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The short-term stability and function of charcoal in soil  
and its relevance to Ghanaian subsistence agriculture

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2017

I hereby declare that this thesis has been composed by myself and that the work therein is my own. This work has not and will not be submitted for any other degree or professional qualification.

Tom Maxfield, Jena, 4<sup>th</sup> January 2017

## **Abstract**

Maintaining an adequate level of soil organic matter and nutrients cycling is crucial to the success of any soil management in the humid tropics. Cover crops, compost, or manure additions have been used successfully to supply nutrients to crops but the benefits of such amendments are often short-lived in the tropics, since decomposition rates are high.

This study focused on charcoal which, when utilised as a soil amendment is termed 'biochar'. Throughout this thesis, the terms 'charcoal' and 'biochar' are used interchangeably depending on the context. Charcoal exhibits physiochemical properties potentially suitable for soil improvement as well as for the safe and long-term storage of carbon in the environment. As a way of investigating its recalcitrance as a carbon store, O:C ratios have been shown to reflect the extent of oxidation and therefore decomposition of charcoal.

This study aimed to fill a gap in the research by describing the effects of biochar on the water retention capacity of soil under laboratory conditions. It also provides a detailed snapshot of the first ten years of recalcitrance under natural conditions, using X-Ray Photoelectron Spectroscopy (XPS) to determine elemental oxygen and carbon ratios of whole charcoal fragments and how these are affected by the surrounding environment over time. Mechanisms of oxidation are described, showing how both biotic and abiotic factors influence the degradation of charcoal in the soil.

It also investigated how these properties affect the nutrient and water retention capability of charcoals of different ages in the laboratory. Results of charcoal/soil mixtures showed significant reduction in nitrate leachate losses with no reduction in performance over a ten year period of residing in the soil. It was also shown that charcoal addition to a sandy soil resulted in a significantly increased available water content. Both these results were argued to support the idea that charcoal is of potential beneficial amendment to sandy, degraded soils.

## CONTENTS

Title page	
Declaration.....	2
Abstract.....	3
Contents page.....	4
<b>1. INTRODUCTION.....</b>	<b>7</b>
<b>1.1 Potential Benefits of biochar.....</b>	<b>7</b>
<b>1.2 Properties of biochar.....</b>	<b>8</b>
1.2.1 Physical properties.....	8
1.2.2 Chemical properties.....	10
1.2.3 Nutrient properties.....	16
<b>1.3 Stability of biochar in soil.....</b>	<b>18</b>
1.3.1 Estimation of long-term stability.....	19
1.3.2 Short-term stability of biochar.....	21
1.3.3 Biochar decay.....	23
<b>1.4 Future research needs regarding biochar attributes and influences on soils .....</b>	<b>27</b>
1.4.1 Soil hydrology .....	27
1.4.2 Nutrient mobility.....	28
<b>1.5 References .....</b>	<b>29</b>
<b>2. WATER RETENTION CHARACTERISTICS OF CHARCOAL/SOIL MIXTURES.....</b>	<b>39</b>
<b>2.1 Abstract.....</b>	<b>39</b>

2.2 Introduction.....	39
2.3 Materials and methods.....	40
2.4 Results and discussion.....	42
2.5 Conclusions.....	51
2.6 References.....	52
<b>3. CHARCOAL WEATHERING OVER A DECADE USING A CHRONOSEQUENCE</b>	
<b>METHODOLOGY.....</b>	<b>55</b>
<b>3.1 Abstract.....</b>	<b>55</b>
<b>3.2 Introduction.....</b>	<b>55</b>
<b>3.3 Materials and methods.....</b>	<b>57</b>
3.3.1 Ghana.....	57
3.3.2 Study sites.....	57
3.3.3 Sample collection.....	58
3.3.4 Sample preparation.....	62
3.3.5 Xray Photoelectron Spectroscopy (XPS).....	63
3.3.6 Quantification of elemental proportions and carbon species from XPS spectra.....	64
3.3.7 Statistical analysis.....	65
<b>3.4 Results and Discussion.....</b>	<b>65</b>
3.4.1 O:C of charcoal surfaces and milled fragments along a chronosequence.....	65
3.4.2 Relative proportions of different functional groups on surfaces and milled charcoal fragments.....	70

3.4.3 Elemental proportions of Al, Si and Fe on and within charcoal fragments....	74
3.4.4 The influence of root incursions on O:C.....	75
3.4.5 O:C along a depth profile into individual charcoal fragments.....	78
<b>3.5 Further discussion and conclusions.....</b>	<b>85</b>
<b>3.6 References.....</b>	<b>87</b>
<b>4. THE CHANGES IN SOIL FUNCTIONALITY OF CHARCOAL OVER A DECADE.....</b>	<b>91</b>
<b>4.1 Abstract.....</b>	<b>91</b>
<b>4.2 Introduction.....</b>	<b>91</b>
<b>4.3 Materials and methods.....</b>	<b>94</b>
<b>4.4 Results and discussion.....</b>	<b>103</b>
<b>4.5 Conclusions.....</b>	<b>119</b>
<b>4.6 References.....</b>	<b>121</b>
<b>5. DISCUSSION.....</b>	<b>124</b>
<b>5.1 Ghanaian agriculture.....</b>	<b>124</b>
<b>5.2 Biochar in Ghanaian agriculture.....</b>	<b>127</b>
<b>5.3 Agriculture in Wenchi District, Brong Ahafo region .....</b>	<b>130</b>
<b>5.4 Potential Biochar feedstocks.....</b>	<b>134</b>
<b>5.5 References.....</b>	<b>137</b>
<b>6 RESEARCH LIMITATIONS, SUGGESTED IMPROVEMENTS AND RECOMMENDATIONS FOR FURTHER WORK.....</b>	<b>138</b>
Acknowledgments.....	144

## **1. INTRODUCTION**

Biochar is described as a porous carbonaceous solid produced by thermochemical conversion of organic materials in an oxygen depleted atmosphere (Lehmann & Joseph 2009). It has physiochemical properties potentially suitable for the safe and long-term storage of carbon in the environment and soil improvement (Baldock & Smernik 2002; Liang et al 2008; Kimetu et al 2009). This introduction provides the background for the following three project objectives:

1. To describe the effect of biochar on soil hydrology.
2. To observe and describe changes in surface chemistry of biochar over time.
3. To assess the mobility of fertiliser in different soil/biochar mixes.

Hypotheses to support these objectives are described at the end of this chapter after an account of the background to this investigation:

### **1.1 Potential benefits of biochar**

Biochar comprises stabilised plant material in which carbon is stored mainly in a highly recalcitrant chemical form. Although little research has been published on the long-term stability of biochar, studies suggest a mean residence time (MRT) for charcoal in soil in the order of millennia, compared to 50 y for bulk soil organic matter (Bird et al 1999; Brodowski et al 2006; Cheng et al 2006; Hammes et al 2008; Lehmann et al 2009). By analogy to charcoal, biochar could provide an effective long-term store of carbon in soil, and thus provide an abatement option for anthropogenic carbon emissions.

Charcoal and biochar addition to tropical soils has been shown to improve crop yields, sometimes dramatically (Lehmann et al 2003b). The most important beneficial functions of biochar are listed below.

a) pH, mineral nutrients and labile carbon: The typically alkaline pH and mineral constituents of biochar (ash content, including N,P,K and trace elements) could

provide important agronomic benefit in many soils, at least in the short- to medium-term, during which time small labile fractions of organic carbon might also be important (Skjemstad et al 1996).

b) Water retention: particularly in poorer-quality sandy or silty soils, the addition of charcoal has been demonstrated to enhance crop yield (Lehmann et al 2003a). This is likely to result, in part, from the enhanced water retention of a typically porous material.

## **1.2 Properties of biochar**

### **1.2.1 Physical Properties**

The presence of biochar in soils can significantly affect properties such as overall texture, structure, pore-size distribution, porosity, particle-size distribution, density and consistency (Brodowski 2004). This in turn directly influences plant growth, as the physical properties of the root zone determines root penetration characteristics as well as the availability of air and water (Lima et al 2005). This section will focus on both the physical properties of biochar, and the subsequent effects on soil physical properties.

#### *Biochar structure*

The physical structure of biochar depends not only upon the organic feedstock used, but also upon the system by which they are made (e.g. pyrolysis or gasification). During pyrolysis, mass and volume of the feedstock are reduced, but the structure and rudimentary porosity of the original material are preserved (Bourke et al 2007). The macroporosity of the remaining mineral and C skeleton originates from the biological cellular structure of the biomass used (Wildman &

Derbyshire 1991). Microscopic analysis has also confirmed the presence of a honeycomb-like structure of pores (of  $\sim 10\mu\text{m}$  in diameter), leading to even smaller meso- and micropores within the biochar (Laine et al 1991).

The operating parameters during pyrolysis process which influence the physical properties of biochar include: heating rate; highest treatment temperature (HTT); pressure; reaction residence time; reaction vessel (orientation, dimensions etc); pre-treatment e.g. drying; input flowrate; and post-treatment e.g. sieving. From all of these parameters, HTT is considered to be the most influential as the physical changes are all temperature dependent (Lehmann & Joseph 2009). For example, one study by Lua et al (2004) on a given feedstock found that pyrolysis temperature had the most significant effect, followed by pyrolysis heating rate.

#### *Soil surface areas and biochar*

Evidence suggests that biochar changes the physical nature of soil, giving similar benefits to those achieved through the addition of other organic amendments (Chan et al 2007a). One of these changes is that to soil surface area, which is an important characteristic concerning: fertility; water, air and nutrient cycling; and microbial activity. Organic matter has been shown to alleviate the problem of waterlogging in clay soils, and also increase the water content of sandy soils (Troeh & Thompson 2005). Biochar has also been experimentally linked to improved soil structure in fine-textured soils (Kolb 2007).

#### *Biochar porosity*

The pore-size distribution of biochar is an important factor in its behaviour in soil processes. Micropores (<2nm in diameter) constitute most of the surface area of biochars, and are responsible for the high adsorptive capacities for micronutrients, water and gases in the soil (Bagreev et al 2001). Increasing HTT generally increases

the surface area of biochar until it reaches the temperature at which deformation occurs. This high temperature causes micropores to enlarge by destroying the walls between adjacent pores, thereby creating both meso- and macropores (Zhang et al 2004).

These pores are also of importance when considering the type of microbial communities that inhabit them. Microbial cells typically range in size from 0.5 to 5µm, and consist predominantly of bacteria, fungi, actinomycetes and lichens (Lal 2006).

#### *Particle size distribution, density & mechanical strength*

The particle sizes and density of biochars is highly dependent upon the nature of the original feedstock material. In most cases the particle size is smaller in the biochar due to shrinkage and attrition during pyrolysis. This is especially true when considering post-handling of the biochar due to its friable nature. Solid density (density on a molecular level) generally increases with increasing process temperature and longer heating residence times. This increase is often accompanied by a decrease in bulk density (bulk density includes the macroporosity within each particle and the inter-particle voids), as demonstrated by Guo & Lua (1998). Mechanical strength is a characteristic used to define the quality of biochar as it relates to its ability to withstand wear and tear during use (Downie et al 2009). It is related to solid density and has a higher mechanical strength than the biomass feedstock from which it was derived.

#### **1.2.2 Chemical properties**

During thermal processing a complex set of chemical reactions occur, resulting in a large degree of chemical heterogeneity within biochars. Still focusing on the

pyrolysis of lignocellulosic materials, Antal & Grønli (2003) describe three major parallel product pathways which affect the chemistry of the resultant biochar:

1. biochar- and gas-forming;
2. liquid- and tar-forming; and
3. gasification and carbonisation pathway.

The relative rates of these pathways are largely determined by the highest heat treatment temperature (HTT), volatile removal rate and particle residence time during pyrolysis (Amonette & Joseph 2008). Lignocellulose degradation occurs at temperatures above  $\sim 120^{\circ}\text{C}$ , and the biochar- and gas-forming pathway dominates up to a temperature of around  $300^{\circ}\text{C}$ . At HTTs of between  $\sim 300$  and  $\sim 600^{\circ}\text{C}$ , the liquid- and tar-forming pathway becomes increasingly important. Biochar yield is reduced, and tars consisting chiefly of anhydrosugars are produced in abundance. With increasing HTTs comes an increase in trapped free radicals which render the resultant biochar extremely reactive towards oxidation.

The gas-forming pathway dominates at HTTs above  $600^{\circ}\text{C}$  due to sufficiently high heat and mass transfer rates during pyrolysis. At these temperatures, biochar, tar and liquid formation are at a minimum and the biochar is carbonised giving carbon contents of up to 90% by weight (Antal & Grønli 2003).

### *Carbon chemistry*

Another classification of the changes that occur over the temperature range just discussed, is the four regions of change as described by Paris et al (2005):

1. dehydration (below  $250^{\circ}\text{C}$ ) of the feedstock and slight depolymerisation of cellulose with little mass loss observed;

2. pyrolysis (between 250 and 350°C) of the cellulose occurs, resulting in significant mass loss by volatilisation. At ~330°C the first signs of aromatic carbon are seen;
3. graphene nucleation (above 350°C) whereby polyaromatic graphene sheets begin to grow at the expense of the amorphous-C matrix; and
4. carbonisation (above 600°C) whereby most of the remaining non-carbon atoms are removed and graphene sheets continue to grow laterally, eventually coalescing.

Within this temperature range of 250-600°C, the proportion of carbon (solid phase) increases from ~40-50% by weight in the feedstock to 70-80% in the resultant biochar. Carbonisation above temperatures of 600°C further increases the carbon content to ~90% except for high mineral-ash biochars e.g. from grasses high in silica.

### *Minerals*

The mineral ash content of feedstocks varies significantly, and the amount and distribution of minerals in biochar is also affected by process conditions. The lowest ash contents (<1% by weight) are generally found in woody feedstocks, whereas grasses and grain husks may contain as much as 24% due to high silica contents (Raveendran et al 1995). Table 1.1 below lists the mineral composition of various feedstocks:

Table 1.1 Ash content and elemental composition of various representative feedstocks

Feedstock	Ash content (wt %)	Al	Ca	Fe	Mg	Na	K	P	Si
		(mg kg <sup>-1</sup> )							
Bagasse	2.9	-	1500	130	6300	90	2700	280	17000
Coconut coir	0.8	150	480	190	530	1800	2400	50	3000
Coconut shell	0.7	70	1500	120	390	1200	2000	90	260
Coir pith	7.1	1700	3100	840	8100	11000	26000	1200	13000
Maize cob	2.8	-	180	20	1700	140	9400	450	9900
Maize stalks	6.8	1900	4700	520	5900	6500	30	2100	13000
Cotton gin waste	5.4	-	3700	750	4900	1300	7100	740	13000
Groundnut shell	5.9	3600	13000	1100	3500	470	18000	280	11000
Millet husk	18.1	-	6300	1000	11000	1400	3900	1300	150000
Rice husk	23.5	-	1800	530	1600	130	9100	340	220000
Rice straw	19.8	-	4800	200	6300	5100	5400	750	170000
Subabul wood	0.9	-	6000	610	1200	90	610	100	200
Wheat straw	11.2	2500	7700	130	4300	7900	29000	210	44000
Olive kernel	2.6	18000	97000	24000	20000	7900	-	-	-
Almond shell	3.4	5000	80000	6100	14000	5500	-	-	-
Forest residue	1.2	4900	130000	10000	19000	4200	-	-	-
Sawdust	0.44	9800	170000	29000	27000	10000	-	-	-
Waste wood	8.8	4900	130000	10000	19000	4200	-	-	-
Willow wood	1.1	20	3900	30	360	150	1400	340	-
Demolition wood	1.9	480	3600	350	420	670	750	60	-
Straw	17.7	5800	8600	3400	3700	3200	22000	600	-
Meat and bonemeal	10.4	7600	260000	4900	13000	5800	23000	100000	-
Oak wood biochar	0.27	1000	350000	3400	16000	6400	98000	5400	4200

Source: Raveendran et al (2005); Skodras et al (2006); and Bourke et al (2007)

There is little evidence reporting the distribution of these inorganic minerals in different biochars, but most are believed to occur as discrete phases separate from the carbonaceous matrix. These include sylvite (KCL), quartz (SiO<sub>2</sub>), amorphous silica, calcite (CaCO<sub>3</sub>), hydroxyapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>), and other minor phases such as calcium phosphates and sulphates, various nitrates, and oxides/hydroxides of Ca, Mg, Al, Ti, Mn, Zn and Fe. Amorphous silica is of particular interest due to its phytolith, or 'plant opal' form which has been shown to be a degradation resilient store of plant carbon (Krull et al 2003; Parr & Sullivan 2005). On the other hand, the

presence of crystalline silica is also of interest as it poses a potentially high respiratory risk during handling.

### *Oils*

Most of the literature focuses on bio-oils released when biomass is pyrolysed, and very little analysis has been carried out revealing the nature of the residual organic molecules on the biochar surface. One research group however (Schnitzer et al 2007) have carried out a detailed analysis of the residual bio-oils from the fast pyrolysis of chicken manure. They grouped the identified compounds into the following six classes:

1. N-heterocyclics;
2. substituted furans;
3. phenol and substituted phenols;
4. benzene and substituted benzenes;
5. carbocyclics; and
6. aliphatics.

Some of these compounds have also been found in smoke and forest fire debris, and have been shown to be important to certain types of soil biological activity. For example: butenolide in the germination of certain seeds (Dixon et al 1995; Vigilante et al 1998); and sesquiterpenes in the triggering of microorganism growth e.g. arbuscular mycorrhizal fungi (Akiyama & Hayashi 2006; Akiyama et al 2005).

### *Surface chemistry*

The rich and varied surface chemistry of biochars exhibits hydrophilic, hydrophobic, acidic and basic properties. The relative contributions of these properties depend upon the feedstock and thermal degradation process used to create the biochar. Functional groups such as OH, NH<sub>2</sub> or O(C=O)R act as electron donors, whereas (C=O)OH, (C=O)H or NO<sub>2</sub> groups act as electron acceptors. Due to the heterogeneity of biochars, these sites may coexist within micrometres of each other on the outer

surfaces and pores of the charred material. In order to provide information about the types of functional groups present on biochar surfaces, X-Ray photoelectron spectroscopy (XPS) is commonly used. This technique has been used to quantify the ageing process of charcoal in soils with regards to surface oxidation (Cheng et al 2008), and will also be employed in this investigation.

In biochars derived from various wastes such as manures and sewage, N and S functional groups are found in a higher abundance than in lignocellulosic biochars. The areas of N groups are centres for high basicity, with low process temperatures yielding amine groups and higher temperatures resulting in pyridine-like compounds incorporated within the biochar (Koutcheiko et al 2007). S functional groups were also seen to change with respect to process temperature. Low temperatures tend to yield sulphonates and sulphates, whereas higher temperatures (>500°C) result in the formation of sulphides (Koutcheiko et al 2007; Knudsen et al 2004). These sulphides are expected to be water insoluble and therefore biologically less available.

The various functional groups above affect the sorption capacity of the biochar for dissolved micronutrients and therefore on soil dynamics. They influence sorption by the nature of their surface charge and by the availability of  $\pi$  electrons. Sorption behaviour is also affected by the amphoteric nature of the functional groups which is dependent upon the pH of the surrounding solution. This behaviour is very complex and is discussed in great detail by Radovic et al (2001). They describe the complex interplay between dispersive hydrophobic interactions, and attraction forces of electrolytes when they are ionized in experimental conditions.

#### *Organo-chemical properties*

Biochar is considered to be highly aromatic (also referred to as 'aryl C'), and this content tends to increase with temperature (Krull et al 2009). The degree of aromaticity and maturation is measured using H/C and O/C ratios, and is often

illustrated in Krevelen diagrams (e.g. Baldock & Smernik 2002). These elemental ratios can be determined using  $^{13}\text{C}$ -nuclear magnetic resonance (NMR) spectroscopy. Using this technique in combination with weight loss data, Almendros et al (2003) report that aromatic structures were formed as a direct result of heating. They also suggested that this transformation of labile compounds into recalcitrant forms has important biochemical implications with regard to greater biochar stability in the soil. It is in this area that further research would help gain a better understanding of the specific differences of biochars from different materials. Krull et al (2009) argue that advanced NMR spectroscopic techniques (e.g. dipolar de-phasing) could shed some light on how the original material may influence the biochar, and at what temperatures the differences may vanish. They also argue that the solvent-extractable component of biochar could be analysed for biomarkers and compound-specific isotopes. This in turn could aid the further characterisation of fresh and aged biochar, aiming to assess the weathering and release of non-aromatic biochar components (which are likely to be responsible for differences in degradability and nutrient status).

### **1.2.3 Nutrient properties**

Often biochar is considered as a fuel for further energy production (Horne & Williams 1996; Tsai et al 2006), and scant evidence exists regarding its nutrient value. Furthermore, information regarding the agronomic value of biochar nutrient content is rarely included in any experimental investigations. Table 1.2 lists nutrient values from various studies, and highlights the large variability in results. This reflects the fact that the composition of biochars depends upon the nature of feedstock and pyrolysis operating conditions used. This is particularly notable with phosphorous which was found in much higher levels in feedstocks of animal origin.

It is also important to mention that the total amounts listed in Table 2 do not reflect the actual bioavailability of nutrients such as organically bound N and S. In contrast,

available K in biochars is typically high and increased K uptake as a result of biochar application has been frequently reported (Lehmann et al 2003a; Chan et al 2007a).

