy in Africa, one of the potential problems will relate to the willingness of farmers to forego an energy source (biochar) once it has been created, which requires transparent certification and monitoring schemes if it is to be used in C credit trading schemes.

To what extent are the motives, practices and input materials that led to the creation of the Terra Preta soils similar or different compared to today's application of biochar to soil? A first obvious difference relates to the variety of inputs used in the formation of Terra Preta, compared to the limited number of inputs (e.g. biochar, or mixtures of biochar and manure) currently proposed. This is an important consideration that determines how far the carbon storage properties (relative to 'average' agricultural soil with organic matter) and agronomic benefits of Terra Preta can reasonably be extrapolated.

The recalcitrance of biochar components is estimated to be potentially hundreds or thousands of years (dependent on biochar properties, environmental conditions, and land use/soil management), or roughly one to two magnitudes higher than the breakdown of OM in the soil (Sections 3.2.1 and 3.2.5.1). Biochar has been identified as the oldest fraction of SOM, confirming it recalcitrance to decomposition and mineralisation (Lehman and Sohi, 2007). The residence time and stability of biochar in Terra Preta soil are fairly robust, but are the result of extensive smallholder agriculture over tens to hundreds of years as opposed to intensive agriculture. The direct translation of these residence times to today's intensive agricultural systems with the use of heavy machinery, and the possible accelerated disintegration and decomposition of biochar particles, with possible effects on biochar recalcitrance, remains questionable.

Sequestering carbon with biochar seems to have potential in theory. Choices of feedstocks are critically related to the larger scale impacts and benefits of biochar. Use of specific organic waste (e.g. papermill waste) may be a reasonable first approach that circumvents the food *vs.* fuel debate (cf. biofuels, van der Velde et al., 2009). Hansen et al. (2008), using illustrative climate change mitigation scenarios, assumed waste-derived biochar to provide only a small fraction of the land use related CO₂ drawdown, with reforestation and curtailed deforestation providing a magnitude more (Kharecha and Hansen, 2009). In line with estimates by Lehman et al. (2006), Hansen et al. (2008) assumed waste-derived biochar to "be phased in linearly over the period 2010-2020, by which time it will reach a maximum uptake rate of 0.16 Gt C yr⁻¹". This illustrates that waste-derived biochar can be a part of the mitigation options, although fundamental uncertainties associated with biochar remain.

5.6 Summary

Biochar can be produced from a wide range of organic feedstocks under different pyrolysis conditions and at a range of scales. The original feedstock used, combined with the pyrolysis conditions will affect the exact physical and chemical properties of the final biochar, and ultimately, the way and the extent to which soil dependent ecosystem services are affected. Preliminary evidence appears to suggest that a tight control on the feedstock materials and pyrolysis conditions (mainly temperature) may be enough in attenuating much of the current concern relating to the high levels of atmospheric pollutants (e.g. PAHs, dioxins) and particulate matter that may be emitted during biochar production, while implications to human health remain mostly an occupational health issue. Health (e.g. dust exposure) and fire hazards associated to production, transport, application and storage need to be considered when determining the suitability of the biochar for a given application, while tight health and safety measures need to be put in place to mitigate such risks for the worker, as well as neighbouring residential areas. The profitability of any biochar operation will depend mainly on its potential to attract revenue as a soil additive and C sink and will be affected by the type of biomass feedstock and that of production (open vs closed, local vs centralised), which can, in turn, result in environmental and economic spillovers. Moreover, the demand for biochar, as a byproduct of pyrolysis, will be influenced by, and will indeed influence, the demand for biofuels, the demand for products such as manure and compost and the price of carbon in the carbon markets. Furthermore, the costs and benefits of a range of biochar operations and scenarios need to be quantified. Cost-benefit analyses ought to cast the net wide by accounting not only for commercial factors but also for social costs and benefits.

6. KEY FINDINGS

This chapter summarises the main findings of the previous chapters, synthesises between these and identifies the key research gaps.

6.1 Summary of Key Findings

This report has highlighted that large gaps in knowledge still exist regarding the effects (including the mechanisms involved) of biochar incorporation into soils. Considerable further research is required in order to maximise the possible advantages of such an application, while minimizing any possible drawbacks. For some potential effects very few or no data are available. For other effects data exist but they do not cover sufficiently the variation in relevant soil-environment-climate-management factors. Table 6.1 provides an overview of the key findings. In view of this, the possibility of qualifying biochar for carbon offset credits within the UNFCC as part of a post-Kyoto treaty seems premature at the present stage. Although an inclusion in the carbon credit systems would certainly boost the nascent biochar industry, current scientific knowledge of large-scale use of biochar in intensive agricultural systems has not reached a sufficient level for safe deployment. Best practices associated with production and application, quality standards, specifications that clarify land use conflicts and opportunities, monitoring of utilisation, and details on minimal qualification requirements for certification of biochar products, require further understanding of the C-sequestration potential and behaviour of biochar in the environment.