Table 1.2. Nutrient content and pHs of biochars from various feedstocks

Feedstock	C	N	C/N	P	K	Production conditions	Source
	(g kg <sup>-1</sup> )						
Wood	708	10.9	65	6.8	0.9	By local farmers	Lehmann et al (2003a)
Green Wastes	680	1.7	400	0.2	1.0	450°C	Chan et al (2007b)
Poultry Litter	380	20	19	25.2	22.1	450°C	Chan et al (2007b)
Sewage sludge	470	64	7	56	-	450°C	Bridle & Pritchard (2004)
Broiler Litter	258	7.5	34	48	30	700°C, steam activated	Lima & Marshall (2005)
Broiler cake	172	6.0	29	73	58	700°C, steam activated	Lima & Marshall (2005)
<i>Eucalyptus deglupta</i>	824	5.73	144	0.6	-	350°C	Rondon et al (2007)
Oil mallee tree*	340	12	28	1.2	7.0	'Moki' method	Blackwell et al (2007)

\* after oil extraction

The C/N ratio is a parameter often used to indicate the ability of organic substrates to mineralise and release inorganic N when applied to soils. Generally, a C/N ratio of 20 is used as a critical limit above which immobilisation of N by microorganisms occurs i.e. it is rendered unavailable to plants (Chan & Xu 2009). Only two of the figures in table 1.2 fall below this limit (sewage sludge and poultry litter), and so one would expect biochars to possibly induce N-deficiency in plants. However, there is a degree of uncertainty whether the C/N criterion is directly applicable to biochars. For example, C/N ratios of Terra Preta soils are usually higher than the adjacent Ferralsol, but they tend to have higher available N (Lehmann et al 2003b). Chan & Xu (2009) also argue that N immobilisation is negligible or transient in

biochars due to the high recalcitrant organic C content which is not easily mineralised.

Little research has been undertaken to identify the optimal pyrolysis conditions necessary to enhance nutrient properties of biochars. Most of the research on pyrolysis of biomass has focused on energy and fuel quality (Horne & Williams 1996 & Tsai et al 2006). These properties are a vital selling point, and their consistent quality is an essential requirement for market development. The high variability shown in various biochars has indeed been found to be a major barrier in developing markets in Australia (Chan et al 2007c).

It has been reported that the most influential operating parameter affecting nutrient composition is pyrolysis temperature. Typically, large amounts of N, K and S are lost via vapourisation, amounting to roughly 50% loss with temperatures exceeding 500°C (Bagreev et al 2001; Shinogi 2004; Lang et al 2005). Furthermore, there is evidence to suggest that the remaining nutrients tend to become less available with further increases in temperature. From a resource conservation point of view, it would therefore be preferable to keep the pyrolysis temperature low e.g. between 400 and 500°C (this would of course vary for different feedstocks). Research opportunities also exist to enhance the nutrient value of biochar by further reaction with nutrients and blending of different feedstocks to tailor the needs of different crops and soils (Chan & Xu 2009).

### **1.3 Stability of biochar in soil**

The stability of biochar is of fundamental importance with regards to its use for environmental management (Lehmann et al 2009). The two reasons for this are: (i) it determines how long C will remain sequestered in the soil, and therefore to what extent it contributes to the mitigation of climate change; and (ii) how long biochar can be beneficial to soil and water quality.

### 1.3.1 Estimation of long-term stability

There is an abundance of evidence to suggest that the longevity of biochar in soils is significantly greater than that of other organic matter (Pessenda et al 2001; Glaser et al 2001; Liang et al 2008). It is typically the oldest C fraction, and residues from forest fires have frequently found to be more than 10,000 years old (reviewed by Preston & Schmidt 2006). Also, radiocarbon dating of biochars found in the Terra Preta soils of the Amazon region have revealed ages of 500-7000 years old (Neves et al 2003). These dates alone are however, not enough to quantitatively conclude the decomposition rate of biochar. Additional information regarding the amount of biochar at deposition is also required in order to carry out a mass-balance calculation.

The availability of such information is unfortunately unlikely due to the lack of archived samples or historical records (Hammes et al 2008). There is also the uncertainty around the time lag between CO<sub>2</sub> fixation into plant biomass and deposition into the soil – which can extend to a few hundred years (Lehmann et al 2009). Nevertheless, data in the scientific literature suggests that biochar has a much greater average stability than plant litter. Global biochar production of only 0.05 to 0.3Gt C yr<sup>-1</sup> (Forbes et al 2006) is less than 0.5% of the 60Gt C yr<sup>-1</sup> estimated for global net primary productivity (Sabine et al 2004), yet biochar concentrations are often above 10% of total organic C in soils (Skjemstad et al 1996, 2002). These data suggest a difference in decomposition rates of at least one order of magnitude. They do however also suggest that biochar is eventually mineralised to CO<sub>2</sub>.

Some estimates of biochar turnover time have been made, including Lehmann et al (2008) who matched annual production of char from savannah fires with measured char stocks in the soil. Strong assumptions for the proportion of char produced per unit biomass burned were made, as was the extent and frequency of biomass burning and production. On a spatial scale of individual sites, they obtained mean

biochar residence times of 1300 to 2600 years under the dryland conditions of Northern Australian woodlands.

Preston & Schmidt (2006) measured biochar stocks in a time series or so-called 'chronosequence' (set of sites with a common history of contrasting duration). Taking samples from a coastal temperate rainforest of Western Vancouver, they obtained a mean residence time of 6623 years. In contrast, Hammes et al (2008) calculated a residence time of just 293 years of biochar produced in Russian steppe natural fires. In both these studies, there was some uncertainty as to how much an effect spatial variability had on the outcome. Even shorter residence times have been reported in other studies e.g. several decades for biochar stocks (termed 'oxidation-resistant elemental carbon, OREC) after savannah burning in Zimbabwe (Bird et al 1999); and just eight years after forest clearing by fire in Kenya (Nguyen et al 2008).

It is important to mention at this point that the methods employed in the above mentioned studies can possibly lead to some erroneous conclusions. Considering only the biochar decomposition as mineralisation to CO<sub>2</sub>, factors such as losses by leaching or erosion are neglected, as well as reburning of biochar by further fires (Czimczik et al 2005). It is also possible that additional biochar could be deposited via sheet erosion from fires in adjacent areas, resulting in an under-estimation of biochar residence time (Lehmann et al 2009).

Although biochar certainly decomposes over time, it appears that the stability of the remaining biochar remains high over long periods of time. Chemical characteristics such of biochar particles have been shown to not change significantly over time e.g. Liang et al (2008) used various X-ray techniques such as X-ray photoelectron spectroscopy (XPS) to show that the aromaticity of biochar particles in Amazonian Dark Earths did not change over time from 700 to 7000 years. Nguyen et al (2008) reported similar findings over 100 years, showing that surfaces of biochar particles

oxidised rapidly within 5 years, while below the ~10nm thick surface layer the O/C ratio remained unchanged.

### **1.3.2 Short-term stability of biochar**

It has been argued that quantification of the easily decomposable fraction of biochar is important for estimating the total amount of biochar ultimately remaining in the soil. Good estimates for mean residence time (MRT) and prediction of long-term decay can be subsequently made (Lehmann et al 2009). Short-term decomposition experiments on fresh biochar include Hamer et al (2004) who conducted 60-day incubation experiments at 20°C. They found a CO<sub>2</sub>-C loss of 0.3 and 0.8% of initial biochar C produced from either oak-wood or maize/rye straw mixture at 800 and 350°C, respectively. Increased incubation temperatures of 250-350°C used by Baldock & Smernik (2002) resulted in a C loss of less than 2% from biochar produced from *Pinus resinosa* (Red Pine) sapwood over 120 days incubation (see Figure 1).

As would be expected, mineralisation of older biochars is even lower. Cheng et al (2008) incubated 130 year old biochars from historical charcoal production sites at 30°C for 50 days, and reported an initial C mineralisation of just between 0.05 and 0.4%. They thus concluded that the mean residence time of these biochars was 1335 years at a mean annual temperature of 10°C. Using a similar calculation approach, Liang et al (2008) reported a mean residence time of 4035 years for biochars in Amazonian Dark Earths.

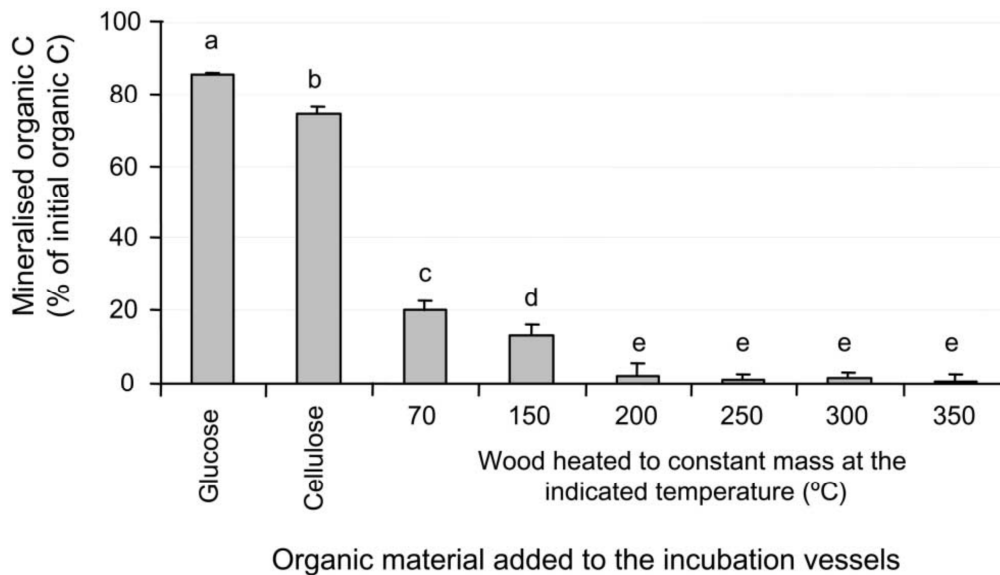


Figure 1.1. Mineralisation at 25°C of organic carbon contained in glucose, cellulose and *Pinus resinosa* sapwood heated to thermal equilibrium at increasing temperatures. Values with different letters are significantly different at  $P < 0.05$  (taken from Baldock & Smernik 2002).

These results contrast with decomposition rates reported by Brodowski (2004), who reported a 16 to 51% loss of biochar (made from maize and rye residues at 350°C) during the first two years. Wardle (2008) even reported no loss after ten years of monitoring biochar decay in a boreal forest soil. Such differences are always caused in some extent to the nature of feedstock and charring conditions, but there are other reasons for such disparity. For example, Hamer et al (2004) and Cheng et al (2008) used analytical approaches which only accounted for the CO<sub>2</sub>-C loss as being indicative of total biochar decay. This approach does not account for the transformation of biochar C to microbial metabolites, resulting in an overestimation of biochar stability.

On the other hand, the molecular marker (benzene polycarboxylic acid, BPCA) method used by Brodowski (2004) would not only classify a transformation of biochar to microbial metabolites as a loss of biochar, but also surface oxidation (Lehmann et al 2009). This would result in an overestimation of C loss, potentially

being very high due to the large surface area of biochars. Another important note to mention here is that incubation experiments reported in the literature frequently made use of a sand medium. This naturally excludes the interactions of clay-biochar and aggregation which potentially increase C stability, thereby overestimating biochar decomposition rates. Lehmann et al (2009) argue that one way to improve estimates of long-term stability by short-term incubation experiments is to use aged biochars (Cheng et al 2008; Liang et al 2008). They also argue that from a C sequestration viewpoint, it may be less relevant in what form the biochar is present in the soil as long as it is not mineralised to CO<sub>2</sub>.

### 1.3.3 Biochar decay

There are various mechanisms of biochar decay in soil, and these are in turn affected by the varying properties of different biochars. The following sections will address these mechanisms and the environmental conditions affecting them.

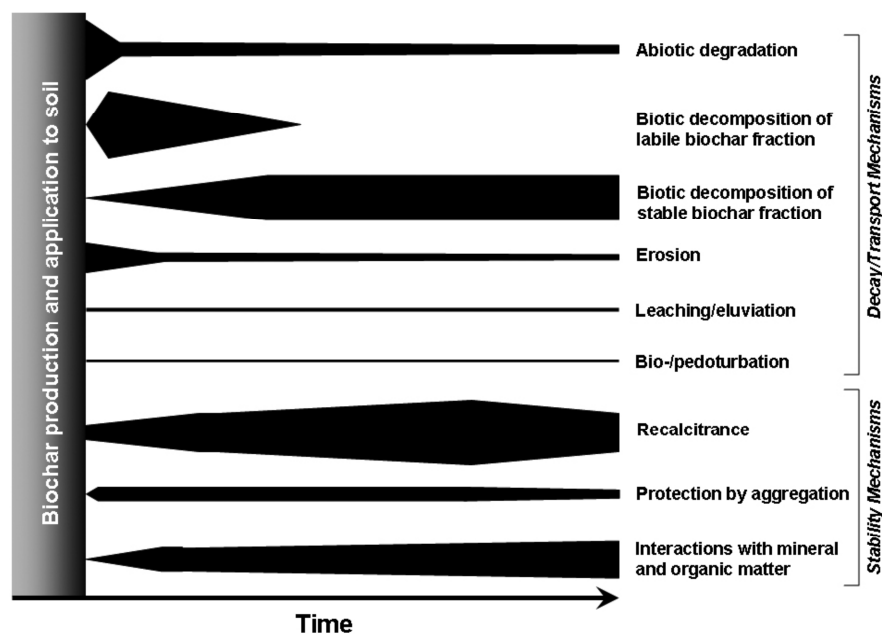


Figure 1.2. Schematic representation of the factors that may influence stability or decay and transport of biochar (importance indicated by the thickness of the bars). Source: Lehmann et al (2009).

### *Biological decomposition*

The organo-chemical and physical structure of biochar are the main reasons for the recalcitrance of biochar (Schmidt & Noack 2000) which appears to be resistant to hydrolytic enzymes. However, biochar can be metabolised by microorganisms, and heterotrophic decomposition is the most important mechanism of biochar decay (Brodowski 2004). Bacteria and fungi have been found on the surfaces and in the pores of biochar, but their relative contribution to this decay is unknown. Fungi e.g. white-rot fungi are more likely to metabolise biochar utilising their extra-cellular enzymes such as laccase (Hockaday 2006). An experiment carried out by Wengel et al (2006) showed an increase in biochar decomposition upon the addition of the basidiomycete fungus *Schizophyllum commune*, leading to an 11% increase in dissolved organic C originating from biochar.

### *Abiotic processes and physical breakdown of biochar*

Hydrolysis and oxidation are the major contributors to degradation during the initial stages of biochar ageing. These processes create negatively charged acidic groups e.g. carboxylate and phenolate on the biochar surfaces (Cheng et al 2006) thereby altering the pH and CEC of the surrounding soil. Although such abiotic mechanisms are not necessarily associated with C loss, they may facilitate subsequent microbial metabolism of otherwise recalcitrant aromatic ring structures.

Over time, the size of biochar particles reduces due to physical breakdown, and this can affect the rate of microbial degradation due to an increased accessible surface area. Nguyen et al (2008) found that after 30 years in a Kenyan oxisol, no particles greater than 50µm in size remained. The extent to which physical breakdown by soil fauna affects the actual stability of the biochar is discussed in the next section.

### *Biochar stabilisation*

Several mechanisms are responsible for the stabilisation of biochar in soil which significantly increase its residence time. These include its intrinsic recalcitrance,

spatial separation of decomposers and substrate, and formation of interactions between mineral surfaces and organic matter (Sollins et al 1996).

The pyrolytic conversion of biomass cellulose and lignin to amorphous structures and turbostratic crystallites increases the recalcitrance of C in the biomass (Paris et al 2005). The differences in stability between biochars produced under different conditions however, has not been fully investigated (Lehmann et al 2009).

Biochar has been found to preferentially reside in soil aggregates rather than as free organic matter (Brodowski et al 2006; Liang et al 2008), which is considered to reduce its accessibility to decomposers. Contrasting evidence to this consideration was however found by Liang et al (2008) who suggested that greater aggregation had no influence on biochar mineralisation in soils with varying percentages of clay.

#### *Assessing biochar decay*

Due to its longevity, direct measures of biochar turnover time may require centuries to millennia, and are therefore experimentally inaccessible. Extrapolations from short term incubation experiments such as those carried out by Baldock & Smernik (2002) and Hamer et al (2004) are problematic because of the heterogeneity and particulate nature of fresh biochar. This problem is represented schematically in the Figure 3 for a hypothetical data set. This example illustrates that long-term decomposition data are necessary to predict biochar decay, and that extrapolations from short-term experiments are likely to fail.

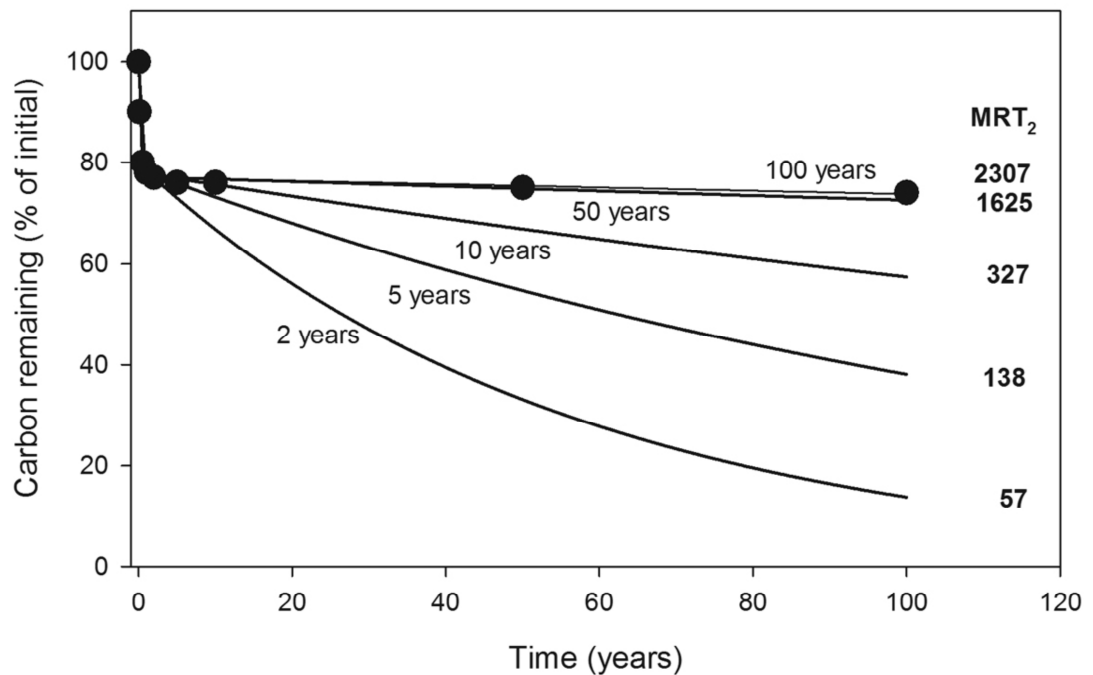


Figure 1.3. Double-exponential model ( $C_{\text{remaining}} = C_1e^{-k_1t} + C_2e^{-k_2t}$ , with 1 and 2 being a labile and stable pool, respectively) fitted to hypothetical data of biochar decay after 0.1, 0.5, 2, 5, 10, 50 or 100 years, assuming data availability for either the first 2, 5, 10, 50 or 100 years

Note: MRT<sub>2</sub> is the mean residence time of the stable pool 2, calculated from the rate  $k_2$ , and is given in years

To overcome this problem, Lehmann et al (2009) argue the need for a comprehensive approach that predicts long-term decay based on easily obtainable characteristics which can be assessed by various rapid test methods.

Firstly, there is a need to establish relationships between biochar properties or rapid stability tests and the proportion of the labile fraction of biochar that will decompose in annual to decadal timescales. This may be achieved by incubation experiments over a few years.

Secondly, the decomposition rate of the stable fraction of biochar could be determined by a combination of long-term incubation experiments with fresh and aged biochar under elevated temperature, and field experiments that either exclude physical losses or allow their quantification.

Thirdly, there is a need to develop a mechanistic understanding of long-term biochar decay as a function of biochar properties and environmental conditions such as climate and soil. A modelling framework could then be applied which recognises stable and labile fractions of biochar, including decomposition products of biochar, which in turn could be validated with long-term field experiments.

#### **1.4 Future research needs regarding biochar attributes and influences on soils**

The physico-chemical properties of biochar affect the functional role it plays in application to soils. There is a large range of characteristics in different biochars, and it is important that these are characterised before the biochars are experimentally applied to agricultural systems. Variations in outcomes are correlated to these characteristics, and so an understanding of how and by what mechanisms biochars influence soil processes is essential. It is also of the utmost importance to determine how these properties of biochars change over time in soil, and how these changes influence their function.

With the overall aim to describe improvements to soil function upon addition of biochar (with regards to growing crops), this thesis focuses on two aspects: soil hydrology and nutrient mobility.

##### **1.4.1 Soil hydrology**

In areas where drought stress effects crop growth, the water holding capacity (WHC) of soils is of the utmost importance to agriculture. Although it has been widely reported that organic amendments generally increase the WHC of soil (Piccolo et al 1996), few studies have detailed the effect of biochar amendment.

Due to its porosity, it has been shown that biochar alone acts as a water retainer (Downie et al 2007; Dünisch et al 2007). Lehmann et al (2003a) went a step further and used lysimeter experiments to show that 'dark earth' soils (i.e. soils containing charred organic material) exhibited a lower water percolation than neighbouring soils. There has been however no published work quantifying the relationship between specific biochar/soil mixtures and water retention.

This study fills this gap by using tension table apparatus to describe the water retention characteristics of different levels of biochar amendments to two different types of soil. The hypotheses to be tested are:

- a) Biochar affects the water retention characteristic of a sandy/clay soil;
- b) The level of biochar addition affects the water retention characteristic of a sandy/clay soil

This information can then be used by agronomists to predict the soil/biochar water storage capacity, water supply to the plants (field capacity) and soil aggregate stability.