Table 6.1 Overview of key findings (numbers in parentheses refer to relevant sections)

	Description	Conditions
Positives	Empirical evidence of charcoal in soils exists (long term)	Biochar analogues (pyrogenic BC and charcoal) are found in substantial quanities in soils of most parts of the world (1.2-1.4)
	The principle of improving soils has been tried successfully in the past	Anthrosols can be found in many parts of the world, although normally of very small spatial extent. Contemplation of Anthrosol generation at a vast scale requires more comprehensive, detailed and careful analysis of effects on soils as well as interactions with other environmental components before implementation (1.2-1.3 and throughout)
	Plant production has been found to increase significantly after biochar addition to soils	Studies have been reported almost exclusively from tropical regions with specific environmental conditions, and generally for very limited time periods, i.e. 1-2 yr. Some cases of negative effects on crop production have also been reported (3.3).
	Liming effect	Most biochars have neutral to basic pH and many field experiments show an increase in soil pH after biochar application when the initial pH was low. On alkaline soils this may be an undesirable effect. Sustained liming effects may require regular applications (3.1.4)
	High sorption affinity for HOC may enhance the overall sorption capacity of soils towards these trace contaminants	Biochar application is likely to improve the overall sorption capacity of soils towards common anthropogenic organic compounds (e.g. PAHs, pesticides and herbicides), and therefore influence toxicity, transport and fate of such contaminants. Enhanced sorption capacity of a silt loam for diuron and other anionic and cationic herbicides has been observed following incorporation of biochar from crop residues (3.2.2)

provision of refugia for microbes whereby they are protected from grazing	biomass and microbial activity, as well as microbial efficieny as a measure of CO ₂ released per unit microbial biomass C. The degree of the response appears to be dependent on nutrient availability in soils
Increases in mycorrhizal abundace which is linked to observed increases in plant productivity	Possibly due to: a) alteration of soil physico-chemical properties; b) indirect effects on mycorrhizae through effects on other soil microbes; c) plant–fungus signalling interference and detoxification of allelochemicals on biochar; or d) provision of refugia from fungal grazers (3.2.6)
Increases in earthworm abundance and activity	Earthworms have been shown to prefer some soils amended with biochar than those soils alone. However, this is not true of all biochars, particularly at high application rates (3.2.6)
The use of biochar analogues for assessing effects of modern biochars is very limited	Charcoal in Terra Preta soils is limited mainly to Amazonia and have received many diverse additions other than charcoal. Pyrogenic BC is found in soils in many parts of the world but are of limited feedstock types and pyrolysis conditions (Chapter 1)
Soil loss by erosion	Top-dressing biochar to soil is likely to increase erosion of the biochar particles both by wind (dust) and water. Many other effects of biochar in soil on erosion can be theorised, but remain untested at present (4.1)
Soil compaction during application	Any application carries a risk of soil compaction when performed under inappropriate conditions. Careful planning and management could prevent this effect (4.6)
Risk of contamination	Contaminants (e.g. PAHs, heavy metals, dioxins) that may be present in biochar may have detrimental effects on soil properties and functions. The ocurrence of such compounds in biochar is likely to derive from either contaminated feedstocks or the use of processing conditions that may favour their production. Evidence suggests that a tight control over the type of feedstock used and lower pyrolysis temperatures (<500°C) may be sufficient to reduce the potential risk for soil contamination (3.2.4)
Residue removal	Removal of crop residues for use as a feedstock for biochar production can forego incorporation of the crop residue into the soil, potentially leading to multiple negative effects on soils (3.2.5.5)
Occupational health and fire hazards	Health (e.g. dust exposure) and fire hazards associated to the production, transport, application and storage of biochar need to be considered when determining the suitability for biochar application. In the context of occupational health, tight health and safety measures need to be put in place in order to reduce such risks. Some of these measures have already proved adequate (5.2)
Reduction in earthworm survival rates (limited number of cases)	High biochar application rates of >67 t ha ⁻¹ (produced from poultry litter) were shown to have a negative effect on earthworm survival rates, possibly due to increases in pH or salt levels (3.2.6)
Empirical evidence is extremely scarce for many modern biochars in soils under modern arable management	Biochar analogues do not exist for many feedstocks, or for some modern pyrolysis conditions. Biochar can be produced with a wide variety of properties and applied to soils with a wide variety of properties. Some short term (1-2 yr) evidence exists, but only for a small set of biochar, environmental and soil management factors and almost no data is available on long term effect (1.2-1.4)
C Negativity	The carbon storage capacity of biochar is widely hypothesised, although it is still largely unquantified and depends on many factors (environmental, economic, social) in all parts of the life cycle of biochar and at the several scales of operation (1.5.2 and Chapter 5)

Microbial habitat and

Negatives

Unknown

Effects on N cycle

provision of refugia for

Biochar addition to soil has been shown to increase microbial

biomass and microbial activity, as well as microbial efficieny as a

N₂O emissions depend on effects of biochar addition on soil

hydrology (water-filled pore volume) and associated microbial processes. Mechanisms are poorly understood and thresholds

largely unknown (1.5.2)

Biochar Loading Capacity (BLC)

BLC is likely to be crop as well as soil dependent leading to potential incompatibilities between the irreversibility of biochar once applied to soil and changing crop demands (1.5.1)

Environmental behaviour mobility and fate

The extent and implications of the changes that biochar undergoes in soil remain largely unknown. Although biochar physical-chemical properties and stabilization mechanisms may explain biochar long mean residence times in soil, the relative contribution of each factor for its short- and long-term loss has been sparsely assessed, particularly when influenced by soil environmental conditions. Also, biochar loss and mobility through the soil profile and into the water resources has been scarcely quantified and transport mechanisms remain poorly understood (3.2.1)

Distribution and availability of contaminants (e.g. heavy metals, PAHs) within biochar

Very little experimental evidence is available on the short- and long-term occurrence and bioavailability of such contaminants in biochar and biochar-enriched soil. Full and careful risk assessment in this context is urgently required, in order to relate the bioavailability and toxicity of the contaminant to biochar type and 'safe' application rates, biomass feedstock and pyrolysis conditions, as well as soil type and environmental conditions (3.2.4)

Effect on soil organic matter dynamics

Various relevant processes are acknowledged but the way these are influenced by combinations of soil-climate-management factors remains largely unknown (Section 3.2.5)

Pore size and connectivity

Although pore size distribution in biochar may significantly alter key soil physical properties and processes (e.g. water retention, aeration, habitat), experimental evidence on this is scarce and the underlying mechanisms can only be hypothesised at this stage (2.3 and 3.1.3)

Soil water retention/availability

Adding biochar to soil can have direct and indirect effects on soil water retention, which can be short or long lived, and which can be negative or positive depending on soil type. Positive effects are dependent on high applications of biochar. No conclusive evidence was found to allow the establishment of an unequivocal relation between soil water retention and biochar application (3.1.2)

Soil compaction

Various processes associated with soil compaction are relevant to biochar application, some reducing others increasing soil compaction. Experimental research is lacking. The main risk to soil compaction could probably be reduced by establishing a guide of good practice regarding biochar application (3.1.1 and 4.6)

Priming effect

Some inconclusive evidence of a possible priming effect exists in the literature, but the evidence is relatively inconclusive and covers only the short term and a very restricted sample of biochar and soil types (3.2.5.4)

Effects on soil megafauna

Neither the effects of direct contact with biochar containing soils on the skin and respiratory systems of soil megafanua are known, nor the effects or ingestion due to eating other soil organisms, such as earthworms, which are likely to contain biochar in their guts (3.2.6.3)

Hydrophobicity

The mechnanisms of soil water repellency are understood poorly in general. How biochar might influence hydrophobicity remains largely untested (3.1.2.1)

Enhanced decomposition of biochar due to agricultural management

It is unknow how much subsequent agricultural management practices (planting, ploughing, etc.) in an agricultural soil with biochar may influence (accelerate) the disintegration of biochar in the soil, thereby potentially reducing its carbon storage potential (3.2.3)

Soil CEC

There is good potential that biochar can improve the CEC of soil. However, the effectiveness and duration of this effect after addition to soils remain understood poorly (2.5 and 3.1.4)

Soil Albedo

That biochar will lower the albedo of the soil surface is fairly well established, but if and where this will lead to a substantial soil warming effect is untested (3.1.3)

6.1.1 Background and Introduction

As a concept biochar is defined as 'charcoal (biomass that has been pyrolysed in a zero or low oxygen environment) for which, owing to its inherent properties, scientific consensus exists that application to soil at a specific site is expected to sustainably sequester carbon and concurrently improve soil functions (under current and future management), while avoiding short- and long-term detrimental effects to the wider environment as well as human and animal health'. Inspiration is derived from the anthropogenically created Terra Preta soils (Hortic Anthrosols) in Amazonia where charred organic material plus other (organic and mineral) materials appear to have been added purposefully to soil to increase its agronomic quality. Ancient Anthrosols have been found in Europe as well, where organic matter (peat, manure, 'plaggen') was added to soil, but where charcoal additions appear to have been limited or non-existent. Furthermore, charcoal from wildfires (pyrogenic black carbon - BC) has been found in many soils around the world, including European soils where pyrogenic BC can make up a large proportion of total soil organic carbon.

Biochar can be produced from a wide range of organic feedstocks under different pyrolysis conditions and at a range of scales. Many different materials have been proposed as biomass feedstocks for biochar. The suitability of each biomass type for such an application is dependent on a number of chemical, physical, environmental, as well as economic and logistical factors. The original feedstock used, combined with the pyrolysis conditions will determine the properties, both physical and chemical, of the biochar product. It is these differences in physicochemical properties that govern the specific interactions which will occur with the endemic soil biota upon addition of biochar to soil, and hence how soil dependent ecosystem functions and services are affected. The application strategy used to apply biochar to soils is an important factor to consider when evaluating the effects of biochar on soil properties and processes. Furthermore, the biochar loading capacity of soils has not been fully quantified, or even developed conceptually.

6.1.2 Physicochemical properties of Biochar

Biochar is comprised of stable carbon compounds created when biomass is heated to temperatures between 300 to 1000°C under low (preferably zero) oxygen concentrations. The structural and chemical composition of biochar is highly heterogeneous, with the exception of pH, which is tipically > 7. Some properties are pervasive throughout all biochars, including the high C content and degree of aromaticity, partially explining the high levels of biochar's inherent recalcitrance. Neverthless, the exact structural and chemical composition, including surface chemistry, is dependent on a combination of the feedstock type and the pyrolysis conditions (mainly temperature) used. These same parameters are key in determining particle size and pore size (macro, meso and micropore; distribution in biochar. Biochar's physical and chemical characteristics may significantly alter key soil physical properties and processes and are, therefore, important to consider prior to its application to soil. Furthermore, these will determine the suitability of each biochar for a given application, as well as define its behaviour, transport and fate in the

environment. Dissimilarities in properties between different biochar products emphasises the need for a case-by-case evaluation of each biochar product prior to its incorporation into soil at a specific site. Further research aiming to fully evaluate the extent and implications of biochar particle and pore size distribution on soil processes and functioning is essential, as well as its influence on biochar mobility and fate.

6.1.3 Effects on soil properties, processes and functions

This section has highlighted the relative paucity of knowledge concerning the specific mechanisms behind the reported interactions of biochar within the soil environment. However, while there is still much that is unknown, large steps have been taken towards increasing our understanding of the effects of biochar on soil properties and processed. Biochar interacts with the soil system on a number of levels. Sub-molecular interactions with clay and silt particles and SOM occur through Van der Waals forces and hydrophobic interactions. It is the interactions at this scale which will determine the influence of biochar on soil water repellency and also the interactions with cations and anions and other organic compounds in soil. These interactions are very char specific, with the exact properties being influenced by both the feedstock and the pyrolysis conditions used.