#### **1.4.2 Nutrient mobility**

As was previously discussed in section 1.2, nutrient mobility in biochar-amended soils has been argued to be influenced by the surface chemistry of the biochar and its ability to retain water and promote soil aggregation. The porous nature of the biochar has been proven to retain water and its associated dissolved nutrients, but the reactive groups present on the biochar surfaces have only been hypothesised to play an important role in nutrient retention.

The aforementioned studies describe how biochar surface chemistry changes over periods of hundreds to thousands of years after exposure to soil, and some laboratory accelerated ageing experiments have shown what happens in the short-term. There are however no published short-term studies which investigate the changes in surface chemistry in a natural environment. This information is considered vital if biochar is to be prescribed for use as a soil-amendment whereby the potential beneficial properties would need to be known both upon application to the soil, and for the following years to come.

This study will investigate the changes in porosity and surface chemistry over a 10 year period and will attempt to quantify the relationship between measured surface

chemistry and its associated nutrient retention. The following hypotheses will be tested:

- c) exposure to the soil causes changes in biochar surface chemistry over time;
- d) exposure to the soil causes changes in biochar porosity over time;
- e) addition of biochar affects the nutrient retention capacity of soil;
- f) biochar surface chemistry affects the nutrient retention capacity of soil/biochar mixes;
- g) biochar porosity affects the nutrient retention capacity of soil/biochar mixes

This will be carried out by measuring the porosity of whole biochar fragments and determining the level of oxidation on the biochar fragment surfaces using XPS, and then using the same fragments in nutrient-retention column experiments. Biochar fragments of various ages up to 10 years of time being exposed to the soil in a natural environment will be used to infer any changes over time.

Finally, a discussion chapter will combine all of the findings from the laboratory experiments and relate them to the current agricultural situation in the studied Brong-Ahafo region of central Ghana. Specific attention will be placed on the local needs of food security, soil management and mitigating the effects of climate change with particular reference to the potential role of biochar in subsistence agriculture.

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## **2. Water retention characteristics of charcoal/soil mixtures**

### **2.1 Abstract**

Gravimetric water release characteristics were determined for two different types of soil with increasing levels of biochar additions. Sieved topsoils were mixed with charcoal at a range of 0-100% by weight, compressed to 50 or 200 kPa, and were subjected to matric potentials from 0 to -1500 kPa using conventional tension table and pressure plate apparatus. Both the sandy and clay soil showed an increased water retention capacity (g/g) with the addition of biochar, and a compression pre-treatment of 200kPa enhanced this effect at the lower matric potentials e.g. a typical charcoal field application rate of 2% (by weight) to a sandy soil resulted in an increased available water content (g/g) of 29%. The data was fitted to a van Genuchten model to develop a good predictive capacity with a coefficient of determination value of around 0.967 (n=16).

### **2.2 Introduction**

It is likely that low soil organic matter contents may be responsible for the low available water capacity and the weak structure of many agricultural soils (Bembridge 1989; Mbagwu 1989; Piccolo et al. 1996). Biochar affects soil physical properties such as soil water retention and aggregation (Piccolo et al. 1996), and it has been argued that these effects may enhance the water availability to crops and decrease erosion (Mbagwu & Piccolo 1997; Piccolo et al. 1996).

The addition of charcoal/biochar to particularly poorer-quality sandy or silty soils in some parts of the world has been demonstrated to enhance crop yield (Shackley & Sohi 2010). An enhancement in crop yield is likely to be partly due to the porous nature of char which enhances the water retention of the material. This porous nature greatly increases the surface area, and as a result soil water retention has

been reported to increase by 18% upon addition of 45% (by volume) charcoal to a sandy soil (Tryon 1948). Glaser et al. (2003) reported that charcoal-rich anthrosols whose surface areas were 3 times higher than those of surrounding soils increased the field capacity by 18%, this being incidentally a likely combination of both biochar and organic matter combined. Gaskin et al. (2007) found that at a high rate of application (up to 22t ha<sup>-1</sup>), biochar resulted in the water content of a loamy sand field being double that of the control at the highest matric potential.

On the other hand, there is evidence to suggest that application of biochar to other soils such as loam results in no changes to soil water content, and in clayey soil the available soil moisture can even decrease with increasing char additions (Tyron 1948; Glaser et al. 2002). It appears therefore, that enhanced soil water retention upon the addition of biochar may only be expected in coarse-textured soils or soils with high distributions of macropores.

An important tool to agronomists is to be able to predict the soil water storage, water supply to the plants and soil aggregate stability. Despite the aforementioned studies showing changes in water content of biochar amended soils, there is no published data which would allow any predictive models to be developed. In this study, the effects of varying levels of biochar addition to both a sandy and a clay soil with respect to water release characteristics was determined using tension table and pressure plate apparatus. The effect of two different soil compression pressures was determined, and available water contents were calculated for the different conditions applied.

## **2.3 Materials & methods**

### *Soils & Char*

Surface soils were collected from two sites, one sandy soil from Woburn experimental farm in Bedfordshire and one clay soil from Rothamsted Research

Centre. These two soils were selected due to their differing physical properties. Both were air-dried and sieved to retain the <2mm fraction for investigation. The charcoal was from hardwood charcoal wastes brought from Brazil which had previously been analysed at source in Brazil to give the following properties:

Table 2.1. Some physical properties of the charcoal used

Moisture %	Ash %	Calorific value MJ/kg	Volatiles %	Fixed Carbon %
37.34	29.46	16.61	28.39	42.14

This charcoal was subsequently sieved to 6mm and washed with tapwater to remove ash. After some storage time, the char was ground sieved and to retain the 0.5-2.8mm fraction and washed with deionised water to remove dusts. Moisture contents of the soils and charcoal were determined by oven drying at 105°C for 24 hours, and particle densities using the pycnometer method.

Table 2.2. Some physical properties of the experimental materials

Substance	% Moisture	Particle density, g/cm <sup>3</sup>
Charcoal	5.43	1.40
Sandy Soil	0.58	2.65
Clay Soil	2.43	2.66

### *Sample preparation*

Soil and charcoal were combined to provide a range of mixtures with varying levels of the two components. The mixtures were wetted (the volume of water added was recorded for later calculation purposes) to enable through mixing of the soil and char giving samples of 0, 1, 2, 10, 50 and 100% by weight of charcoal. Triplicate samples of these mixtures were packed into cylindrical plastic cores (50-mm

internal diameter, 25-mm height) and were either uniaxially compressed to 50 or 200 kPa and the core weight, sample weight and sample volume were all recorded.

#### *Water release characteristic*

The cores were saturated in deionised water overnight before being placed on a tension plate connected to a water reservoir. To ensure good hydraulic connectivity, a small amount of kaolin paste (roughly the consistency of double cream) was deposited between the core and plate, and steel weights (180g) were rested on top of the core. The water reservoir was lowered progressively to give a range of matric potentials between 0 and -30 kPa. At each potential, the soil cores were weighed (roughly every 48 h), ensuring prior removal of any kaolin residue.

After each weighing, fresh kaolin paste was applied and the hydraulic contact re-established. To cover the greater matric potentials of -100, -300 and -1500kPa, duplicate sets of cores were placed in pressure plate apparatus for 2, 2 and 3 weeks respectively. At presumed equilibration after this time, samples were removed and water contents were determined using oven drying at 105°C for 24 h.

## **2.4 Results & Discussion**

#### *Bulk density and porosity*

The addition of charcoal to both soils decreased the bulk density and increased its porosity as shown in figures 2.1 and 2.2 below.

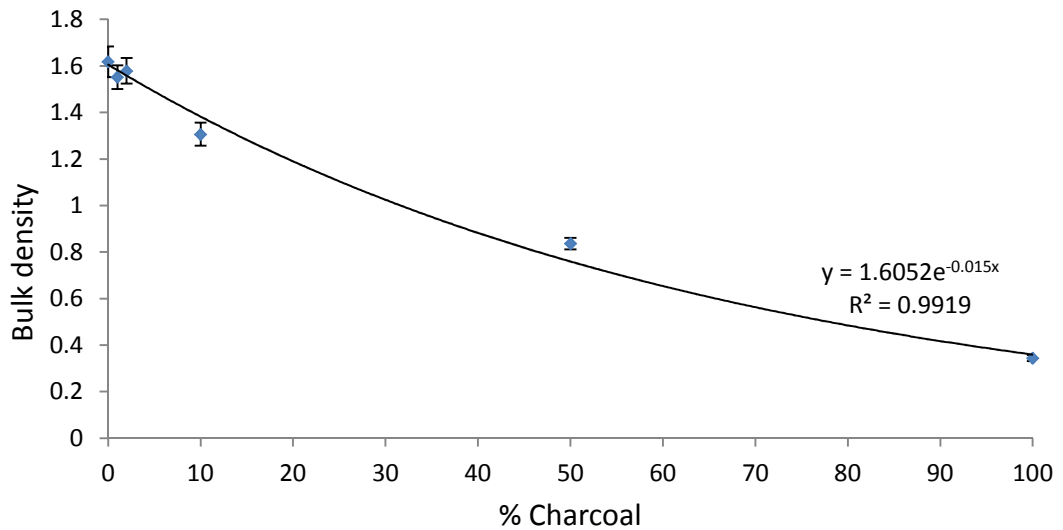


Figure 2.1 The exponential relationship between % charcoal and bulk density of charcoal/soil mixtures. Error bars denote standard deviation around the mean of 10 analyses.

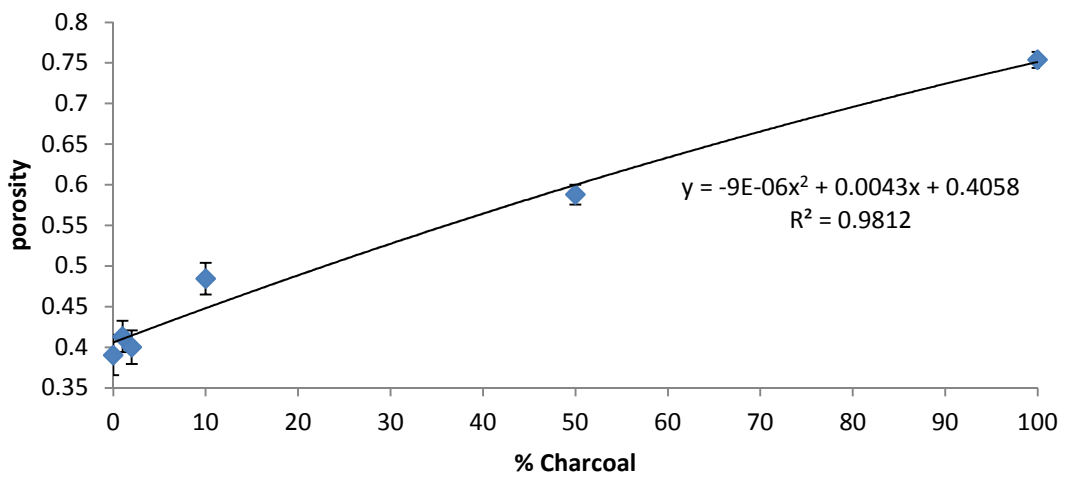


Figure 2.2. The exponential relationship between % charcoal and porosity of charcoal/soil mixtures. Error bars denote standard deviation around the mean of 10 analyses.

### *Water release characteristic*

The addition of charcoal altered the water release characteristic of the two soils in question. Although levels of 50% and 100% charcoal were also included in this experiment, it was found that kaolin intrusion into the sample cores had

significantly skewed the results. This was attributed to the apparent affinity of charcoal for kaolin absorption.

Figure 2.3 shows an increased water retention capacity for both soils, and more prominently so in the sandy soil. It is in the sandy soil that there is a progressive increase in water content as more charcoal is added, and this effect is stronger at the higher compression value of 200kPa.

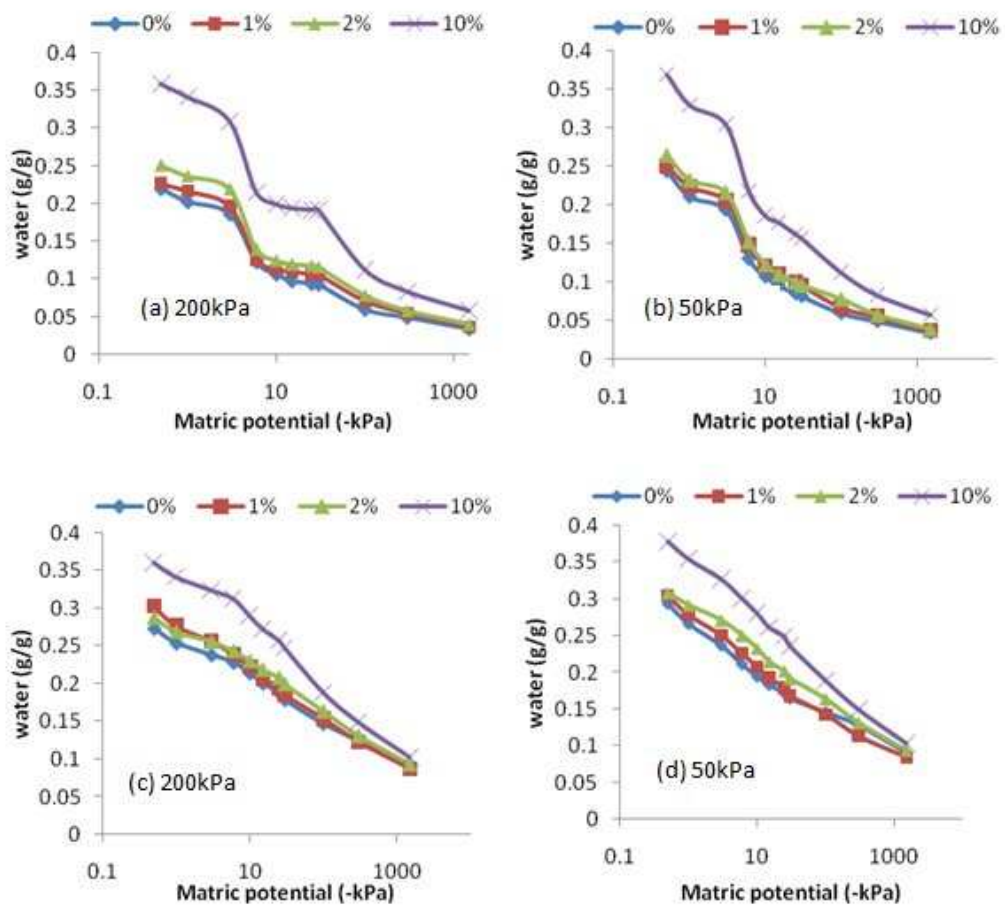


Figure 2.3. Gravimetric water release characteristics for a sandy soil (a & b) and clay soil (c & d) after sample compression of either 200kPa (left) or 50kPa (right). Curves are based on triplicate analysis with negligible variation (standard deviation around the mean < 0.005 in all cases).

Addition of charcoal did not affect the permanent wilting point (PWP) of any of the soil mixes, but it did significantly increase the field capacity ( $P < 0.01$ ), thereby increasing the available water content (AWC). Table 2.1 illustrates this increase in AWC, e.g. a 200kPa compressed sandy soil with a 2% (by weight) char supplement will exhibit a 29% increase in available water content.

Table 2.3 also shows that a higher compression of soil cores results in a significantly higher AWC (g/g) across the board ( $P < 0.01$ ). This can be attributed to the overall reduction of pore size and therefore greater affinity to bind water over the range of matric potentials. Additionally, the gravimetric water release characteristic data in figure 2.3 can be used to reflect the dual porous nature of soil (Dexter et al., 2008). The two compression treatments resulted in differences in field capacity (at -30kPa) at which the larger soil pores are drained, but the permanent wilting point (at -1500kPa) was largely unaffected.

Table 2.3. Effects of Biochar addition on water retention capacity (g/g) of two different soils. Figures are derived from triplicate analysis with negligible variation (standard deviation around the mean  $< 0.005$  in all cases).

Soil	% Char	Soil water constants (g/g)					
		FC		PWP		AWC	
		50*	200*	50*	200*	50*	200*
Sandy	0	0.08	0.09	0.03	0.03	0.05	0.06
	1	0.10	0.11	0.04	0.04	0.06	0.07
	2	0.10	0.12	0.04	0.04	0.06	0.08
	10	0.16	0.19	0.06	0.06	0.10	0.13
Clay	0	0.16	0.18	0.09	0.09	0.07	0.09
	1	0.17	0.19	0.08	0.09	0.08	0.10
	2	0.19	0.20	0.09	0.09	0.10	0.11
	10	0.24	0.25	0.10	0.10	0.13	0.15

\* These values of 50 and 200 represent the compression (kPa) used during sample preparation.

There is a significant difference in FC, PWP and AWC of charcoal amended soils compared to the soil alone (t-test,  $P < 0.01$ ), with a most marked increase in constants for the 10% charcoal amendment. There is no significant difference between 1% and 2% additions ( $P > 0.01$ ), but there is between the 10% and other treatment levels. Additionally, there is a significant increase in all constants in the clay when compared to the sandy soil ( $P < 0.01$ )

However, it was observed that the charcoal and soil exhibit such contrasting particle densities (1.40 and 2.65 respectively), that the interpretability of the g/g water results was deemed to possibly be misleading. The results listed in table 4.3 were therefore converted into a volumetric unit,  $\text{g}/\text{cm}^3$  (see table 2.4 below).

Table 2.4. Effects of Biochar addition on water retention capacity ( $\text{g}/\text{cm}^3$ ) of two different soils. Figures are derived from triplicate analysis with negligible variation (standard deviation around the mean  $< 0.005$  in all cases).

Soil	% Char	Soil water constants ( $\text{g}/\text{cm}^3$ )					
		FC		PWP		AWC	
		50*	200*	50*	200*	50*	200*
Sandy	0	0.11	0.14	0.06	0.05	0.05	0.09
	1	0.13	0.16	0.05	0.05	0.08	0.11
	2	0.13	0.17	0.05	0.05	0.07	0.12
	10	0.17	0.23	0.07	0.07	0.10	0.16
Clay	0	0.23	0.30	0.13	0.13	0.09	0.17
	1	0.22	0.30	0.13	0.13	0.09	0.17
	2	0.25	0.31	0.15	0.15	0.10	0.16
	10	0.24	0.33	0.13	0.13	0.11	0.20

\* These values of 50 and 200 represent the compression (kPa) used during sample preparation.

The  $\text{g/cm}^3$  results show the relationships between all parameters of the sandy soil remain the same, but the interpretation of the clay data is changed dramatically. There is now no significant difference of any of the constants with respect to different levels of charcoal addition ( $P > 0.05$ ). This can be attributed to the already high water retention capacity of clay soils which is little affected by the presence of char. It has even been reported that the presence of up to 20% charcoal (by weight) in clay soils may even increase percolation, thereby decreasing the soil's overall water holding capacity (Tryon 1948), but this was not found to be the case in this experiment.

On the other hand, volumetric results may not be so representative as the sample core volume was not recorded during the course of each experiment. It was observed that the volume of some of the sample cores was not constant i.e. particularly the tension table cores with charcoal additions showed a visual increase in volume as a result of swelling. The pressure plate cores however showed a certain degree of compression from the steel weight resting on top of the core.

#### *Data Modelling*

Water release characteristic data were fitted to a van Genuchten model detailed below:

$$\theta(\psi) = \theta_r + \frac{\theta_s - \theta_r}{[1 + (\alpha |\psi|)^n]^{1-1/n}}$$

where

$\theta(\psi)$  is the water retention curve [ $\text{L}^3\text{L}^{-3}$ ];

$|\psi|$  is suction pressure ([L] or cm of water);

$\theta_s$  is saturated water content [ $\text{L}^3\text{L}^{-3}$ ];

$\theta_r$  residual water content [ $\text{L}^3\text{L}^{-3}$ ];

$\alpha$  is related to the inverse of the air entry suction,  $\alpha > 0$  ( $[L^{-1}]$ , or  $cm^{-1}$ ); and,

$n$  is a measure of the pore-size distribution,  $n > 1$  (dimensionless).

Table 2.5. Parameters of the van Genuchten function of gravimetric water content (g/g) in 50kPa and 200kPa compressed soils.

Soil	Char %	Compression (kPa)	Indicators of goodness-of-fit		Van Genuchten function parameters $\theta = (\theta_s - \theta_r)(1 + (\alpha h)^n)^m$				
			MSE	$R^2$	$\theta_s$	$\theta_r$	$\alpha$	$n$	$M$
Sandy	0	50	$7.75 \times 10^{-4}$	0.984	0.228	0.037	0.491	30.899	0.019
		200	$7.44 \times 10^{-4}$	0.981	0.211	0.032	0.522	16.148	0.029
	1	50	$5.72 \times 10^{-4}$	0.989	0.237	0.034	0.508	30.899	0.015
		200	$1.18 \times 10^{-3}$	0.971	0.222	0.030	0.591	16.148	0.024
	2	50	$8.74 \times 10^{-4}$	0.925	0.248	0.042	0.487	30.899	0.017
		200	$1.52 \times 10^{-3}$	0.970	0.244	0.033	0.556	16.148	0.025
	10	50	$1.67 \times 10^{-3}$	0.984	0.349	0.039	0.576	30.899	0.012
		200	$3.27 \times 10^{-3}$	0.955	0.351	0.030	0.609	30.904	0.010
Clay	0	50	$1.56 \times 10^{-4}$	0.993	0.293	0.000	1.847	30.896	0.005
		200	$5.17 \times 10^{-4}$	0.973	0.336	0.000	7.404	25.170	0.005
	1	50	$3.68 \times 10^{-4}$	0.980	0.304	0.000	1.353	30.896	0.005
		200	$1.33 \times 10^{-3}$	0.942	0.290	0.000	0.563	30.904	0.005
	2	50	$3.26 \times 10^{-4}$	0.985	0.300	0.000	0.533	30.896	0.005
		200	$2.38 \times 10^{-3}$	0.899	0.355	0.000	7.404	25.170	0.005
	10	50	$9.23 \times 10^{-4}$	0.975	0.367	0.000	0.520	30.896	0.006
		200	$1.14 \times 10^{-3}$	0.973	0.342	0.000	0.224	30.904	0.006

Goodness of fit values in table 2.5 indicate that the data fits the van Genuchten model well, with an average coefficient of determination of 0.967 ( $n = 16$ , mean =  $0.967 \pm 0.025$ ). There is no significant difference in the goodness of fit indicator between sandy and clay soils ( $P > 0.01$ ), and level of charcoal addition does not significantly affect the accuracy of the model ( $P > 0.01$ ). Below in figures 2.4 and 2.5 are graphs depicting the relationship between experimental and modelled data.