There has been some evidence to suggest that biochar addition to soil may lead to loss of SOM via a priming effect in the short term. However, there is only very little research reported in the literature on this subject, and as such it is a highly pertinent area for further research. The fact that Terra Pretas contain SOM as well as char fragments seems to demonstrate that the priming effect either does not exist in all situations or if it does, perhaps it only lasts a few seasons and it appear not to be sufficient to drive the loss of all native SOM from the soil. Biochar has the potential to be highly persistent in the soil environment, as evidenced both by its presence in Terra Pretas, even after millennia, and also as evidenced by studies discussed in this section. While biochars are highly heterogeneous across scales, it seems likely that properties such as recalcitrance and effects on water holding capacity are likely to persist across a range of biochar types. It also seems probable, that while difference may occur within biochars on a microscale, biochars produced from the same feedstocks, under the same pyrolysis conditions are likely to be broadly similar, with predictable effects upon application to soil. What remains to be done are controlled experiments with different biochars added to a range of soils under different environmental conditions and the precise properties and effects identified. This will lead towards biochars possibly being engineered for specific soils and climate where specific effects are required.

After its initial application to soil, biochar can function to stimulate the edaphic microflora and fauna due to various substrates, such as sugars, which can be present on the biochar's surface. Once these are metabolised, biochar functions more as a mineral component of the soil rather than an organic component, as evidenced by its high levels of recalcitrance meaning that it is not used as a carbon source for respiration. Rather, the biochar functions as a highly porous network the edaphic biota can colonise. Due to the large inherent porosity, biochar particles in soil can provide refugia for

microorganisms whereby they may often be protected from grazing by other soil organisms which may be too large to enter the pores. This is likely to be one of the main mechanisms by which biochar-amended soils are able to harbour a larger microbial biomass when compared to non-biochar amended soils. Biochar incorporation into soil is also expected to enhance overall sorption capacity of soils towards trace anthropogenic organic contaminants (e.g. PAHs, pesticides, herbicides), in a stronger way, and mechanistically different, from that of native organic matter. Whereas this behaviour may greatly contribute to mitigating toxicity and transport of common pollutants in soil, biochar aging over time may result in leaching and increased bioavailability of such compounds. On the other hand, while the feasibility for reducing mobility of trace contaminants in soil might be beneficial, it might also result in their localised accumulation, although the extent and implications of this have not been experimentally assessed.

Soil quality may not be necessarily improved by adding biochar to soil. Soil quality can be considered to be relatively high for supporting plant production and provision of ecosystem services if it contains carbon in the form of complex and dynamic substances such as humus and SOM. If crop residues are used for biochar, the proportion of carbon going into the dynamic SOM pool is likely to be reduced, with the carbon being returned to the soil in a relatively passive biochar form. The proportion of residues which are removed for pyrolysis versus the proportion which is allowed to remain in the soil will determine the balance between the dynamic SOM and the passive biochar and so is likely to affect soil quality for providing the desired roles, be it provision of good use as crop or timber, or functioning as a carbon pool. Biochar also has the potential to introduce a wide range of hazardous organic compounds (e.g. heavy metals, PAHs) into the soil system, which can be present as contaminants in biochar that has been produced either from contaminated fedstocks or under processing conditions which favour their production. While a tight control over the feedstock type and processing conditions used can reduce the potential risk for soil contamination. experimental evidence of the occurrence and bioavailability and toxicity of such contaminants in biochar and biochar-enriched soil (over time) remain scarce. A comprehensive risk assessment of each biochar product prior to its incoporation into soil, which takes into account the soil type and environmental conditions, is therefore, paramount.

Increased crop yields are the most commonly reported benefits of adding biochar to soils. A full search of the scientific literature led to a compilation of studies used for a meta-analysis of the effects of biochar application to soils and plant productivity. Meta-analysis techniques (Rosenberg et al., 1997) were used to quantify the effect of biochar addition to soil on plant productivity from a range of experiments. Our results showed a small overall, but statistically significant, positive effect of biochar application to soils on plant productivity in the majority of cases, covering a range of both soil and crop types. The greatest positive effects were seen on acidic free-draining soils with other soil types, specifically Calcarosols showing no significant effect. No statistically significant negative effects were found. There was also a general trend for concurrent increases in crop productivity with increases in pH up on biochar addition to soils. This suggests that one of the main mechanisms

behind the reported positive effects of biochar application to soils on plant productivity may be a liming effect. These results underline the importance of testing each biochar material under representative conditions (i.e. soil-environment-climate-management factors).

The degree and possible consequences of the changes biochar undergo in soil over time remain largely unknown. Biochar loss and mobility through the soil profile and into water resources has so far been scarcely quantified and the underlying transport mechanisms are poorly understood. This is further complicated by the limited amount of long-term studies and the lack of standardised methods for simulating biochar aging and for long-term environmental monitoring.

6.1.4 Biochar and soil threats

This chapter has described the interactions between biochar and 'threats to soil'. For most of these interactions, the body of scientific evidence is currently insufficient to arrive at a consensus. However, what is clear is that biochar application to soils will effect soil properties and processes and thereby interact with threats to soil. Awareness of these interactions, and the mechanisms behind them, is required to lead to the research necessary for arriving at understanding mechanisms and effects on threats to soil, as well as the wider ecosystem.

6.1.5 Wider issues

Biochar can be produced from a wide range of organic feedstocks under different pyrolysis conditions and at a range of scales. The original feedstock used, combined with the pyrolysis conditions will affect the exact physical and chemical properties of the final biochar, and ultimately, the way and the extent to which soil dependent ecosystem services are affected. Preliminary evidence appears to suggest that a tight control on the feedstock materials and pyrolysis conditions (mainly temperature) may be enough in attenuating much of the current concern relating to the high levels of atmospheric pollutants (e.g. PAHs, dioxins) and particulate matter that may be emitted during biochar production, while implications to human health remain mostly an occupational health issue. Health (e.g. dust exposure) and fire hazards associated to production, transport, application and storage need to be considered when determining the suitability of the biochar for a given application, while tight health and safety measures need to be put in place to mitigate such risks for the worker, as well as neighbouring residential areas. The profitability of any biochar operation will depend mainly on its potential to attract revenue as a soil additive and C sink and will be affected by the type of biomass feedstock and that of production (open vs closed, local vs centralised), which can, in turn, result in environmental and economic spillovers. Moreover, the demand for biochar, as a byproduct of pyrolysis, will be influenced by, and will indeed influence, the demand for biofuels, the demand for products such as manure and compost and the price of carbon in the carbon markets. Furthermore, the costs and benefits of a range of biochar operations and scenarios need to be quantified. Cost-benefit analyses ought to cast the net wide by accounting not only for commercial factors but also for social costs and benefits.

6.2 Synthesis

The aim of this report was to review the state-of-the-art regarding the interactions between biochar application to soils and effects on soil properties, processes and functions. Adding biochar to soil is not an alternative to reducing the emissions of greenhouse gasses. Minimising future climate change requires immediate action to lower greenhouse gas emissions and harness alternative forms of energy (IPCC, 2007).

6.2.1 Irreversibility

The irreversibility of biochar application to soils has implications for its development. Once biochar has been applied to soils, it is virtually impossible to remove. This irreversibility does not have to be a deterrent from considering biochar. Rather, the awareness of its irreversibility should lead to a careful case-by-case assessment of its impacts, underpinned by a comprehensive body of scientific evidence gathered under representative soil-environmentclimate-management conditions. Meta-analyses, an example of which on the relationship between biochar and crop productivity is presented in this report, can provide a valuable method for both signalling gaps in knowledge as well as providing a quantitative review of published experimental results. The results of meta-analyses can then be used to feed back to directing funding for more research where needed, and/or to inform specific policy development. Objectivity of systematic reviews on biochar is of paramount importance. In the medical sciences this has been resolved by the founding of an independent organisation (the Cochrane Collaboration), which provides regularly updated systematic reviews on specific healthcare issues using a global network of volunteers and a central database/library. A similar approach, although at a different scale, could be envisaged to ensure that the most robust and up to date research informs policy concerning biochar. Alternatively, this task could be performed by recognised, independent scientific institutions that do not (even partially) depend on conflicting funding, and that have the necessary expertise.

6.2.2 Quality assessment

The evidence reviewed in this report has highlighted potential negative as well as positive effects on soils and, importantly, a very large degree of unknown effects (see Table 6.1; and Section 6.3). Some of the potential negative effects can be 'stopped at the gate', i.e. by not allowing specific feedstocks that have been proven to be inappropriate, and by regulating pyrolysis conditions to avoid undesirable biochar properties (a compulsory biochar quality assessment and monitoring approach could prove effective). Other potential negative effects on soils, or the wider ecosystem, need to be regulated on the application side, i.e. at the field scale, taking into account the soil properties and processes as well as threats to soil functions. Similarly, biochar properties can be 'engineered' (to an extent), through controlled use of feedstocks and pyrolysis conditions, to provide necessary benefits to soil functions and reduce threats when applied to fields that have specific soil-environmental-climatic-management conditions. However, the current state-of-the-art regarding the effects of biochar on soils has a substantial lack of

information on relevant factors (see Section 6.3). Results from research into the relative importance of these factors, and the associated environmental and soil management conditions, needs to drive further extension and development of a biochar quality assessment protocol.

6.2.3 Scale and life cycle

Relevant factors for producing biochar with specific properties are feedstock characteristics and pyrolysis conditions, thereby affecting the scale and method of operation. The optimal scale of operation, from a soil improvement and climate adaptation perspective, will differ for different locations, as the availability of feedstocks and the occurrence of soil-environment-climatemanagement conditions changes along with land use. The optimal scale of operation, from a climate mitigation perspective, is, intuitively, the smallest scale. However, full life cycle assessment studies to evidence this have not been found. It is possible that at a larger scale of operation, if not production then at least application, a more complementary situation exists with larger concomitant reductions in CO₂ equivalent emissions by the ability to forego or reduce certain operations. For example, a farm on a fertile floodplain, with good water availability, may produce biochar from feedstocks on the farm with good water and nutrient retention properties. If this is applied to soils on the same farm, it may allow a reduction of a single fertiliser pass. However, if the biochar is sold (or traded) to the farm next door, which may be on soils with low water and nutrient retention, then there may be a reduction of two fertiliser passes and a substantial reduction in irrigation, for example. It is possible, therefore, that the CO₂ equivalents saved on the farm next door are more than the CO₂ equivalent emissions produced during transport from one farm to the other. This is of course just one hypothetical example of how off-site biochar distribution does not necessarily decrease the carbon negativity of the technology. One critical factor affecting this is the way long-lived specific beneficial effects of specific biochars will be under specific conditions. Experimental studies of sustained effects, e.g. nutrient and water retention, of different soil-environment-climate-management combinations are needed to feed into life cycle assessment studies. It is possible that the optimum scale of operation, in terms of global warming mitigation, will be different in different parts of Europe and the world.

6.2.4 Mitigation/adaptation

Besides global warming mitigation, biochar can also be viewed from the perspective of adaptation to climate change. In the future, climate change looks likely to increase rainfall intensity, if not annual totals, for example thereby increasing soil loss by water erosion, although there is much uncertainty about the spatio-temporal structure of this change as well as the socio-economic and agronomic changes that may accompany them. Independent from changes in climate, the production function of soil will become increasingly more important, in view of the projected increase in global human population and consequent demands for food. More than 99% of food supplies (calories) for human consumption come from the land, whereas less than 1% comes from oceans and other aquatic ecosystems (FAO, 2003).