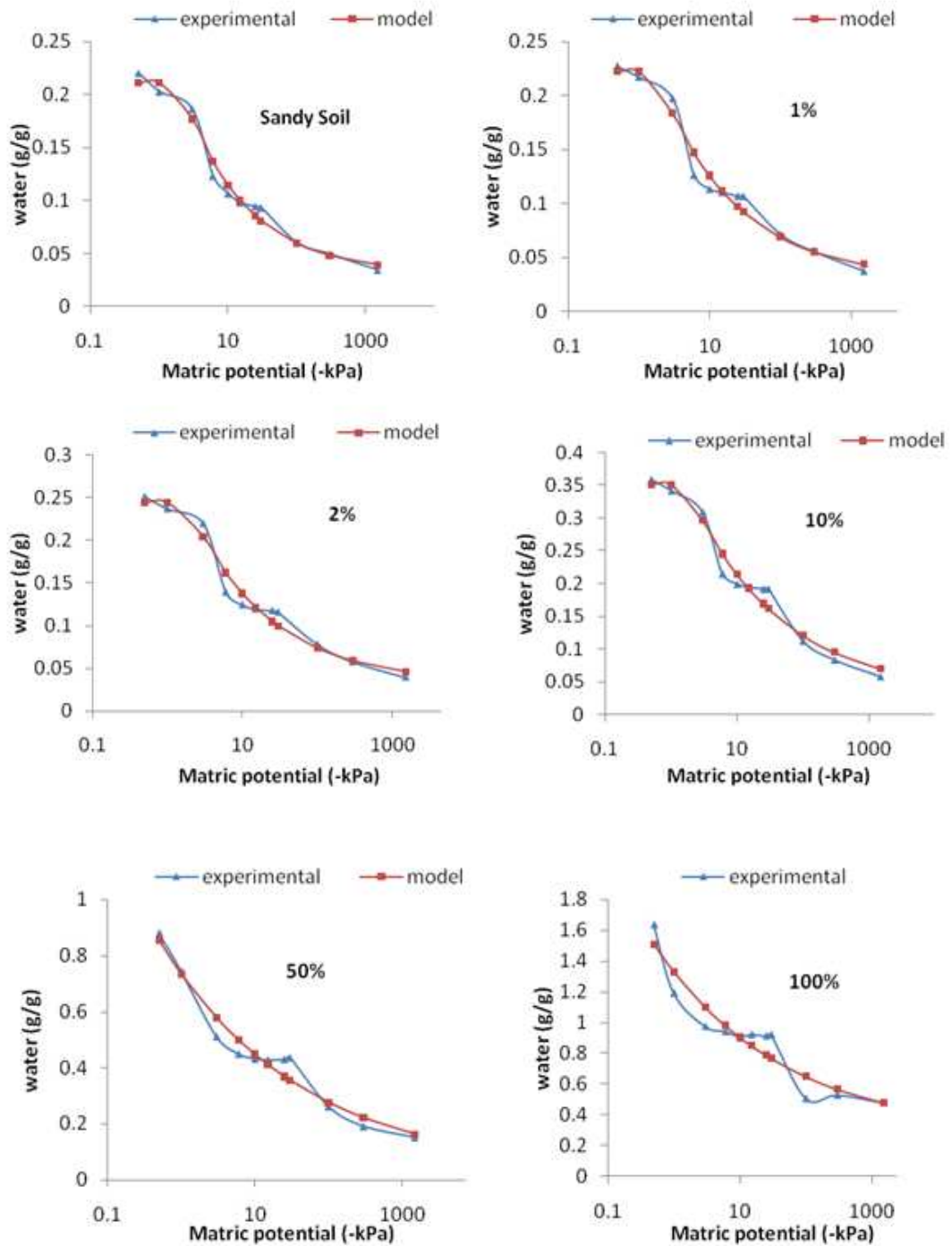


Figure 2.4. Gravimetric water release characteristics for all 200kPa compressed sandy soil/char mixes fitted to a van Genuchten model. Percent figures on the graphs represent the level of char addition by weight.

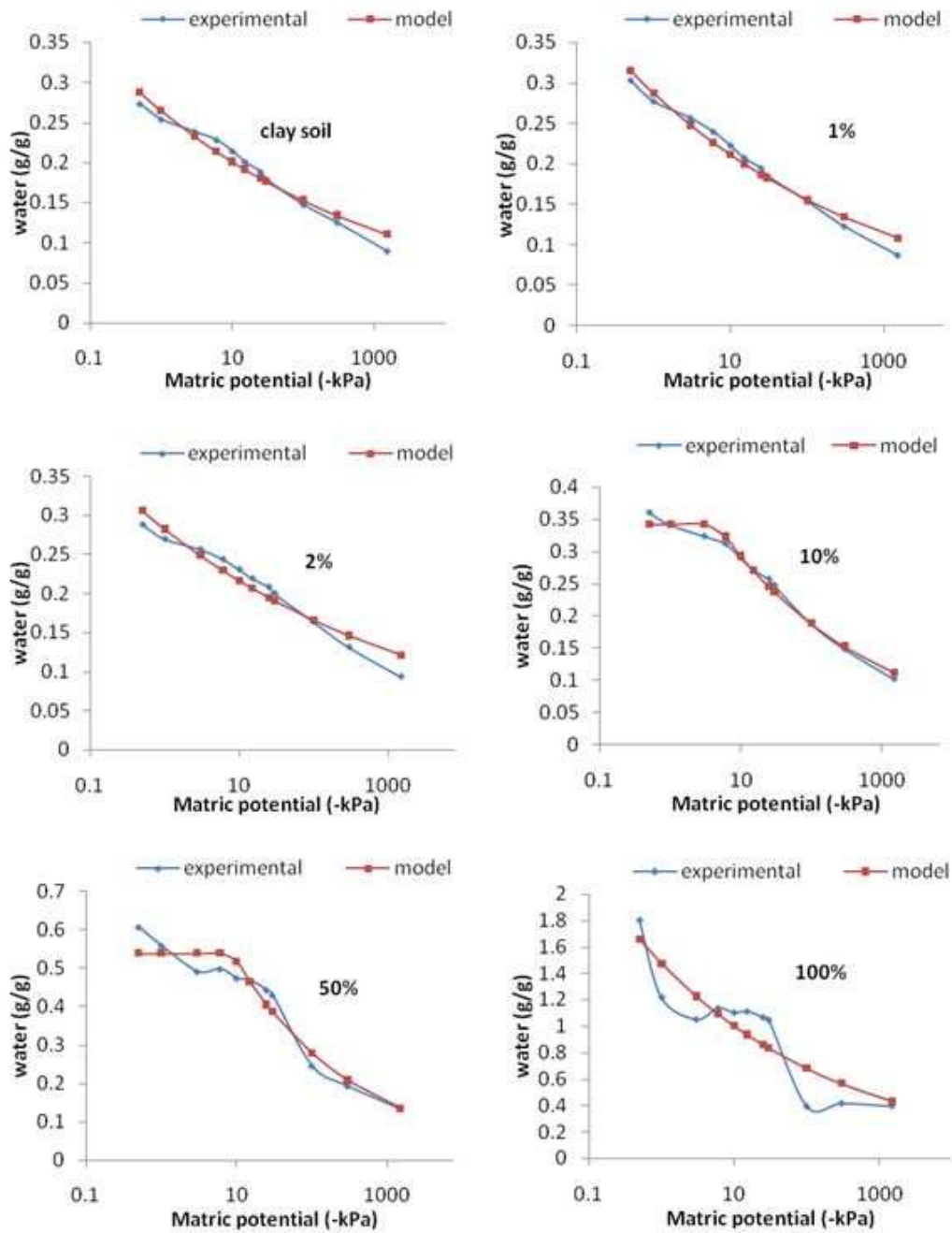


Figure 2.5. Gravimetric water release characteristics for all 200kPa compressed clay soil/char mixes fitted to a van Genuchten model. Percent figures on the graphs represent the level of char addition by weight

The curves obtained for 50 and 100% charcoal addition can be discarded due to the unwanted absorption of kaolinite described earlier in this chapter. The curves obtained for lower levels of charcoal addition exhibit an interestingly different

shape to those from the modelled data. There is a distinct step-wise reduction in water content with increasing matrix potential. This is particularly the case for the sandy soil mixtures, where water contents rapidly drop around -2 kPa, then level off somewhat at -10 kPa before rapidly dropping again around the - 30 kPa matrix potential. This finding is most likely due to the presence of different size pores in the charcoal which release water at different suction pressures.

## 2.5 Conclusions

This study showed that detailed water release characteristics can be obtained for charcoal/soil mixtures of up to 10% charcoal (by dry weight). The method was deemed not suitable for the concentrations of 50% and 100%, due to the unforeseen absorption of the kaolin paste by the charcoal fragments. Application rates in the published field experiments do not exceed 10 % (Rondon et al 2004; Yamato et al 2006; Steiner et al 2007; Kimetu et al 2008; Sinclair et al 2008) and so this lack of information was not considered a great loss. It has also been argued that generally, applications of around 2% are the most practicable with regards to cost-benefit and availability of feedstock (Steiner 2006).

As is to be expected, there is a significant relationship between % charcoal in the soil and porosity of the mixture. The overall increase in porosity upon charcoal addition is the most likely explanation for the increase in water retention capacity. According to IUPAC value ranges, charcoal has been reported to contain a large proportion of micropores ( $<2 \times 10^{-3} \mu\text{m}$ ) (Tseng & Tseng 2006), which would trap water held by capillary forces. Mesopores ( $2-50 \times 10^{-3} \mu\text{m}$ ) and macropores ( $>50 \times 10^{-3} \mu\text{m}$ ) known to be also contained within charcoal (Bornemann et al 2007) would potentially act in tandem with micropores as a water reservoir in the soil, releasing the water at different matrix potentials. These varying sizes of pores could possibly explain the step-wise nature of the water retention curves illustrated in this study.

This study also found that charcoal proportionally increases the water retention capacity more in sandy soil than in clay soil. This is to be expected as sandy soil is abundant with macropores which, as described by the British Society of Soil Science, can contribute to the rapid flow of water through soil by gravity. Clay on the other hand, exhibits an already high water retention capacity mostly due to the relative abundance of micropores.

The van Genuchten model can be fitted well to the data from these experiments allowing a predictive capacity for sandy soil/char mixes up to 10% char. The same cannot be said with such certainty concerning clay soil/char mixes due to the reported residual water content ( $\theta_r$ ) of 0 for the clay in table 2.5 (clay having a considerable residual water content). This as-of-yet unreported finding for sandy soil could be of great interest to agronomists with respect to drought mitigation strategies and responses to climate change-induced irregular rainfall patterns. This is of particular interest for sandy soils, as clay soils (especially compacted clays) are more likely to exhibit water-logging as opposed to water deficiency in agriculture.

There is however some ambiguity as to whether the unit measurement (g/g) or (g/cm<sup>3</sup>) reflects the true nature of the water retention results in this study. Although conclusions were unchanged with the sandy soil, a completely different story for the clay was apparent. This implies that a cautious approach should be taken when interpreting data from this method of investigation.

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### **3. CHARCOAL WEATHERING OVER A DECADE USING A CHRONOSEQUENCE**

#### **METHODOLOGY**

##### **3.1 Abstract**

X-ray Photoelectron Spectroscopy (XPS) was used to characterise charcoal fragments recovered from historical production sites of different ages. O:C ratios were calculated and used as an analogue to weathering extent in and around the separate fragments of charcoal. Results showed a significant difference in O:C of different ages ( $P < 0.05$ ), and it is only after the 5<sup>th</sup> year that any general increase in O:C. of fragment surfaces was recorded, but there was no significant relationship with the proportion any of the oxidised groups (C-O, C=O and COOH) and time of charcoal exposure ( $P > 0.1$ ). Root incursions were found to have a significant effect on the oxidation of the immediately surrounding material ( $P < 0.01$ ) suggesting that root exudates are oxidising the surrounding charcoal and thus play an important role in biochar decay. O:C was also shown to significantly reduce as one penetrates further into the charcoal fragment ( $P < 0.01$ ), with a more consistent degree of oxidation penetration along the central transport vessels of whole charcoal branches.

##### **3.2 Introduction**

Maintaining an adequate level of soil organic matter and nutrients cycling is crucial to the success of any soil management in the humid tropics. Cover crops, compost, or manure additions have been used successfully to supply nutrients to crops, whilst also helping to retain applied mineral fertilizers better (Goyal et al 1999). However, the benefits of such amendments are often short-lived in the tropics, since decomposition rates are high (Jenkinson & Ayanaba 1977) and the added organic matter is usually mineralised to CO<sub>2</sub> within only a few cropping seasons (Bol et al 2000).

Management of biochar may overcome some of these limitations and provide an additional soil management option. This study focuses on charcoal which, when utilised as a soil amendment is termed 'biochar'. Charcoal exhibits physiochemical properties potentially suitable for soil improvement as well as for the safe and long-term storage of carbon in the environment. Its beneficial functions relevant to this study are the pH alteration of acidic soils, and nutrient retention/release; and water retention: particularly in poorer-quality sandy or silty soils, the addition of charcoal has been demonstrated to enhance crop yield (as shown in the previous chapter).

The longevity of these reported beneficial properties of biochar is related to its physical and chemical stability in the soil, the influencing factors of which can be split into two categories: inherent chemical recalcitrance; and interaction with mineral surfaces. This study addresses both. As a way of investigating recalcitrance, O:C ratios have been shown to reflect the extent of oxidation and therefore decomposition of charcoal (Cheng et al 2006). This oxidation has been attributed towards both abiotic (Puri 1963, 1970; Billinge & Evans 1984; Adams et al 1988) and biotic processes (Shneour 1966; Baldock & Smernik, 2002; Hamer et al 2004), which have both been demonstrated in short-term experiments under laboratory conditions. There are also studies which describe the oxidation of charcoal over longer periods of up to a hundred years (e.g. Nguyen et al 2008) in agricultural fields.

This study aims to fill a gap in the research by providing a detailed snapshot of the first ten years of weathering under natural conditions, using X-Ray Photoelectron Spectroscopy (XPS) to determine elemental O and C ratios of whole charcoal fragments. To describe the interaction with mineral surfaces, XPS was also used to determine the relative elemental proportions of Al, Si & Fe present within the charcoal. Analysing samples from both the surface and the sub-surface (henceforth termed 'above-ground' and 'below-ground' respectively) of the soil allowed for a comparison between samples, thereby inferring the role of mineral interaction and soil biota with regards to charcoal ageing.

### **3.3 Materials and methods**

#### **3.3.1 Ghana**

The Wenchi municipality in the Brong Ahafo region of Ghana was chosen for fieldwork due to the reported use of slash and char agriculture. Assisted by the Agricultural Extension Service (AES), many visits to scores of farms and smallholdings within a 30km radius were carried out.

It was noted that despite there being no deliberate incorporation of charred material into the soil, many farms (especially in forest frontier lands) produced their own charcoal from felled hardwood trees, and many of these production sites remained undisturbed i.e. they were at the fringes of the plantations and had not been tilled and no crops had been planted on them. Since one of the original objectives was to investigate the change in properties of biochar over time, these charcoal (analogous to biochar) production sites became the focus of investigation.

#### **3.3.2 Study sites**

The study sites used in this work were located in Wenchi District, central Ghana in the Brong Ahafo region. This area falls within the forest-savannah transitional agro-ecological zone of Ghana, with an altitude of about 300 m above sea level and a mean annual temperature of around 26°C. The soils in the area (developed on Voltain sandstones) are mainly lixisols which are well-drained, friable and porous sandy loams. Nutrients are concentrated in the topsoil organic matter and the soil mineral matter has little capacity to supply or retain nutrients. The rainy season is from April to October with a short dry spell in August. The mean annual rainfall is 1271 mm with an average number of 107 rainy days.

From the many farms surveyed, one was deemed to be the most suitable for sample collection. This particular farm was at the frontier of a forested area, and the farmer had felled trees to make way for his maize, yam and cassava plantations. Charcoal was produced at the site of felling, and in each case the stump of the tree used remained beside the charring site. The farmer had a poorly 12 year old child, and had recorded what work he had carried out each year as well as events in his child's life. It was therefore possible to determine the age of a particular charcoal production site. This information was confirmed by repeat interviews and discussions with his wife.

Charcoal production sites within a ~1 km radius were located which could provide historic samples of charcoal (analogous to biochar) which had resided in the soil for up to 10 years. These samples were to become the foundation of work carried out in chapters 3 & 4 of this thesis.

### **3.3.3 Sample collection**

Fragments from past charcoal production sites in Ghana were collected for subsequent analysis. These production sites shared similar attributes: near identical soil type; same production method; hardwoods (of 3 different species of tree) used; the sites themselves were positioned to the side of any agricultural fields, and have been left undisturbed since the time of production. Charcoal samples from both the soil surface and sub-surface were taken as the differences between the two sets of samples could give insight into the role of soil in charcoal stabilisation. In addition, soils were collected from both the production sites and from nearby agricultural fields as reference materials.

A chronosequence methodology was applied to samples of increasing age, going back a maximum of 10 years for the charcoal fragments. The age of these samples was confirmed by one farmer who had been producing charcoal on his land with

roughly the same method since he had acquired the land. Potential variability of charcoal quality arising from this rough method is discussed at the end of the chapter.

The ages of charcoal samples collected were 2 months, 1 year, 1.5 years, 2 years, 3 years, 4 years, 5 years, 7 years, 8 years and 10 years old. There were three separate sub-sets of samples aged 3 years (i.e. the farmer made three batches of charcoal at different sites within the same month) which were collected to potentially investigate the variability between different species of hardwood tree.

Plate 3.1. Future charcoal production site.



A felled tree (in this case a cashew), is cut into ~3m segments with a chainsaw and heaped in a pile to dry for at least one dry season. A small fire is then lit at the base, and the whole mound covered first with fresh leaves and then smothered with a layer soil. The smouldering fire is then left for a minimum 3-4 days or until the smoke stops. The charcoal will then be bagged up and sold to a local charcoal merchant or shared between family and friends for cooking.

Plate 3.2. Past charcoal production site with the stump of the tree used



As with all other sites, this 2-year old site at the side of the field had been left untouched since its use. Charcoal fragments remain on the surface, as well as mixed in with the scorched soil below. Only a few plants were able to grow on the scorched soil of sites 2 years old or younger. Surrounding each of these sites however, was abundant fungal and visibly lush vegetation growth akin to ‘fairy circles’ found around cowpats in UK arable grassland. At sites older than 2 years, the soil had recovered to a more natural state, exhibiting similar properties to the surrounding farmland. The implications of these varying soil types are discussed in detail at the end of this chapter.

A second visit to this site a month later (plate3.3) revealed a use for this previously barren spot. This farmer planted watermelon around the perimeter of the site, stating that melon grew best there and the warmth from the black surface sped up the ripening of the fruits.

Plate 3.3. Watermelon spreading across the charcoal production site



All sites aged 3 years and over had subsequently overgrown with either the ubiquitous elephant grass or a local weed called acheampong (see plate 3.4).

Plate 3.4. Three years of fallow plant growth



Plate 3.5. Photographs of charcoal fragments recovered from the soil subsurface showing the various cracks and fissures which facilitate the penetration of oxidation.



The photographs above in plate 3.5 depict typical examples of charcoal fragments used in this study. Top left shows the curved outer surface of an intact branch with a deep fissure penetrating its interior. Top right shows the white streaks of fine root incursions along pre-existing plant structures which are shown in this study to have an effect on the surrounding level of oxidation. Bottom left illustrates the cracked surface which is a dominating feature of all fragments recovered, and bottom right shows how these cracks become encrusted with soil. All these features were investigated with regards to their influence on the overall oxidation of charcoal in the soil.

### **3.3.4 Sample preparation**

As can be seen in Plate 3.5, most of the charcoal fragments recovered from agricultural lands showed varying degrees of soil and organic matter encrustation.

This was found to interfere too strongly with the intended analysis – obtained peaks were shifted and distorted, which was reflected by the considerable presence of e.g. aluminium, iron, silicon and calcium. It was therefore decided that this mineral material would need to be removed prior to analysis. This was carried out by very light brushing and rinsing with de-ionised water. Care was taken to ensure no removal of the upper layer of charcoal occurred. Subsequent microscopic investigations proved this to be an adequate method – this being confirmed by the lack of mineral peaks found on the surfaces after cleaning.

### **3.3.5 X-ray photoelectron spectroscopy (XPS)**

XPS was used to characterise both the surfaces of charcoal fragments and finely milled powders to give bulk properties of the same fragments. XPS measurements can probe a maximum sampling depth of 10nm and therefore provide information regarding surface properties. XPS was also used to characterise transects running into the centre of fragments, as well as areas around root incursions (see figure 3.1 below). XPS measurements were performed using a system that uses a focused monochromatic Al K $\alpha$  X-ray (1486.7 eV) source and a spherical section analyser. The instrument has a 16-element multichannel detector. The X-ray beam was 100W and 40 $\mu$ m wide, and was incident normal to the sample. Narrow scan, high-resolution spectra of C1s, O1s, Fe2p, Al2p and Si2p were collected using a pass energy of 48.75 eV.