A common way of thinking about adapting food production to climate change is by genetically engineering crops to survive and produce under adverse and variable environmental conditions. This may well work, if risks to the environment are minimised and public opinion favourable. However, other soil functions are likely to still be impaired and threats exacerbated, such as increased loss of soil by erosion. Improving the properties of soil will increase the adaptive capacity of our agri-environmental systems. The ClimSoil report (Schils et al., 2008) reviews in detail the interrelation between climate change and soils. One of their conclusions is that land use and soil management are important tools that affect, and can increase. SOC stocks. In this way, the soils will be able to function better, even under changing climatic conditions. In arable fields, SOM content is maintained in a dynamic equilibrium. Arable soil is disturbed too much for it to maintain greater contents of SOM than a specific upper limit, which is controlled by mainly clay contents and the soil wetness regime. Biochar, because of its recalcitrance, and possibly because of its organo-mineral interaction and accessibility provides a means of increasing the relevant functions of soils beyond that which can be achieved by OM alone in arable systems.

Biochar application to soils, therefore, may play both a global warming mitigation and a climate change adaptation role. For both, more research is needed before conclusive answers can be given with a high degree of scientific certainty, particularly when considering specific soil-environment-climate-management conditions and interactions. However, it may be the case that in certain situations the biochar system does not mitigate global warming, i.e. is C neutral or positive, but that the enhanced soil functions from biochar application may still warrant contemplation of its use.

As far as the current scientific evidence allows us to conclude, biochar is not a 'silver bullet' or panacea for the whole host of issues ranging from food production and soil fertility to mitigating (or more correctly 'abating') global warming and climate change for which it is often posited. The critical knowledge gaps are manifold, mainly because the charcoal-rich historic soils, as well as most experimental sites, have been studied mostly in tropical environments, added to the large range of biochar properties that can be produced from the feedstocks currently available subjected to different pyrolysis conditions. Biochar analogues, such as pyrogenic BC, are found in varying, and sometimes substantial amounts in soils all over the world. As well as causing some difficulty with predicting possible impacts of biochar addition to soil, the large variety in biochar properties that can be produced actually provides an opportunity to 'engineer' biochar for specific soilenvironment-climate-management conditions, thereby potentially increasing soil functioning and decreasing threats to soil (and/or adapting to climate change). What is needed is a much better understanding of the mechanisms concerning biochar in soils and the wider environment. Although the research effort that would be required is substantial, the necessary methods are available.

6.3 Knowledge gaps

Table 6.1 lists 'unknown' effects of biochar on soil properties, processes and functions. For 'known' positive or negative effects, Table 6.1 also discusses (briefly but with reference to more elaborate discussions in the report) the soil-environment-climate-management conditions for which the effects are valid and where they are not (known). From the viewpoint of biochar effects on soil functions and soil threats, a number of key issues emerge that are discussed in the subsections below. Biochar research should aim to reach a sufficient level of scientific knowledge to underpin future biochar policy decisions. This review indicates that a large number of questions related to biochar application to soils remain unanswered. The multitude of gaps in current knowledge associated with biochar properties, the long-term effects of biochar application on soil functions and threats, and its behaviour and fate in different soil types (e.g. disintegration, mobility, recalcitrance, interaction with SOM), as well as sensitivity to management practices, require more scientific research.

6.3.1 Safety

While the widespread interest in biochar applications to soils continues to rise, issues remain to be addressed concerning the potential for soil contamination and atmospheric pollution associated to its production and handling, with potentially severe health, environmental and socio-economic implications. The irreversibility of biochar incorporation into soil emphasises the urgent need for a full and comprehensive characterisation of each biochar type in regard to potential contaminants (mainly heavy metals and PAHs), as influenced by biomass feedstock and pyrolysis conditions. Very little focus has been paid to the long-term distribution of such contaminants in biochar-enriched soils and bioavailability to the micro- and macro-biota. In this context, risk assessment procedures for these compounds need to be re-evaluated on a case-by-case basis, based on bioavailable concentrations (rather than initial concentrations in biochar) and accounting for the influence of NOM on their desorption from biochar over time. This would allow understanding the true implications of their presence in biochar on human, animal and ecosystem health over a wide range of soil conditions, while enabling relation of toxicity to biochar type and safe application rates, as well as feedstock characteristics and pyrolysis conditions. Similarly, the emission of atmospheric pollutants during biochar production requires careful qualitative and quantitative analysis. It will provide a sound basis for the development and/or optimisation of feedstock and pyrolysis operational conditions (as well as technologies) required to tackle these pollutants.

6.3.2 Soil organic matter dynamics

Biochar can function as a carbon sink in soils under certain conditions. However, the reported long residence times of biochar have not been confirmed for today's intensive agricultural systems in temperature regions. Disintegration of biochar is likely to be stimulated by intensive agricultural practices (tilling, plouging, harrowing) and use of heavy machinery, thereby potentially reducing residence times. Work is required to better elucidate the biochar loading capacity of different soils, for different climatic conditions in order to maximise the amount of biochar which can be stored in soils without impacting negatively on soil functions. In addition to crop yields, research

should also focus on threshold amounts of biochar that can be added to soils without adverse consequences to soil physical properties, such as priming by increasing the pH or dedcreasing water-filled pore space, hydrophobic effects, or soil chemical properties, e.g. adding a high ash content (with salts) biochar to a soil already at risk of salinisation, or other ecosystem components, e.g. particulate or dissolved organic C reaching ground/surface waters. Therefore, the biochar loading capacity should vary according to environmental conditions as well as biochar 'quality', specific to the environmental conditions of the site (soil, geomorphology, hydrology, vegetation).