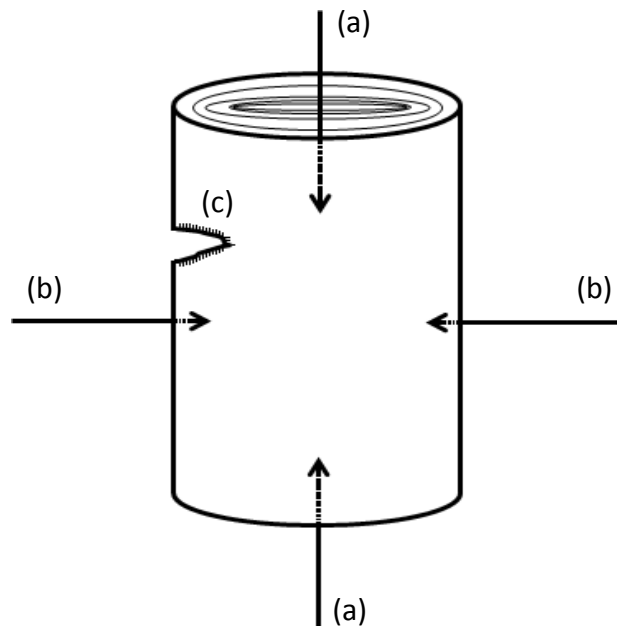


Figure 3.1. Graphic illustration of three oxidation pathways on a charred branch of hardwood: (a) Tangential section along the naturally porous transport channels running through the branch; (b) Transverse section through the outer layers of bark; and (c) around cracks and fissures which break the surface of the charred material.

### 3.3.6 Quantification of elemental proportions and C species from XPS spectra

XPS spectra were peak-fitted to separately identify C-bonded O species and different C forms. This was achieved using a non-linear least squares curve fitting program (as described in Cheng et al 2006), with a Shirley background correction on regions from 280 to 295 eV. The C1s binding energy of aromatic C (C-C, C=C and C-H) was assigned at 284.6 eV. A shift of 1.6 ( $\pm 0.15$ ), 3.0 ( $\pm 0.15$ ) and 4.5 ( $\pm 0.1$ ) above 284.6 eV was defined as C-O, C=O and COO respectively (as per Proctor & Sherwood 1982 and Cheng et al 2006). Identical Full-Width Half Maximum (FWHM) values were set at 1.88, 1.53, 1.60 and 1.76 for peaks at 284.6, 286.2, 287.6 and 289.1 eV respectively. These values were determined from measurements of 96 separate samples.

### **3.3.7 Statistical analysis**

Statistical data analysis was carried out using Genstat (16.1). Standard linear regression analysis was performed to calculate regression coefficients and their 95% confidence intervals. The *F* statistic and *p* value were used to signify the relationship between age of charcoal fragment and extent of surface oxidation. A normal distribution of data was checked before ANOVAs were applied and analysis of residuals was used to determine outliers. Significant differences in measurements between charcoal fragments of different ages were then tested using one-way analysis of variance (ANOVA) with blocks. Any outliers found were subsequently excluded from the analysis. Age effects were deemed significant if  $p \leq 0.05$  unless otherwise stated.

## **3.4 Results and discussion**

### **3.4.1 O:C of charcoal surfaces and milled fragments along a chronosequence**

The ratio of oxygen to carbon will theoretically increase over time due to the slow oxidation of the chemically recalcitrant carbon structures in the charcoal. XPS analysis was carried out to investigate how this oxidation progressed over a period of ten years. XPSPEAK 4.1 software was employed which gave an output listing the relative proportions of carbon and oxygen in the sample, thus enabling the calculation of oxygen to carbon ratios (O:C).

An initial round of analysis was carried out on charcoal samples recovered from belowground. Three fragments from each age subset of samples were selected at random. Three different surfaces of each fragment were analysed, giving a total of nine results for each age of sample. This was done to ascertain whether there was a relationship between the surface chemistry of charcoal fragments and how long they had been exposed to the environment.

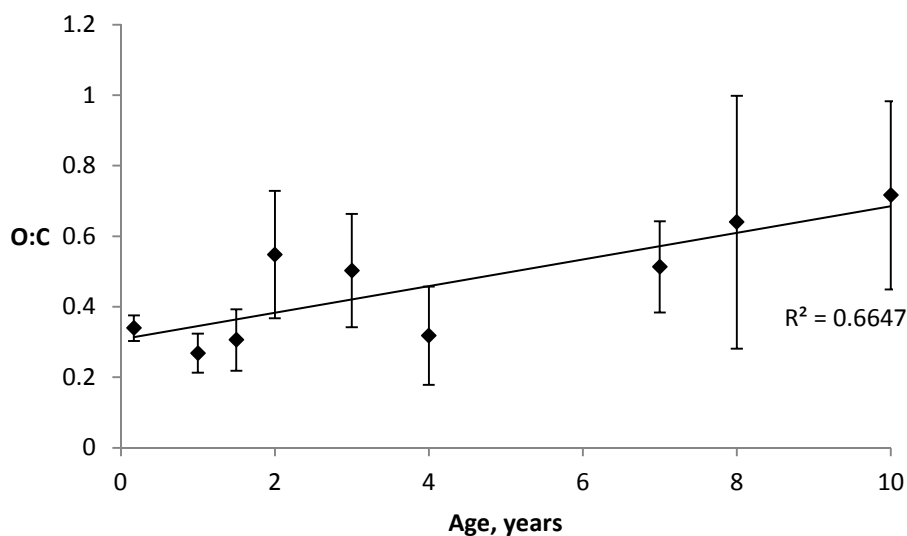


Figure 3.2. The change in O:C of charcoal fragment surfaces over a decade. Three fragments of each age were analysed in triplicate except the 3 year old sample which consisted of 9 separate fragments from three different sites. Error bars denote standard deviation around the mean of 9 analyses.

Figure 3.2 highlights the high variability of O:C on the surface of charcoal fragments which is at its greatest for samples of a greater age e.g. the relative standard deviation (RSD) of 9 analyses of the 8 and 10 year old sets was 56% and 37% respectively. Only the samples of fewer than two years of age showed a RSD of below 30%, with the youngest sample exhibiting the least variance with 11%. A one way ANOVA test revealed that there is a statistically significant difference in O:C between the fragments of different ages ( $P= 0.012$ ), and a gradual trend of increasing O:C with time.

The high variance between replicates however led to some concern. From visual observation, it became apparent that the analysed surface was not necessarily the surface that had been exposed to the environment since the day the charcoal was produced e.g. a ten year-old sample could have fragmented in the soil after just 4 years thereby exposing a 'fresh' surface which subsequently would have only been exposed for 6 years. Therefore a more selective sampling process was carried out.

Further analysis was carried out only on the curved surface of charcoal fragments which were derived from whole branches of wood. That way, the above-mentioned fragmentation effect could be minimised.

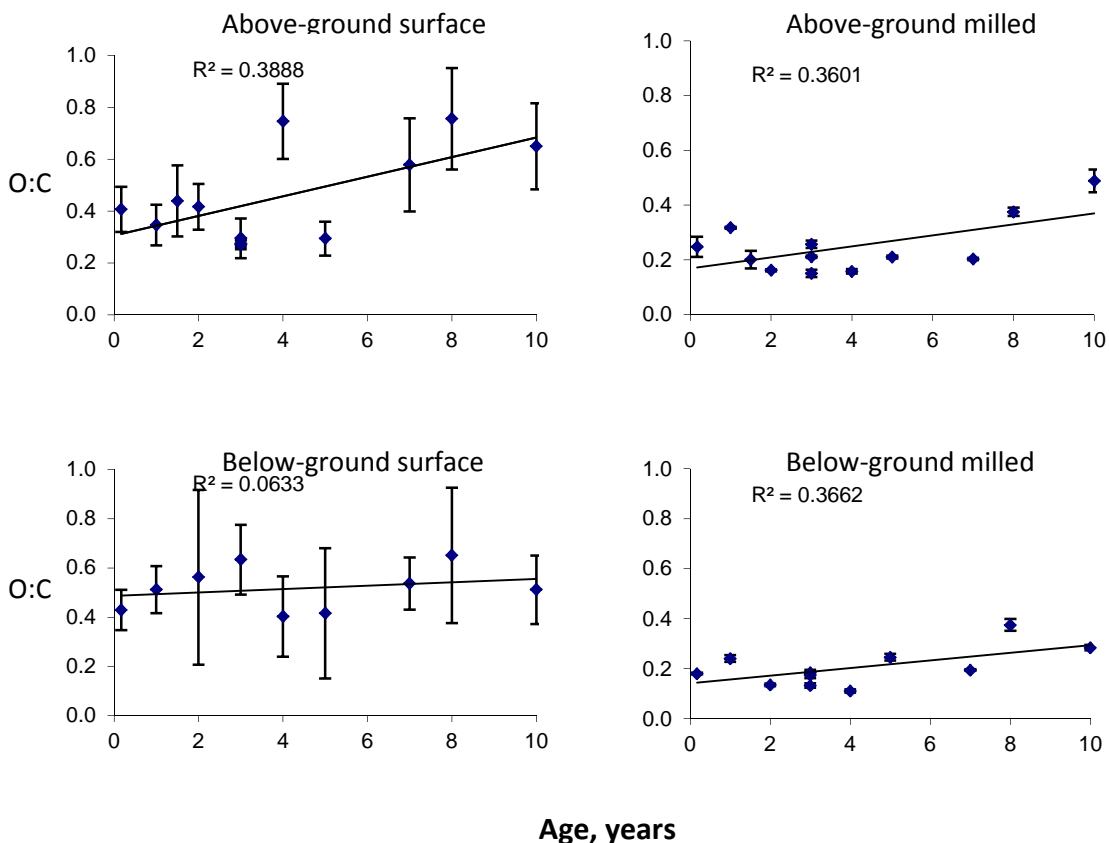


Figure 3.3. O:C ratios of charcoal fragments of increasing age. The top graphs are from charcoal recovered from above-ground, and the bottom graphs are from below-ground samples. Error bars show standard deviation around the mean of 9 analyses.

The same variability seen in figure 3.2 was also exhibited when analysing the surfaces of whole branches of charcoal recovered from belowground, reflecting their inherent heterogeneous nature. The replicate results for belowground fragments in figures 3.2 and 3.3 show a mean RSD of 31% and 37% respectively. The mean RSD for above-ground replicates however, is lower at 21%. A similar pattern is not observed for the milled sample results which show very little variability (with a

mean RSD between replicates of 5%), reflecting the more homogenous nature of a sample which has been milled and mixed thoroughly.

General trends over the entire 10 years are not clear from these results as the low  $R^2$  values indicate. The first 4 years give very noisy data, and it is only after the 5<sup>th</sup> year that any general increase in O:C. One way ANOVA analysis between all replicates shows a significant difference in O:C of different ages ( $P < 0.05$ ), but linear regression shows a weak relationship between O:C and age of sample.

To illustrate the potential differences between charcoal fragments recovered from both above- and belowground, table 3.1 below lists a summary of the differences in O:C.

Table 3.1. Comparison of oxidation levels of both surface and sub-surface recovered charcoal fragments.

Age (years)	O:C ratios					
	Aboveground		Belowground		Difference	
	surface	milled	surface	milled	surface	milled
0.17	0.43	0.18	0.41	0.25	0.02	-0.07
1	0.51	0.24	0.35	0.32	0.17	-0.08
1.5	-	-	0.44	0.20	-	-
2	0.76	0.13	0.42	0.16	0.35	-0.03
3	0.62	0.16	0.28	0.21	0.34	-0.04
4	0.40	0.11	0.75	0.16	-0.34	-0.05
5	0.42	0.25	0.29	0.21	0.12	0.04
7	0.54	0.19	0.58	0.20	-0.04	-0.01
8	0.65	0.37	0.76	0.38	-0.10	0.00
10	0.51	0.28	0.65	0.49	-0.14	-0.20

Table 3.1 shows that charcoal fragments recovered from belowground are consistently very slightly more oxidised than their aboveground counterparts. This would infer that processes occurring within the soil have a stronger oxidation potential than simply being exposed to the atmosphere e.g. heterotrophic decomposition by soil bacteria and fungi as reported by Baldock & Smernik (2002). However, a two-sample t-test revealed that there was no significant difference

between aboveground and belowground O:C for both the whole ( $P>0.05$ ) and milled ( $P>0.05$ ) charcoal fragments.

Results from figure 3.2 show the heterogeneous nature of the charcoal surfaces as the levels of oxidation vary from one 200 $\mu\text{m}$  wide area to the next. This variability is vastly reduced when the sample is milled, and the O:C is much lower confirming the hypothesis that most oxidation is limited to the surface of the charcoal fragments (Lehmann et al 2009). To expand on this theory, this study investigated the 'depth' of oxidation penetration, along a transect of depth into the charcoal fragment (as described in Figure 3.1) and is reported in the following section of 3.4.5.

#### *Comparison of different tree species*

The charcoal samples collected comprised of three different hardwood species, known locally as 'Srono', 'Senya' and 'Kande'. Due to concern that these different woods would produce charcoals of different properties, a comparison analysis was carried out on XPS-derived O:C data. The only available samples to compare were the three 3 year old sets of samples which comprised two Srono trees and one Senya. Results from the surfaces of both above- and belowground fragments were pooled, as well as the results from the milled charcoal powders.

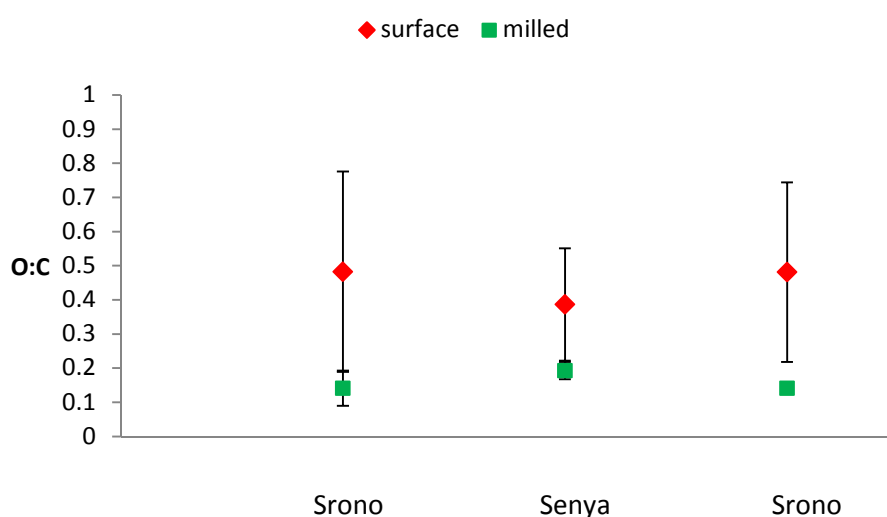


Figure 3.4 An O:C comparison of three different sub-sets of samples of the same age. Error bars denote standard deviation around the mean of 18 analyses.

There was found to be no significant difference in O:C of fragment surfaces or milled powders between the different types of tree. This implies that the type of tree should not significantly influence any investigations into physico-chemical properties over time, but it should also be noted that a very high variability in fragment surface results could be masking any underlying trends. This is also a very small set of samples, and so any differences found could simply be due to natural variation e.g. in charcoal production conditions. A much larger set of analyses of the three species of tree covering all ages would therefore help to iron out any variation and allow more definite conclusions to be made.

### **3.4.2 Relative proportions of different functional groups on surfaces and milled charcoal fragments**

A more detailed picture of the nature of the observed oxidation was gained by peak-fitting the XPS spectra to reveal the % relative contribution of four different functional groups. Group parameters (FWHMs) are listed in section 3.3.6 of this chapter and follow those employed by Cheng et al (2006). The spectrum in figure 3.5 below illustrates the output of the XPSPEAK 4.1 software employed to analyse the XPS peak data once the FWHM values had been manually entered. The light blue line along the top of the figure is an indicator of goodness-of-fit, the dark blue line is the running average of the jagged red signal line, the orange line is the fitted-peaks and the green line is the base signal.

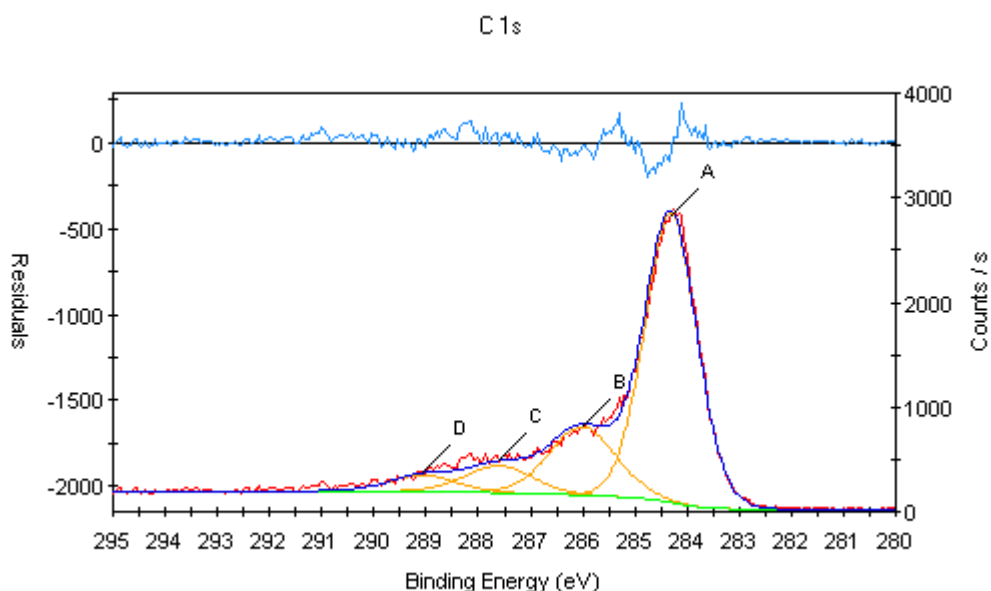


Figure 3.5. XPS spectrum of the C1s electron on the surface of a 6 year old fragment of charcoal. 'A' denotes C-H; 'B' is C-O; 'C' is C=O; and 'D' is COO.

The results show the overall proportional dominance of aromatic-C (C-H) in all samples as denoted by the strong signal at peak 'A'. Reflecting the O:C results, greater proportions of oxidised carbon groups are to be found on the surfaces of all charcoal fragments than in the bulk results of the milled fragments. This confirms the argument of Lehmann et al (2009) who hypothesised that oxidation of biochar would be mainly confined to the surface of the fragments.

Table 3.2 below lists the mean relative abundance of the different groups in all samples as well as the associated variance in results from the nine XPS spectra for each age of sample.

Table 3.2 Percentages of functional carbon groups present on the surface and within milled charcoal fragments showing standard deviation (SD) around the mean of 9 analyses.