6.3.3 Soil biology

Owing to the vital role that the soil biota plays in regulating numerous ecosystem services and soil functions, it is vital that a full understanding of the effects of biochar addition to soil is reached before policy is written. Due to the very high levels of heterogeneity found in soils, with regard to soil physical, chemical and biological properties, extensive testing is needed before scientifically sound predictions can be made regarding the effects of biochar addition to soils on the native edaphic communities under a range of climatic conditions. Much of the data currently reported in the literature shows a slight, but significant positive effect on the soil biota, with increased microbial biomass and respiration efficiency per unit carbon, with associated increases in above ground biomass production reported in the majority of cases. There is currently a major gap in our understanding of the influence of biochar addition to soils on carbon fluxes. This is vital to increase our understanding of interactions between the soil biota and biochar as it will help to unravel the mechanisms behind any possible priming effect, as well as nutrient transfer and interactions with contaminants introduced with biochar. A very suitable method for probing this interaction would be the use of Stable Isotope Probing (SIP), which can be used with other molecular techniques to trace the flow of carbon from particular sources through the soil system. Pyrolysing biomass labeled with a stable isotope and measuring its emission from the soil will allow accurate measures of its recalcitrance over time. Conducting controlled atmosphere experiments with stable isotope-labelled CO2 will enable assessing the observed increased microbial respiration and investigation of whether this increase is due to a more efficient use of plant provided substrates (in case the label is detected in soil respiration), or if a priming effect has occurred leading to increased metabolisation of the SOM (in case the label is not detected).

6.3.4 Behaviour, mobility and fate

Physical and chemical weathering of biochar over time has implications for its solubilisation, leaching, translocation through the soil profile and into water systems, as well as interactions with other soil components (including contaminants). Up to now, biochar loss and environmental mobility have been quantified scarcely and such processes remain poorly understood. In addition, the contribution of soil management practices and the effects of increasingly warmer climates, together with potential greater erosivity as potential key mechanisms controlling biochar fate in soil, have also been assessed insufficiently up to now.

An effective evaluation of the long-term stability and mobility of biochar, including the way these are influenced by factors relating to biochar physicochemical characteristics, pyrolysis conditions and environmental factors, is paramount to understanding the contribution that biochar can make to improving soil processes and functioning, and as a tool for sequestering carbon. Such knowledge should derive from long-term studies involving a wide range of soil conditions and climatic factors, while using standardised methods for simulating biochar aging and for long-term environmental monitoring.

6.3.5 Agronomic effects

Biochar has shown merit in improving the agronomic and environmental value of agricultural soils in certain pilot studies under limited environmental conditions, but a scientific consensus on the agronomic and environmental benefits of biochar has not been reached yet. It remains difficult to generalise these studies due to the variable nature of feedstocks, their local availability, the variability in resulting biochar and the inherent biophysical characteristics of the sites it has been applied to, as well as the variability of agronomic practices it could be exposed to. Furthermore, there is a lack of (long-term) studies on the effects of biochar application in temperate regions. Direct and indirect effects of biochar on soil hydrology (e.g. water availability to plants) need to be studied experimentally for representative conditions in the field and in the laboratory (soil water retention - pF - curves) before modelling exercises can begin. Ultimately, in those conditions where biochar application is beneficial to agriculture and environment, it should be considered as part of a soil conservation package aimed at increasing the resilience of the agroenvironmental system combined with the sequestration of carbon. The key is to identify the agri-soil management strategy that is best suited at a specific site. Other carbon sequestration and conservation methods, such as no-till, mulching, cover crops, complex crop rotations, mixed farming systems and agroforestry, or a combination of these, needs to be considered. In this context the interaction of biochar application with other methods warrants further investigation.

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Title: Biochar Application to Soils - A Critical Scientific Review of Effects on Soil Properties,

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Abstract

Biochar application to soils is being considered as a means to sequester carbon (C) while concurrently improving soil functions. The main focus of this report is providing a critical scientific review of the current state of knowledge regarding the effects of biochar application to soils on soil properties and functions. Wider issues, including atmospheric emissions and occupational health and safety associated to biochar production and handling, are put into context. The aim of this review is to provide a sound scientific basis for policy development, to identify gaps in current knowledge, and to recommend further research relating to biochar application to soils. See Table 1 for an overview of the key findings from this report. Biochar research is in its relative infancy and as such substantially more data are required before robust predictions can be made regarding the effects of biochar application to soils, across a range of soil, climatic and land management factors.

Definition

In this report, biochar is defined as: "charcoal (biomass that has been pyrolysed in a zero or low oxygen environment) for which, owing to its inherent properties, scientific consensus exists that application to soil at a specific site is expected to sustainably sequester carbon and concurrently improve soil functions (under current and future management), while avoiding short- and long-term detrimental effects to the wider environment as well as human and animal health." Biochar as a material is defined as: "charcoal for application to soils". It should be noted that the term 'biochar' is generally associated with other co-produced end products of pyrolysis such as 'syngas'. However, these are not usually applied to soil and as such are only discussed in brief in the report.

Biochar properties

Biochar is an organic material produced via the pyrolysis of C-based feedstocks (biomass) and is best described as a 'soil conditioner'. Despite many different materials having been proposed as biomass feedstock for biochar (including wood, crop residues and manures), the suitability of each feedstock for such an application is dependent on a number of chemical, physical, environmental, as well as economic and logistical factors. Evidence suggests that components of the carbon in biochar are highly recalcitrant in soils, with reported residence times for wood biochar being in the range of 100s to 1,000s of years, i.e. approximately 10-1,000 times longer than residence times of most soil organic matter. Therefore, biochar addition to soil can provide a potential sink for C. It is important to note, however, that there is a paucity of data concerning biochar produced from feedstocks other than wood, but the information that is available is discussed in the report. Owing to the current interest in climate change mitigation, and the irreversibility of biochar application to soil, an effective evaluation of biochar stability in the environment and its effects on soil processes and functioning is paramount. The current state of knowledge concerning these factors is discussed throughout this report.