Age, years	Group	above ground surface		aboveground milled		belowground surface		belowground milled	
		mean %	SD	mean %	SD	mean %	SD	mean %	SD
0.17	A	61.3	7.2	74.4	2.2	68.0	3.6	88.0	3.6
0.17	B	19.3	2.9	15.4	1.8	16.0	3.7	0.0	0.0
0.17	C	15.2	4.9	7.1	1.3	10.9	2.6	11.1	3.6
0.17	D	4.2	2.4	3.2	0.1	5.2	3.0	0.9	0.0
1	A	58.8	4.7	79.3	3.8	66.4	7.5	72.8	6.3
1	B	19.8	4.3	7.3	4.1	18.0	4.0	13.7	5.9
1	C	11.2	1.8	8.7	0.9	9.2	2.4	8.8	0.8
1	D	10.1	2.4	4.8	0.8	6.4	1.6	4.6	1.1
2	A	59.4	11.5	88.5	2.5	70.2	1.8	90.1	1.4
2	B	23.4	9.6	0.8	1.1	15.6	1.8	0.0	0.0
2	C	12.3	3.7	7.1	1.2	8.8	0.7	7.1	0.9
2	D	4.9	2.6	3.5	1.0	5.5	0.6	2.8	0.5
3	A	49.5	4.5	86.9	4.1	64.8	2.4	79.3	2.0
3	B	25.6	1.5	1.9	2.1	19.0	2.7	10.5	1.7
3	C	15.3	2.5	7.5	0.5	9.5	1.1	5.8	0.3
3	D	9.6	1.1	3.6	1.5	6.6	1.4	4.5	0.6
3	A	56.1	2.4	79.4	0.0	62.3	4.9	88.3	6.2
3	B	22.3	4.2	12.9	0.0	19.6	4.5	0.0	0.0
3	C	13.5	4.5	5.4	0.0	11.7	2.2	9.9	6.1
3	D	8.1	1.7	2.3	0.0	6.4	2.0	1.9	0.1
4	A	59.0	7.2	90.1	0.3	53.3	5.1	84.8	1.0
4	B	15.2	2.6	0.0	0.0	15.7	4.1	0.0	0.0
4	C	15.2	3.2	7.0	0.6	18.9	2.3	14.1	0.3
4	D	10.5	4.2	2.9	0.4	12.1	3.2	1.1	1.0
5	A	63.2	9.9	86.9	0.9	70.1	7.2	69.7	4.3
5	B	13.0	2.8	1.4	0.8	13.7	5.5	17.1	3.0
5	C	16.4	8.5	7.3	0.6	10.7	3.4	7.2	0.4
5	D	7.5	2.8	4.4	0.2	5.6	1.7	6.1	0.9
7	A	50.7	7.8	78.3	1.5	63.6	7.6	95.8	1.7
7	B	21.3	4.4	10.4	0.9	19.8	5.5	0.0	0.0
7	C	19.5	5.0	6.4	0.6	11.9	1.6	4.1	1.9
7	D	8.5	4.9	5.0	0.5	4.7	3.0	0.1	0.2
10	A	58.1	12.7	84.5	1.8	66.0	2.9	86.3	0.0
10	B	14.1	3.6	0.0	0.0	15.2	3.3	0.0	0.0
10	C	17.4	4.5	13.0	1.1	14.8	2.1	12.2	2.0
10	D	10.4	4.9	2.5	1.1	4.1	1.8	1.6	0.3

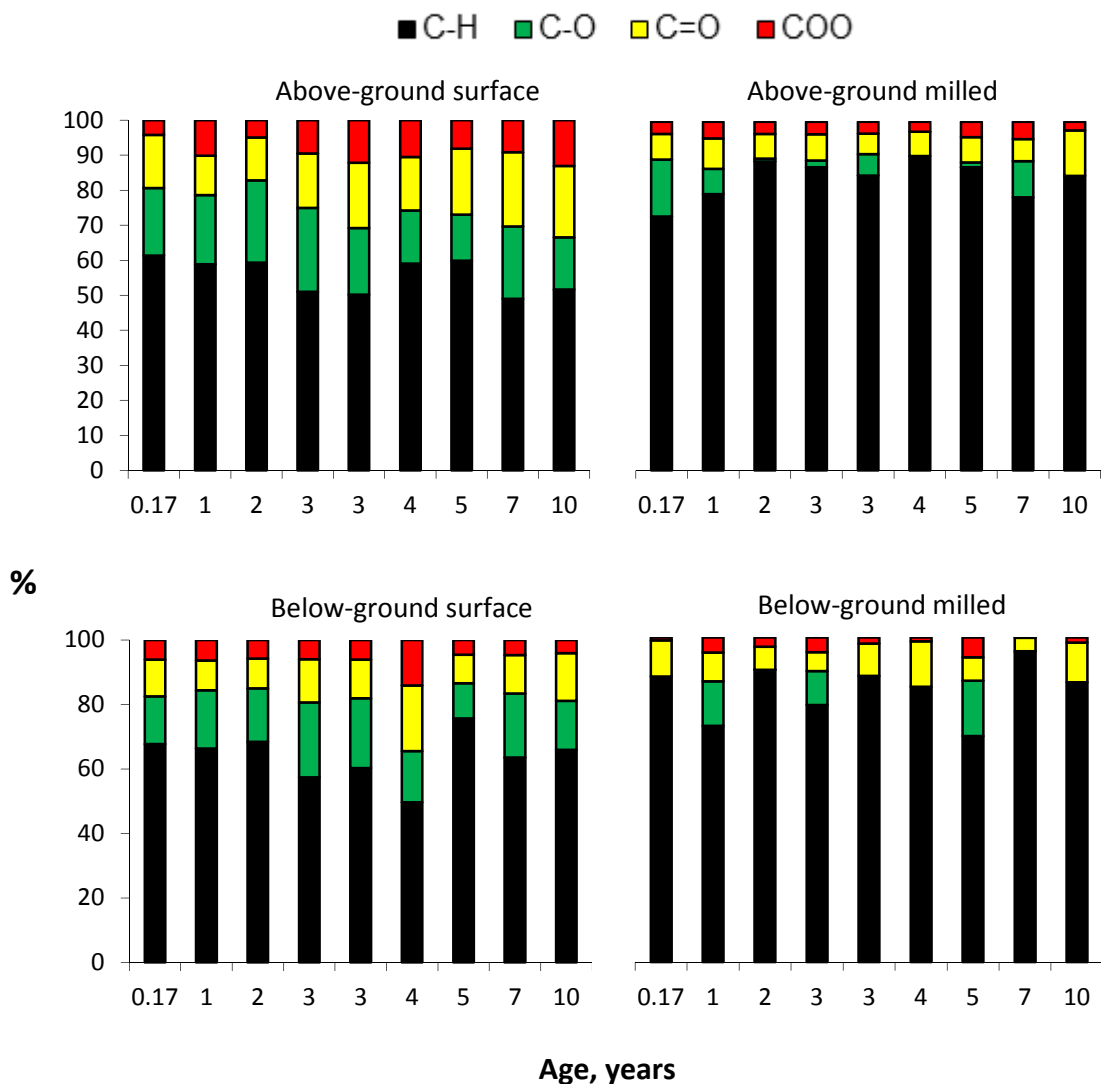


Figure 3.6. Percentages of functional carbon groups present on the surface and in milled charcoal fragments recovered from above-ground (top) and below-ground (bottom).

There is no statistically significant difference between samples recovered from below- and above-ground with regards to the functional groups present ( $P > 0.1$ ). Simple regression analysis also reveals there to be no significant relationship with any of the oxidised groups over time ( $P > 0.1$ ). Most surprising is the 7 and 10 year old milled charcoal fragments from belowground which exhibit the lowest proportion of oxidised groups of all the ages. This does not concur with the XPS data presented in figure 3.3, and will be discussed at the end of this chapter.

There is however, a significant difference between the level of non-oxidised carbon (C-H) between aboveground and belowground samples ( $P < 0.05$ ). Table 3.2 below lists a summary of a comparison between these two sets of samples.

Table 3.2. Comparison of the relative abundance of functional groups between above- and below-ground samples. 'Difference values' are achieved by subtracting the 'below ground' result from the 'above ground'. Standard deviation values are derived from the mean of 9 analyses.

Group	% Contribution					
	Above ground		Below ground		Difference	
	Surface	Milled	Surface	Milled	Surface	Milled
C-H	58.01± 3.37	83.71± 1.35	64.95± 2.26	83.88± 2.27	-6.94	-0.17
C-O	18.50± 2.13	4.81± 1.44	16.95± 1.22	4.59± 2.08	1.55	0.23
C=O	15.13± 2.06	7.76± 0.32	11.82± 0.81	8.92± 2.04	3.31	-1.16
COO	8.36± 1.22	3.71± 0.44	6.28± 0.89	2.62± 0.44	2.08	1.10

### 3.4.3 Elemental proportions of Al, Si and Fe on and within charcoal fragments

Encrustation of biochar fragments with minerals is frequently visible in the soil (Lehmann 2007). A rapid association of biochar surfaces with soil minerals containing aluminium, silicon and iron within the first decade of incorporation in to the soil has also been reported (Nguyen et al 2008). It is however not clear whether these interactions are lending more stability to the biochar by reducing surface oxidation and thereby decomposition.

It was therefore deemed of interest to investigate whether charcoal fragments collected in this study exhibited any relationship between mineral association and level of oxidation. Figure 3.7 below illustrates the levels of Al, Si and Fe found on the surfaces of charcoal fragments using XPS.

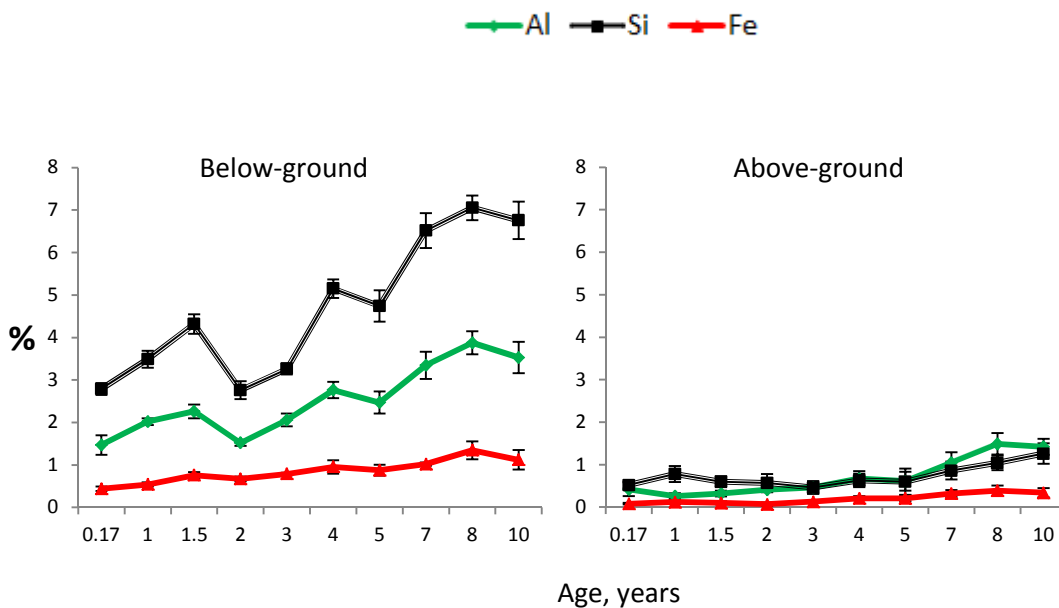


Figure 3.7. Proportional amounts of elements found on the surface of a charcoal fragment recovered from the soil-subsurface (left) and surface (right). 100% constitutes C, O, Al, Si and Fe from XPS spectra. Error bars denote the standard deviation around 9 analyses.

A clear difference between samples from above- and under-ground was measured for the presence of aluminium, silicon and iron. Figure 3.6 above illustrates how, over time, the levels of all three elements increase. These elements are either adsorbed onto the charcoal surfaces, or bound ionically to the acidic functional groups such as COO.

There were no significant amounts of Al, Si or Fe on the milled fragments (<0.1% collectively), confirming that the mineral presence is chiefly restricted to the surfaces of charcoal fragments. The significance of this find will be discussed at the end of this chapter.

#### 3.4.4 The influence of root incursions on O:C

Biochar can be metabolised by microorganisms and heterotrophic decomposition has been reported to be the most important mechanism of biochar decay (Schneour 1966; Baldock & Smernik 2002; Brodowski 2002). Bacteria and fungi have been

detected on the surfaces and in the pores of biochar (Laird et al 2008) and it is known that white-rot fungi can metabolise coal and wood (Hofrichter et al 1999). Abundant extracellular enzymes found in white-rot fungi have also been shown to degrade biochar (Hockaday 2006).

These are the only reported biological influences on biochar decay, and it was therefore of great interest to observe that many fragments of charcoal contained root hairs within their porous structure. Roots ranging from 200µm to 1mm had penetrated their way into the interior of the fragment, often following channels within the natural structure of the original tree.

Plant roots are known to exude a wide variety of compounds which can regulate the soil microbial community in their immediate vicinity and also change the chemical and physical properties of the soil (Nardi et al 2000). It was therefore hypothesised that there would be an effect on the biochar oxidation level in areas immediately surrounding the root hairs, thus influencing overall biochar decay in soil systems.

Charcoal fragments were cut open and observed under the microscope for evidence of root hairs. Three fragments of different ages recovered from under-ground which exhibited clear root incursions were analysed with XPS to reveal the contribution of roots to the oxidation of charcoal interiors. A fine X-ray beam of 40µm together with the microscope built in to the XPS instrument were used to target specific areas. With each sample, three areas at least 4 mm away from the root were analysed (avoiding the exposed oxidised surfaces), together with three areas immediately surrounding the root (without targeting the fine root hairs themselves) to give the following results:

Table 3.3. Summary of XPS-derived O:C showing the increased oxidation around root incursions. Standard deviations result from 3 separate analysis points on each fragment.

Age, years	O:C of charcoal Interior	O:C of area around root	O:C increase at root
1	0.40 ± 0.02	0.59 ± 0.04	0.19
3	0.18 ± 0.04	0.38 ± 0.02	0.20
10	0.28 ± 0.01	0.52 ± 0.09	0.24

The root incursions found in three separate fragments of different age charcoals were found to have a significant effect on the oxidation of the immediately surrounding material (t-test,  $P < 0.01$ ). This supports the hypothesis that oxygen originating from the roots is oxidising the surrounding charcoal.

It was of interest to see how the effect of roots compared to the level of oxidation present on the exposed surfaces of the charcoal fragments. The surfaces of the three ages of samples were therefore analysed to give the following results:

Table 3.3. Summary of XPS-derived O:C showing the oxidation levels on the surface of charcoal fragments of different ages as well as around root incursions. Standard deviations result from 3 separate analysis points on each fragment.

Age, years	O:C of charcoal interior	O:C of area around root	O:C of fragment surface
1	0.40 ± 0.02	0.59 ± 0.04	0.35 ± 0.08
3	0.18 ± 0.04	0.38 ± 0.02	0.27 ± 0.02
10	0.28 ± 0.01	0.52 ± 0.09	0.65 ± 0.17

These results show that there is a significant difference ( $P < 0.01$ ) between the O:C of areas around root incursions and the O:C of charcoal surfaces. With exception to

the oldest 10 year old sample, the activity of the roots shows a greater oxidation potential than the charcoal being exposed to other environmental factors.

This oxidation in combination with root growth and expansion would contribute to the physical break-up of the fragment and exposure of more surfaces to potential degradation processes in the soil.

#### **3.4.5 O:C along a depth profile into individual charcoal fragments**

##### *Transverse section profile*

It has been reported that oxidation of biochar surfaces is limited to the outer layer exposed to the environment (Nguyen et al 2008). This was deduced from the fact that biochar fragment surfaces exhibit a higher level of oxidation than the results from a milled sample. There are no published studies which detail just how deep into a biochar fragment this oxidation occurs – vital information when predicting the potential decay of biochar in a soil system.

As described in figure 3.1 (b), the following results describe the extent of oxidation penetration along a transverse section or ‘horizontal’ profile i.e. from the outer bark to the core of the fragment. As a preliminary analysis, one of the oldest available samples was analysed using XPS. Single analysis points penetrating progressively deeper into the centre of the fragment reveal the following results:

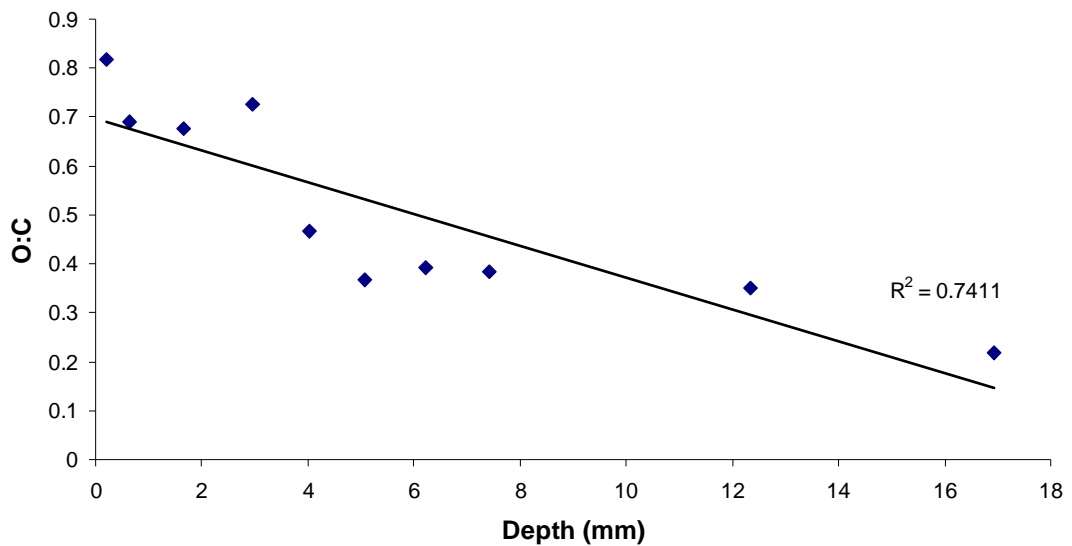


Figure 3.8. Oxidation penetration (shown by O:C) into a single 10-year-old charcoal fragment with a radius of ~18mm recovered from belowground.

Results from this analysis demonstrate that in this one fragment, oxidation is indeed generally limited to the surfaces, but will also penetrate further than expected due to cracks and fissures in the structure of the charcoal. XPS analysis of areas around root incursions also demonstrated an as-of-yet unreported biotic degradation of charcoal by plant roots – something which has previously only been shown with microbial incubation studies (Hamer et al 2004; Cheng et al 2008; Liang et al 2008).

Further analysis was subsequently carried out on charcoal fragments of all ages recovered from both above- and belowground. Figure 3.11 below is a preliminary illustration of the scatter of data.

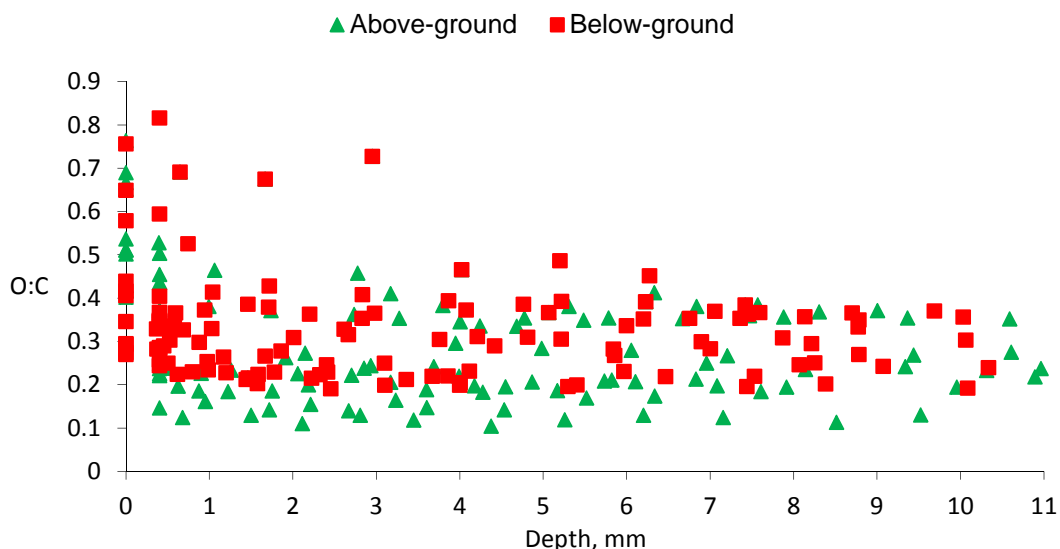


Figure 3.9. XPS data revealing the depth of oxidation for charcoal fragments of all different ages recovered from both above-ground (mean O:C = 0.33) and below-ground (mean O:C = 0.29).

The scatter in figure 3.9 illustrates the wide variability of results obtained from such samples. The above-ground samples exhibit some of the highest O:C ratios, and overall are significantly different ( $n = 122$ , mean =  $0.28 \pm 0.12$ ) than the below-ground samples ( $n = 132$ , mean =  $0.32 \pm 0.09$ ). Additionally, the above-ground samples show a minimum O:C of around 0.1, whereas the minimum below-ground ratio is around 0.2. This would again suggest that interaction with the soil leads to a greater extent of oxidation than being merely exposed to the atmosphere.

In order to investigate the relationship between depth and O:C further, data were collated into bins. Measurements at 0 – 1 mm depth were classified as '1', and 1 - 2 mm depth as '2' and so on, unto a maximum depth of 11 mm. The results were split into above- and belowground sets and are illustrated in the figure below.

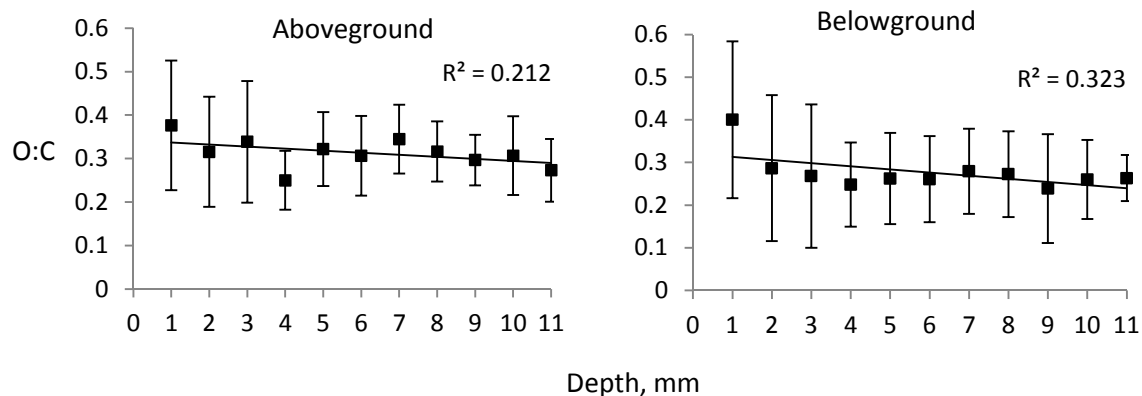


Figure 3.10. The relationship between XPS derived O:C values and depth into charcoal fragments recovered from aboveground (left) and belowground (right). Error bars denote standard deviation around the mean of at least 6 measurements.

There is a significant relationship between O:C and depth into fragment ( $P < 0.01$ ), with a general downward trend of O:C over depth as shown by regression analysis. There is however a large variability between replicates, especially between the 1 and 3 mm mark. This reflects both the heterogenous nature of biochar near-surfaces as well as the fact that there are many different starting points at depth 0 – 1 mm for the different ages of char e.g. the belowground O:C of the 1 year old sample starts at 0.40 on the surface, whereas the 10 year old starts at 0.65.

Carrying out statistical analysis on binned data such as this could confound the matter, and so it was deemed necessary to illustrate the data by separating out the different ages of charcoal as shown in figure 3.11 below. Again, the data points are from single measurements running along a profile in to the centre of each fragment. Replicate analysis at each depth would have been preferable, but time constraints on use of the XPS instrument did not allow this.

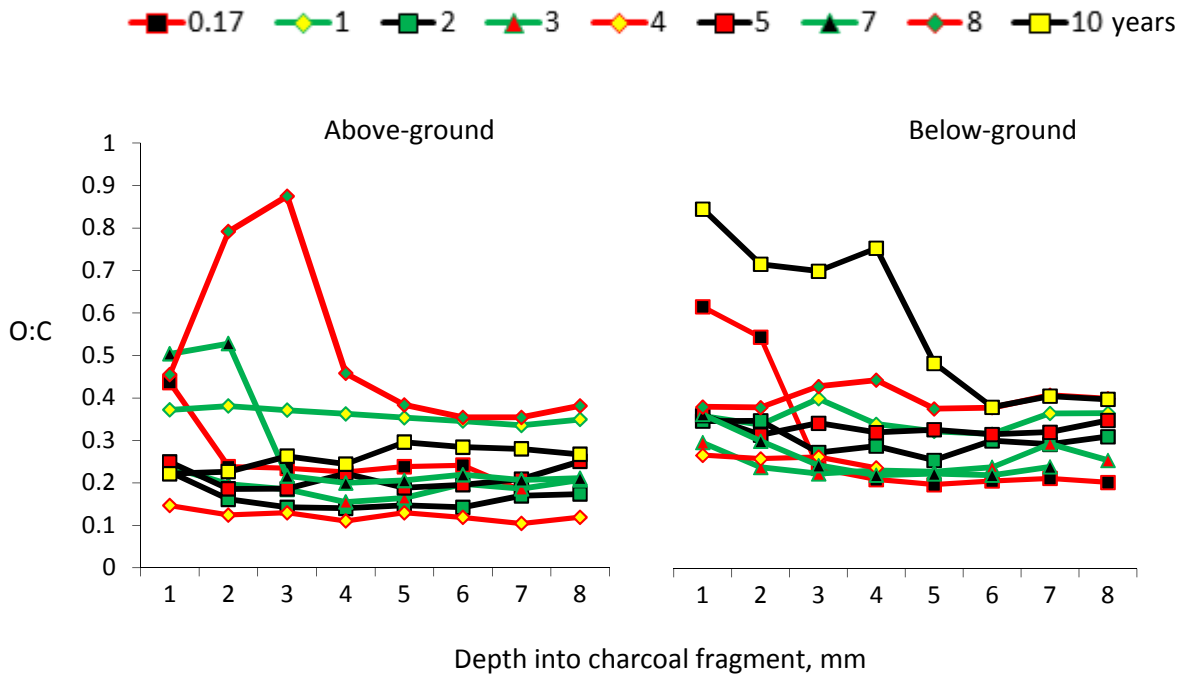


Figure 3.11. XPS data showing the relationship between depth into the fragment and O:C for charcoal of different ages recovered from above-ground (left) and below-ground (right). Ages in years of the charcoal fragments are listed in the top legend.

Again, there is a significant difference in O:C between Above- and belowground samples ( $P < 0.01$ ), with the belowground samples exhibiting an overall greater level of oxidation as mentioned before. The highest O:C are to be found at depths of under 4 mm, and there is no overall linear trend of a reduction in O:C as one progresses deeper in to the charcoal fragments. Possible explanations for this finding will be discussed at the end of this chapter.

#### *Tangential section profile*

As described in figure 3.1 (a), the following results describe the extent of oxidation penetration along a tangential or 'vertical' profile i.e. from the tip of an intact branch of charcoal into its interior.



Figure 3.12. Graphic illustration depicting the extent of oxidation in charred hardwood branches over time. Depth error margins represent the standard deviation around two analyses.

5 individual branch fragments of different ages from both above- and under-ground were analysed with XPS. Compared to penetration from the bark to interior, a much more consistent degree of oxidation penetration was observed when analysing along the central transport vessels of the charcoal branch. This is evident in the much lower variability in results shown in Figure 3.11.

It is shown that how year on year, the extent to which oxidation penetrated, from which a rough rate of 1mm per year can be estimated. Depth of oxidation was deemed to be the point at which no further increase in O:C occurred. Due to this relatively linear relationship between depth and oxidation penetration (when compared to depths along a profile described in figure 3.1b), it was deemed of interest to investigate the change in functional groups along a profile. The same methods described in section 3.4.2 were applied to estimate relative proportions of C-H, C-O, C=O and COO along the tangential profile. The results are illustrated in figure 3.13 below.

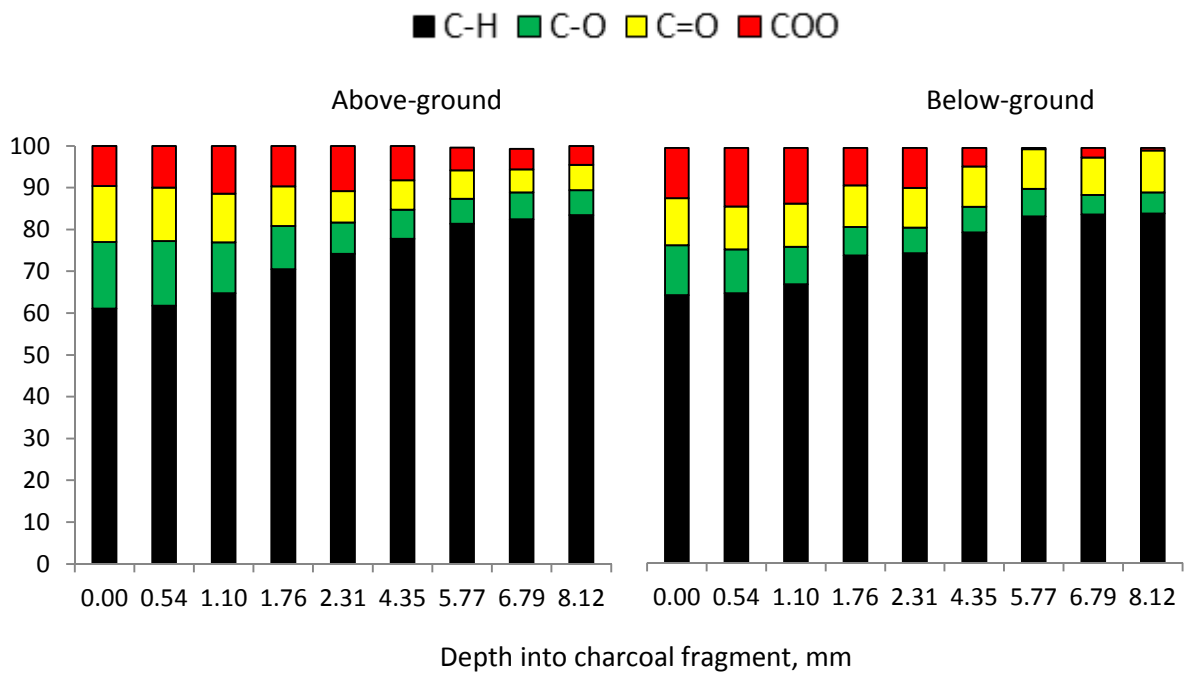


Figure 3.13. Relative proportions of functional groups along a vertical depth profile into charcoal fragments recovered from above- and below ground.

The results in figure 3.13 show a much more uniform progression with depth than those for the cross-section depth profile shown in figure 3.5. With depth, C-H increases as the oxidised groups decrease. This is in part due to the fact that all proportions are obliged to equal 100%, but this is not deemed significantly distort the story the data is telling.

The relatively uniform plant structures running vertically through a branch (xylem and phloem) were deemed to be the conduits along which oxidation processes could progress. Water contained within these structures will most likely provide a medium for both biotic and abiotic agents to travel within, allowing a more consistent penetration than that afforded by cracks and fissures in addition to plant structures found along a cross-sectional profile.

### 3.5 Further Discussion and Conclusions

An increase in O:C is observed for the 8 and 10 year old charcoal samples, but there is no evidence of a relationship between time up until that point and oxidation. Cheng et al (2008) report a rapid oxidation of biochar in the first few years of exposure to the soil, but describing the rate at which this occurs is not possible in this study. Charcoal has been shown to last for hundreds of years in the soil in other studies (Bird et al 1999; Cheng et al 2006; Forbes et al 2006; Liang et al 2008), and so it is possible that what we are observing here is just the 'noise' to be expected over a decade.

Oxidation is mainly restricted to surface of charcoal, but its physical structure affects the extent of oxidation, whereby physical weathering, soil interaction and root incursions all play a role in promoting subsequent degradation processes. The determination of the longevity of charcoal in the soil has been reported to be a very rough estimation indeed (Lehmann et al 2006), and is largely based on laboratory incubation experiments and conceptual models of decay (Baldock & Smernik 2002; Brodowski 2004; Hamer et al 2004). It is claimed that oxidation of biochar particles start at its surfaces (Cheng et al 2006) and typically remains restricted to the near-surface regions for several millennia (Lehmann et al 2005; Liang et al 2006; Cohen-Ofri et al 2007).

However, biotic factors are not taken into account such as the root incursions described in this study which was shown to increase the bulk O:C over just a short period of 10 years. Additionally, the increasing acidic functional groups could increase the hydrophilicity of charcoal and enhance further physical, chemical, and biological weathering, such as breaking and reducing its particle size, leaching to deeper soil horizons, and dissolution or export from the soil profile.

Minerals increasingly associate with charcoal surfaces over 10 years, but do not appear to affect the extent of oxidation over such a short period of time. Their reported role in masking the potentially beneficial properties of functional groups present on the charcoal surface (Glaser et al 2000; Brodowski et al 2005) is subject to further investigation in this study. There is however an uncertainty with the charcoal-associated minerals found in this study. It could not be proven with the methods employed whether they were adsorbed to the charcoal surfaces or whether there was simply soil encrusted in the pore spaces. Every care was taken to remove soil particles under a microscope at low resolution, but additional experimentation would be necessary (e.g. adsorption isotherm investigations carried out by Lehmann et al 2002) to substantially back up any claims of mineral interference.

A statistically significant difference in O:C between charcoal fragments recovered from above- and below-ground was found in this study. These differences highlight the fact that charcoal degradation is controlled by both abiotic and biotic processes to varying degrees. The relative contribution of biotic and abiotic mechanisms to biochar decay is still not known (Lehmann et al 2009), and this study cannot contribute to the current state of knowledge. For example, it became clear that the categorisation of charcoal fragments as being 'aboveground' samples was not sufficient to observe any significant differences between being fully or partially exposed to the soil. Especially in the older samples, fragments were actually embedded in the soil, with at least one surface fully exposed to any of the biotic soil processes described in the preceding chapters. Substantial conclusions cannot therefore be made regarding the effects of biotic vs. abiotic influences on charcoal oxidation.

A major weakness in this investigation is the lack of a '0' year old charcoal subset of samples. Without this, it is very difficult to attribute observed changes in surface chemistry to the effects of time. It is conceivable that observed variations in

charcoal properties are merely a result of variations in charcoal production conditions (temperature, oxygen supply etc), species of tree used or even which part of the original tree was analysed. There is however one piece of evidence that oxidation increases over a decade, and that is the experiment which found the increasing O:C along a transect described in figure 3.1a.

There is also a considerable amount of uncertainty regarding the XPS peak-fitting procedure which provided all the data regarding O:C, and more importantly the proportion of functional groups present (which required a greater level of interpretation). XPS spectra of charcoal surfaces showed a great deal of noise and the subsequent goodness-of-fit indicators were not as good as those obtained for milled (and therefore more homogenous) samples. Perhaps due to this uncertainty, no significant relationships were found, which subsequently negates any further avenues of discussion in the next chapter.

There is however an over-arching and previously unreported environmental significance to the results in this chapter. That being that there are no significant changes of the studied properties of charcoal over a period of ten years. What this means in an agricultural context will be the subject of the next chapter.

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## **4. The changes in soil functionality of charcoal over a decade**

### **4.1 Abstract**

The relationship between physical and chemical properties of charcoal from historical production sites of different ages with fertiliser retention in soil was investigated. Properties including functional groups (e.g. COOH), O:C and porosity were considered in conjunction with their effects on the retention of an inorganic fertiliser using soil leaching columns in the laboratory. After 12 successive water additions to mimic natural rainfall events, all charcoal treatments of different ages resulted in a reduction in the total amount of nitrate leached through the columns when compared to the control. Whole fragment/soil mixtures showed a mean reduction of  $26.4\% \pm 10.9$  ( $n = 30$ ) and milled charcoal/soil mixtures by  $23.6\% \pm 2.3$  ( $n = 30$ ). There was however no significant difference of  $\text{NO}_3$  reduction between samples of different ages ( $P > 0.05$ ), indicating that charcoal's ability to retain nitrate remains unchanged after 10 years of exposure to the soil.

### **4.2 Introduction**

A major problem related to highly-weathered oxisol soils in the Wenchi district of Ghana is a high rate of nitrogen leaching during episodes of heavy rainfall, leading to a contamination hazard in shallow groundwaters as well as being an undesired loss of nutrients to the farmer (Osei Adade, pers. comm.) Several options have been proposed for reducing nutrient leaching in agriculture. Lehmann et al (2003) proposed that nutrient leaching reductions are possible through either the application of slow-release forms of fertilisers, or increasing adsorption sites for longer retention of applied fertilisers.

The continuous application of fertiliser during the growing season, specifically timed to supply nutrients during crop growth stages of maximum water and nutrient uptake, has also been suggested as a means to combat increased nutrient leaching (Laird et al 2010). However, these options are all costly short-term solutions to the problem of mineral fertiliser leaching (Laird et al 2010).

Biochar has been suggested as an effective, long-term tool for reducing the adverse impacts of mineral fertiliser leaching on surface and groundwater quality (Lehmann et al. 2003; Steiner et al. 2008). The amendment of sandy soils with biochar is especially beneficial as research has shown it to provide greater water holding capacity (Tryon 1948 and chapter 2 of this thesis). Empirical evidence suggests that the retention of soil water with its associated dissolved nutrients, together with the increase in electrostatic adsorption sites is possible through biochar additions (Lehmann et al. 2003).

In recent years, most of the biochar research on nutrient leaching has been studied parallel to the application of either inorganic or organic N fertiliser sources. For example, Ding et al (2010) investigated the influence of bamboo charcoal (biochar) on N retention at different soil depths using multi-layered soil columns. It was found that biochar retained  $\text{NH}_4\text{-N}$  for a longer time period, providing evidence that biochar addition to soils may delay inorganic  $\text{NH}_4\text{-N}$  leaching, and thus benefit crops for optimal N utilisation. This would particularly be the case for the sandy soils of the study area where downpour events were responsible for rapid leaching of added inorganic fertiliser from the soil. It was reasoned that because charcoal has a highly porous structure, leaching of  $\text{NH}_4\text{-N}$  was reduced because of charcoal's adsorptive properties.

Recent studies have also been conducted on the effect of N leaching on organic N sources. Laird et al. (2010) found that the manure treated soils plus biochar reduced

total inorganic N ( $\text{NO}_3$  and  $\text{NH}_4$ ) leaching by 11 % in comparison to the manure treated soils receiving no biochar.

Biochar has been shown to possess great potential in reducing N losses by means of nutrient leaching experiments. These above-mentioned studies speculate on the responsible mechanisms for this, yet there is scant empirical evidence linking determined physico-chemical properties with nutrient retention. This study will attempt to make this link by quantifying the relationship between the measured parameters of porosity and O:C with the ability of soil/charcoal mixes to retain nitrogen.

### *Objectives*

The main aim of this study was to examine the effect of locally produced charcoal on potentially reducing or preventing leaching of inorganic fertiliser in a typical Ghanaian sandy soil. This will be carried out utilising a column-leaching method. Current data on the effect of biochar amendment on nutrient leaching through soils (reviewed by Warnock et al 2007) describes various explanations for the possible mechanisms of nutrient retention e.g. porous structure or adsorption sites. There is however no empirical evidence to quantify the relationship between physico-chemical properties of biochar and its ability to retain nutrients.

This study aims to fill this gap by selecting charcoals of known porosity & O:C properties and subjecting them to soil leaching experiments. In addition, this study will look at the leaching of nutrients contained in charcoal after application to the soil. The levels of plant available inorganic N remaining in the soil and charcoal-amended soil after the leaching period will also be investigated.

The agronomic benefits of fresh char added to the soil are well documented (Lehmann et al 2003; Downie et al 2007; Dünisch et al 2007), but the timescale of

biochar change in an agronomic context is not clear yet. This study will define the changes of specific properties responsible for soil improvement over a period of a decade. Those properties in question are:

- Particle and bulk density
- Oxidised functional groups
- Water retention characteristics
- Nutrient retention

### **4.3 Materials & Methods**

#### *Charcoal sample selection*

For practical reasons, nutrient leaching experiments were carried out using a selection of previously analysed charcoal fragments. The criteria for selection were: low variability of O:C from triplicate analysis using XPS (some samples provided such a wide range of results that they were not deemed appropriate for further investigation); equal representation of samples recovered from both aboveground and belowground; actual amount of charcoal available (there was simply not enough of recovered sample to enable triplicate analysis for some of the samples); and the range of properties of different samples needed to be as wide as possible in order to detect any potential influence on nutrient retention. The table below lists all the potential sample candidates, and those subsequently selected for this experiment.

#### *Charcoal*

Locally produced charcoal from known species of hardwood tree was collected. The charcoal was produced in the following traditional way: first, the tree is felled, sawed into ~ 2m sections and piled up at the side of the field and left for several

months; at the end of a dry season a small fire is lit at the base of the pile; once going, the pile is covered first with a layer of fresh leaves, then with a layer of soil to exclude air; the pile is then left for 2-3 days to smoulder until fully extinguished; most of the charcoal is exported for sale, leaving behind remnant fragments which were taken for analysis. Ten samples (from a possible 24) from these fragments were chosen to represent the full range of O:C and porosity values obtained through analysis, and are listed below in Table 4.1. Prior to mixing with soil, the charcoal fragments were cut into sections of roughly equal size (1cm<sup>3</sup>).

### *Soil*

Sieved (<4 mm) oven-dried (105°C) loamy-sand oxisol collected from agricultural fields in Wenchi District, Ghana.

Table 4.1. Properties of the candidate samples for experimentation. U/O denotes whether the sample was recovered from Belowground or aboveground.

Age, years	U/O	Surface O:C	Milled O:C	Porosity	Weight available, g	Source tree	To be used?
1	O	0.43	0.24	0.70	154	Srono	NO
<b>1</b>	<b>U</b>	<b>0.35</b>	<b>0.32</b>	<b>0.74</b>	<b>97</b>	<b>Srono</b>	<b>YES</b>
1.5	O	-	-	0.73	53	Senya	NO
<b>2</b>	<b>U</b>	<b>0.42</b>	<b>0.16</b>	<b>0.69</b>	<b>36</b>	<b>Senya</b>	<b>YES</b>
3	O	0.50	0.17	-	70	Srono	NO
<b>3</b>	<b>O</b>	<b>0.69</b>	<b>0.18</b>	<b>0.85</b>	<b>54</b>	<b>Senya</b>	<b>YES</b>
3	U	0.73	0.21	-	89	Srono	NO
<b>3</b>	<b>U</b>	<b>0.27</b>	<b>0.26</b>	<b>0.80</b>	<b>35</b>	<b>Senya</b>	<b>YES</b>
<b>4</b>	<b>O</b>	<b>0.40</b>	<b>0.11</b>	<b>0.89</b>	<b>40</b>	<b>Senya</b>	<b>YES</b>
5	U	0.29	0.21	0.80	72	Senya	NO

Table 4.1 continued

5	O	0.42	0.25	0.68	124	Senya	NO
<b>7</b>	<b>O</b>	<b>0.54</b>	<b>0.19</b>	<b>0.67</b>	<b>83</b>	<b>Kande</b>	<b>YES</b>
7	U	0.58	0.20	0.57	68	Kande	NO
<b>8</b>	<b>U</b>	<b>0.76</b>	<b>0.38</b>	<b>0.77</b>	<b>70</b>	<b>Kande</b>	<b>YES</b>
<b>8</b>	<b>O</b>	<b>0.65</b>	<b>0.37</b>	<b>0.70</b>	<b>112</b>	<b>Kande</b>	<b>YES</b>
<b>10</b>	<b>U</b>	<b>0.65</b>	<b>0.49</b>	<b>0.54</b>	<b>94</b>	<b>Kande</b>	<b>YES</b>
<b>10</b>	<b>O</b>	<b>0.51</b>	<b>0.28</b>	<b>0.70</b>	<b>79</b>	<b>Kande</b>	<b>YES</b>

#### *Particle and bulk density*

Particle density was obtained using the pycnometer method from Smith & Mullins (1991). Bulk density was determined by the ratio of mass to volume of individual charcoal fragments. All analyses were carried out in triplicate. Porosity ( $\phi$ ) was then determined by calculation from the direct measurement of particle ( $\rho_{\text{particle}}$ ) and bulk density ( $\rho_{\text{bulk}}$ ) using the following equation:

$$\phi = 1 - \frac{\rho_{\text{bulk}}}{\rho_{\text{particle}}}$$

Figure 4.1 below illustrates the porosities of the selected samples and shows the relationship between porosity and O:C. There is a significant difference in porosity between different ages of charcoal ( $P < 0.05$ ), but regression analysis shows a very weak trend of decreasing porosity over time, as is revealed by the low  $R^2$  values.

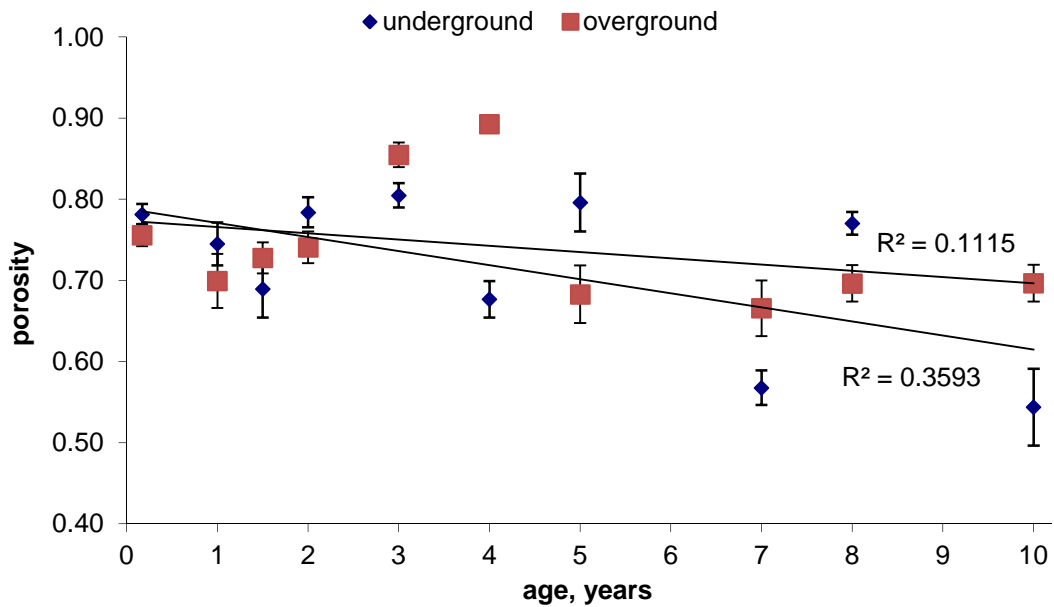


Figure 4.1. Relationship between age of charcoal and its porosity. Error bars show standard deviation around the mean of triplicate results.