Pyrolysis conditions and feedstock characteristics largely control the physico-chemical properties (e.g. composition, particle and pore size distribution) of the resulting biochar, which in turn, determine the suitability for a given application, as well as define its behaviour, transport and fate in the environment. Reported biochar properties are highly heterogeneous, both within individual biochar particles but mainly between biochar originating from different feedstocks and/or produced under different pyrolysis conditions. For example, biochar properties have been reported with cation exchange capacities (CECs) from negligible to approximately 40 cmolc g⁻¹, and C:N ratios from 7 to 500, while the pH is normally neutral to basic. While this heterogeneity leads to difficulties in identifying the underlying mechanisms behind reported effects in the scientific literature, it also provides a possible opportunity to engineer biochar with properties that are best suited to a particular site (depending on soil type, hydrology, climate, land use, soil contaminants, etc.).

Effects on soils

Biochar characteristics (e.g. particle and pore size distribution, surface chemistry, relative proportion of readily available components), as well as physical and chemical stabilisation mechanisms of biochar in soils, determine the effects of biochar on soil functions. However, the relative contribution of each of these factors has been assessed poorly, particularly under the influence of different climatic and soil conditions, as well as soil management and land use. Reported biochar loss from soils may be explained to a certain degree by abiotic and biological degradation and translocation within the soil profile and into water systems. Nevertheless, such mechanisms have been quantified scarcely and remain poorly understood, partly due to the limited amount of long-term studies, and partly due to the lack of standardised methods for simulating biochar aging and long-term environmental monitoring. A sound understanding of the contribution that biochar can make as a tool to improve soil properties, processes and functioning, or at least avoiding negative effects, largely relies on knowing the extent and full implications of the biochar interactions and changes over time within the soil system.

Extrapolation of reported results must be done with caution, especially when considering the relatively small number of studies reported in the primary literature, combined with the small range of climatic, crop and soil types investigated when compared to possible instigation of biochar application to soils on a national or European scale. To try and bridge the gap between small scale, controlled experiments and large scale implementation of biochar application to a range of soil types across a range of different climates (although chiefly tropical), a statistical meta-analysis was undertaken. A full search of the scientific literature led to a compilation of studies used for a meta-analysis of the effects of biochar application to soils and plant productivity. Results showed a small overall, but statistically significant, positive effect of biochar application to soils on plant productivity in the majority of cases. The greatest positive effects were seen on acidic free-draining soils with other soil types, specifically calcarosols showing no significant effect (either positive or negative). There was also a general trend for concurrent increases in crop productivity with increases in pH up on biochar addition to soils. This suggests that one of the main mechanisms behind the reported positive effects of biochar application to soils on plant productivity may be a liming effect. However, further research is needed to confirm this hypothesis. There is currently a lack of data concerning the effects of biochar application to soils on other soil functions. This means that although these are qualitatively and comprehensively discussed in this report, a robust meta-analysis on such effects is as of yet not possible. Table 1 provides an overview of the key findings - positive, negative, and unknown - regarding the (potential) effects on soil, including relevant conditions.

Preliminary, but inconclusive, evidence has also been reported concerning a possible priming effect whereby accelerated decomposition of soil organic matter occurs upon biochar addition to soil. This has the potential to both harm crop productivity in the long term due to loss of soil organic matter, as well as releasing more CO₂ into the atmosphere as increased quantities of soil organic matter is respired from the soil. This is an area which requires urgent further research.

Biochar incorporation into soil is expected to enhance overall sorption capacity of soils towards anthropogenic organic contaminants (e.g. PAHs, PCBs, pesticides and herbicides), in a mechanistically different (and stronger) way than amorphous organic matter. Whereas this behaviour may greatly mitigate toxicity and transport of common pollutants in soils through reducing their bioavailability, it might also result in their localised accumulation, although the extent and implications of this have not been assessed experimentally. The potential of biochar to be a source of soil contamination needs to be evaluated on a case-by-case basis, not only with concern to the biochar product itself, but also to soil type and environmental conditions.

Implications

As highlighted above, before policy can be developed in detail, there is an urgent need for further experimental research in with regard to long-term effects of biochar application on soil functions, as well as on the behaviour and fate in different soil types (e.g. disintegration, mobility, recalcitrance), and under different management practices. The use of representative pilot areas, in different soil ecoregions, involving biochars produced from a representative range of feedstocks is vital. Potential research methodologies are discussed in the report. Future research should also include biochars from non-lignin-based feedstocks (such as crop residues, manures, sewage and green waste) and focus on their properties and environmental behaviour and fate as influenced by soil conditions. It must be stressed that published research is almost exclusively focused on (sub)tropical regions, and that the available data often only relate to the first or second year following biochar application.

Preliminary evidence suggests that a tight control on the feedstock materials and pyrolysis conditions might substantially reduce the emission levels of atmospheric pollutants (e.g. PAHs, dioxins) and particulate matter associated to biochar production. While implications to human health remain mostly an occupational hazard, robust qualitative and quantitative assessment of such emissions from pyrolysis of traditional biomass feedstock is lacking.

Biochar potentially affects many different soil functions and ecosystem services, and interacts with most of the 'threats to soil' outlined by the Soil Thematic Strategy (COM (2006) 231). It is because of the wide range of implications from biochar application to soils, combined with the irreversibility of its application that more interdisciplinary research needs to be undertaken before policy is implemented. Policy should first be designed with the aim to invest in fundamental scientific research in biochar application to soil. Once positive effects on soil have been established robustly for certain biochars at a specific site (set of environmental conditions), a tiered approach can be imagined where these combinations of biochar and specific site conditions are considered for implementation first. A second tier would then consist of other biochars (from different feedstock and/or pyrolysis conditions) for which more research is required before site-specific application is considered.

From a climate change mitigation perspective, biochar needs to be considered in parallel with other mitigation strategies and cannot be seen as an alternative to reducing emissions of greenhouse gases. From a soil conservation perspective, biochar may be part of a wider practical package of established strategies and, if so, needs to be considered in combination

with other techniques.

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