It can therefore be assumed that there is no relationship between age of the sample and its porosity, indicating that the physical structure of the charcoal is not significantly changed over a period of ten years. There is also no significant difference in porosity between the above- and belowground fragments ( $P > 0.01$ ) suggesting that the pore space within the belowground samples is not being filled in by any material from the surrounding soil.

Variation in results from triplicate analysis is acceptable throughout, with the 10 year old belowground sample showing the highest variability ( $n = 3$ , mean =  $0.54 \pm 0.05$ ). This could be due to environmental influences on biochar decay over time affecting some fragments more than others e.g. root incursions altering the pore structure.

From the samples selected above in table 4.1, the following ranges were available for investigation: a surface O:C of 0.27 to 0.76; a milled O:C of 0.11 to 0.49; and a porosity of 0.54 to 0.89. These ranges were deemed large enough to investigate the

potential effect of different charcoal properties on fertiliser retention in this experiment.

### *Soil*

The soil was a rich orange-coloured ferrasol characteristic of a highly weathered tropical soil, and showed the particle size distribution of a sandy loam (ISSS). A Beckman Coulter LS Particle Size Analyser was used to determine the following particle sizes and their fraction by volume: Clay (<2 $\mu$ m) 16%; Silt (2-20 $\mu$ m) 31%; Fine sand (20-200 $\mu$ m) 42%; and coarse sand (200-2000 $\mu$ m) 11%.

Soil was collected onsite at the perimeter of a cultivated maize plot of one of the participating farmers. This site was chosen due to the following reasoning: it was of a locally typical nature as determined by visual inspection and hand texturing; it had not had any fertiliser addition; there had been no burning in the area (minimising the potential presence of charred material); and lastly, the farmer gave his consent. Roughly 10 kilos of topsoil (down to a maximum depth of 20cm) was taken, air-dried for 2 weeks then transported back to the UK, oven dried for 18h at 70°C and stored in a large container bin until use.

### *Fertiliser*

99.995% purity ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) was used as the inorganic fertiliser for this experiment. A single application of 56mg NH<sub>4</sub>NO<sub>3</sub> dissolved in 10ml de-ionised water was applied to each column, representing an average rate of 100kg N ha<sup>-1</sup> in Ghanaian agriculture (SRID 2010). This amounted to a total of 12.6mg NH<sub>4</sub> and 43.4mg NO<sub>3</sub> applied to each treatment column.

### *Soil leaching apparatus*

The apparatus was constructed by hand using PVC tubing connected to a wooden stand. 25 cm long sections with a diameter of 5cm were cut and secured into place as shown in plate 4.1. Aluminium foils were moulded around the top of the tubes throughout the experiment to minimise water loss by evaporation, but allow some gas exchange to minimise the development of anaerobic conditions within the column.

Plate 4.1. Photograph of leaching apparatus and collection flasks.



Many dry runs were conducted to investigate the basic flow dynamics of the individual columns prior to use. Different packing techniques were explored and then one perfected to attain a uniform leachate rate with each separate packing. An appropriate rate of 'rainwater' inundations was also attained after conducting simple trial and error procedures. This was considered to be essential to minimise

the potential variability in leaching rate between the individual columns, which could arguably affect the outcome of the experiment.

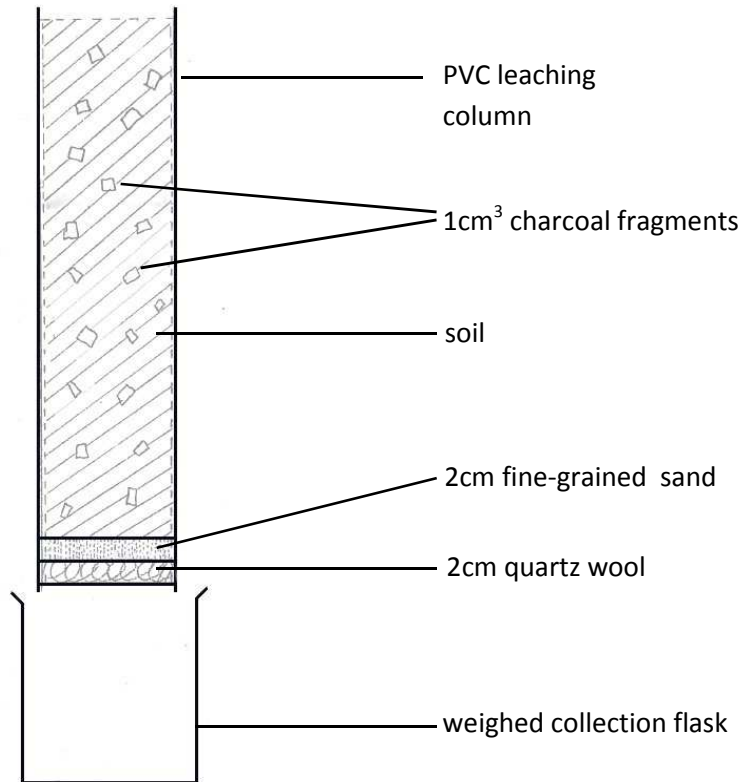


Figure 4.2. Illustration of leaching apparatus.

### *Method*

Below is a list of the various treatments which were all carried out in triplicate, resulting in 36 separate leaching columns:

1. Control 1 (soil alone)
2. Control 2 (soil + fertiliser)
3. 3 Year-old aboveground charcoal + fertiliser
4. 4 Year-old aboveground charcoal + fertiliser

5. 7 Year-old aboveground charcoal + fertiliser
6. 8 Year-old aboveground charcoal + fertiliser
7. 10 Year-old aboveground charcoal + fertiliser
8. 1 Year-old belowground charcoal + fertiliser
9. 2 Year-old belowground charcoal + fertiliser
10. 3 Year-old belowground charcoal + fertiliser
11. 8 Year-old belowground charcoal + fertiliser
12. 10 Year-old belowground charcoal + fertiliser

a) Soil was sterilised in an oven at 103°C for ~16 hours prior to use. This was carried out to minimise the effect of nitrifying/denitrifying bacteria on the leaching experiment. Soil columns were packed with 800g of this soil (with or without charcoal) by tamping the columns as the soil is added. All columns were carefully packed to achieve an initial bulk density of about 1.5 g cm<sup>-3</sup>. There is just one level of charcoal treatment at 2% charcoal d/w i.e. 784g of oven-dry soil is mixed with 16g of charcoal fragments or milled charcoal accordingly.

b) 80ml of de-ionised water was added to all columns to reach an estimated field capacity of 0.1g water per gram of sandy soil.

c) 10ml of a 5.60g/l NH<sub>4</sub>NO<sub>3</sub> solution was added to the appropriate treatments with a pipette, ensuring an even distribution on the soil surface.

d) Weighed beakers were placed under the columns to collect the leachate.

e) 80ml of de-ionised water was added to all columns every three days to represent the mean precipitation rates during the wet growing season in Ghana (equivalent of 40mm downpour events from personal observation, 2011).

f) Leachate was collected and weighed after each 'rainfall event' for six weeks. Leachate samples were centrifuged, filtered using Whatman 42 filter paper and then taken immediately for analysis. On three occasions it was necessary to freeze the samples for preservation until analysis was possible. Samples for  $\text{NH}_4$  and  $\text{NO}_3$  represent the leachate from each 'rainfall' event. Colorimetric analysis gave leaching rates as well as cumulative leaching for the 6 week study.

g) After the six week experiment, all soil/charcoal mixtures are analysed for extractable  $\text{NH}_4$  and  $\text{NO}_3$  using a 2M KCl extraction method taken from Mulvaney (1996):

h) 50 g of the soil/charcoal mixture was placed in 500ml bottles with 100ml 2M KCl extraction solution. Stoppered bottles were shaken for one hour on a rotary agitator; decanted until a clear supernatant solution was obtained; centrifuged for 5 minutes then filtered using a Whatman 42 filter paper.

i) The filtrate is then used for the colorimetric determination of  $\text{NH}_4$  and  $\text{NO}_3$ .

These steps were carried out for two separate experiments – one to investigate the effect of whole charcoal fragments, and one for milled charcoal/soil mixes. The following step was only carried out for the whole charcoal fragment experiment:

j) Remaining charcoal fragments from each of the columns were also analysed for residual  $\text{NH}_4$  and  $\text{NO}_3$ , following the procedure stated above in (h). Charcoal fragments from each column were removed and brushed to clean off adhering soil particles. Triplicate samples were pooled to give one ~16g sample for each age of charcoal. These were subjected to KCl extraction on 6 sequential occasions.

k) Thus, with all inputs and outputs of fertiliser measured and recorded, a mass balance calculation was made possible for the entire run of experiments. This

calculation assumed there were no external losses of nutrient e.g. via denitrification.

#### *Statistical analysis*

Statistical data analysis was carried out using Genstat (16.1). Standard linear regression analysis was performed to calculate regression coefficients and their 95% confidence intervals. The *F* statistic and *p* value were used to signify the relationship between age of charcoal fragment and extent of nitrate/ammonium in the leachate. A normal distribution of data was checked before ANOVAs were applied and analysis of residuals was used to determine outliers. Significant differences in % nitrate/ammonium in the leachate between charcoal (of different ages)/soil mixtures were then tested using one-way analysis of variance (ANOVA) with blocks. Any outliers found were subsequently excluded from the analysis. Age effects were deemed significant if  $p \leq 0.05$  unless otherwise stated.

### **4.4 Results & Discussion**

#### *Whole charcoal fragments/soil mix*

After 12 water additions, cumulative totals of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  began to plateau, and after the 13th addition, leaching experiments ran to an end as results fell below the limit of quantification for the colorimeter. Figures 4.3 and 4.4 below show the cumulative amounts of both  $\text{NO}_3^-$  and  $\text{NH}_4^+$  collected from the leaching columns.

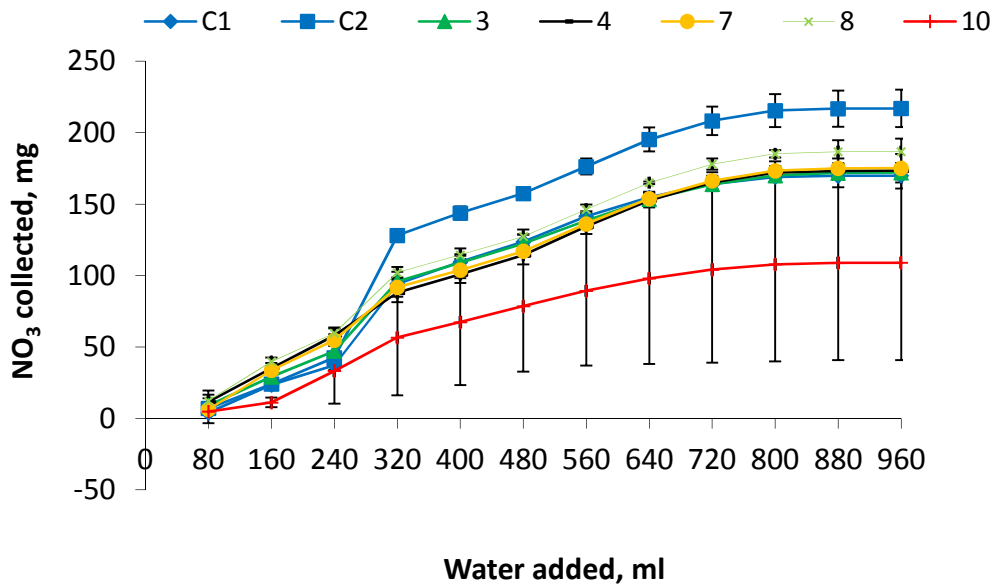


Figure 4.3. Nitrate collected from the various treatments. Fragments of charcoal recovered from aboveground were used in the charcoal/soil mixtures. The legend describes the age of the charcoal concerned; with C1 being soil alone and C2 soil plus NH<sub>4</sub>NO<sub>3</sub>. Error bars denote standard deviation around the mean of 3 analyses.

All treatments show a reduction in the total amount of nitrate leached through the columns after 12 additions of water when compared to the C2 control (soil with fertiliser added). With the exception of the 10 year old aboveground charcoal sample (which showed too high a variation in results to be accepted as valid – see discussion later), all treatments exhibit a similar level of nitrate retention, with the 8 year old sample showing the least. No significant difference of total NO<sub>3</sub> collected between samples of different ages was detected ( $P > 0.05$ ).

Interestingly, the C1 control (soil alone) did not result in a significantly different amount of total NO<sub>3</sub> collected than the charcoal amended columns ( $P > 0.05$ ). The most likely explanation for this is the presence of considerable levels of nitrate in the soil to begin with. The significance of this finding is discussed in detail at the end of the chapter.

Figure 4.4 below shows the results from treatments of soil/charcoal fragments recovered from belowground.

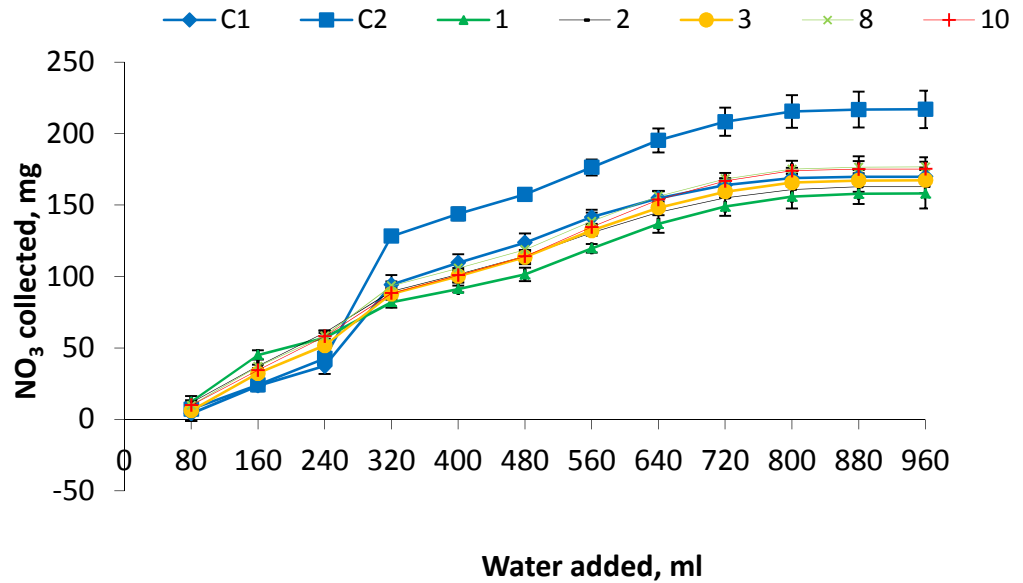


Figure 4.4. Nitrate collected from the various treatments. Fragments of charcoal recovered from belowground were used in the charcoal/soil mixtures. The legend describes the age of the charcoal concerned; with C1 being soil alone and C2 soil plus  $\text{NH}_4\text{NO}_3$ . Error bars denote standard deviation around the mean of 3 analyses.

Again, all treatments exhibit a significant reduction in nitrate collected in the leachate and similar to the aboveground samples, there is no significant difference of total  $\text{NO}_3$  collected between samples of different ages ( $P > 0.05$ ), indicating once more that age of sample appears to play no role in level of nitrate retention.

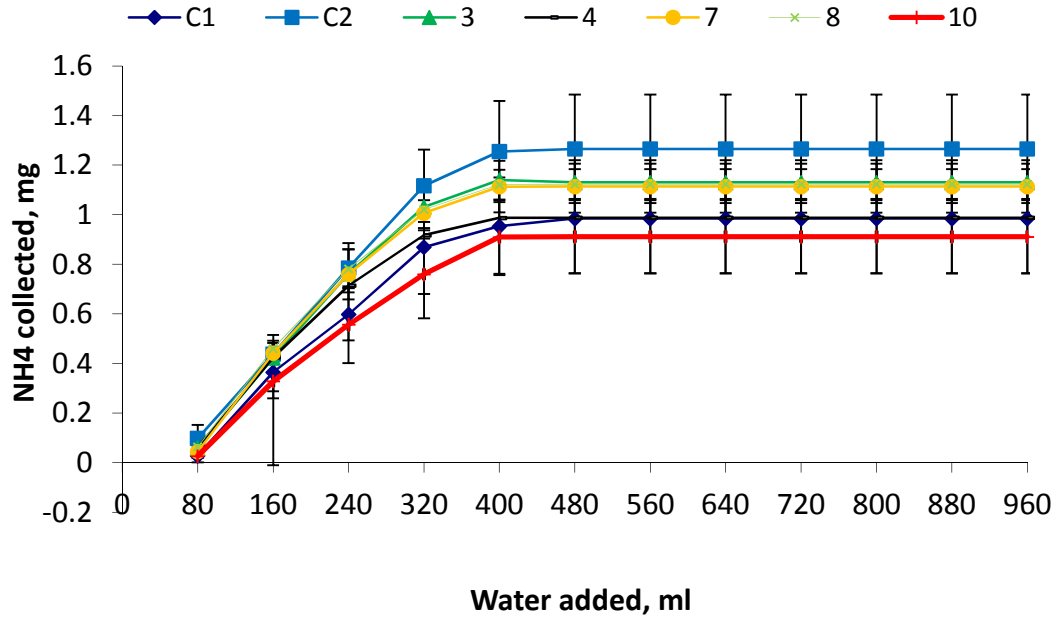


Figure 4.5. Ammonium collected from the various treatments. Fragments of charcoal recovered from aboveground were used in the charcoal/soil mixtures. The legend describes the age of the charcoal concerned; with C1 being soil alone and C2 soil plus  $\text{NH}_4\text{NO}_3$ . Error bars denote standard deviation around the mean of 3 analyses.

Ammonium reduction mirrors the nitrate reduction of the same sample. Results begin to plateau around the 5<sup>th</sup> addition, after only 1-2% of the total added ammonium had accumulated in the leachate. All treatments show a reduction in the total amount of ammonium leached through the columns after 12 additions of water when compared to the C2 control (soil with fertiliser added). With the exception of the 10 year old aboveground charcoal sample (which showed too high a variation in results to be accepted as valid – see discussion later), all treatments exhibit a similar level of ammonium retention. No significant difference of total  $\text{NH}_4^+$  collected between samples of different ages was detected ( $P > 0.05$ ).

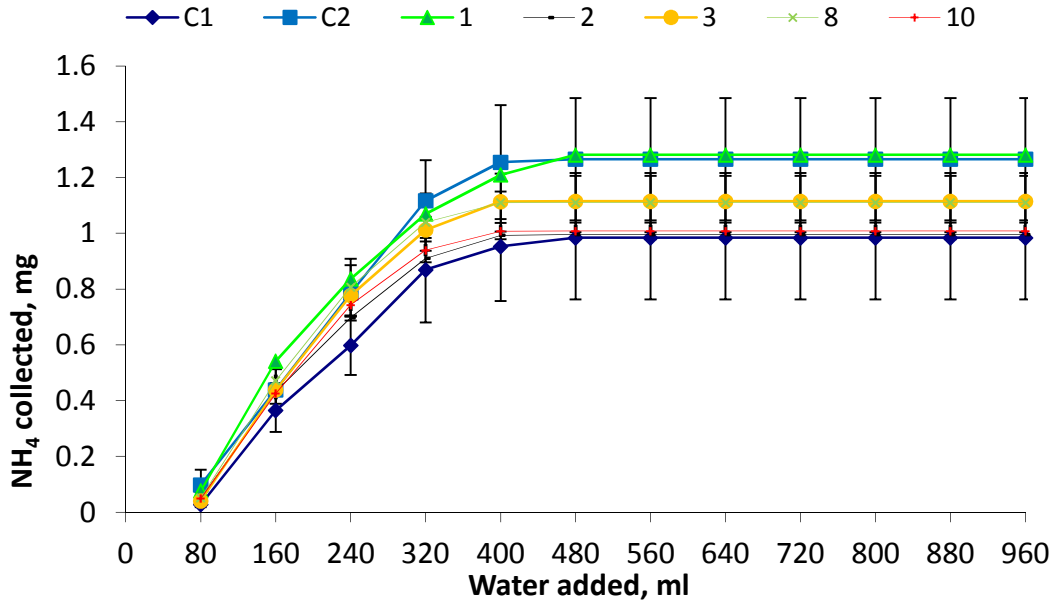


Figure 4.6. Ammonium collected from the various treatments. Fragments of charcoal recovered from belowground were used in the charcoal/soil mixtures. The legend describes the age of the charcoal concerned; with C1 being soil alone and C2 soil plus  $\text{NH}_4\text{NO}_3$ . Error bars denote standard deviation around the mean of 3 analyses.

Interestingly, the level of ammonium reduction in the leachate is lower than for nitrate, with the 1 year old sample showing no difference in retention to the control. This suggests that charcoal has a minimal effect on ammonium leaching through the soil. The percent recovery of ammonium was also very low – ranging from 0 to 2% of the total added at the beginning of the experiment suggesting that it is tightly bound within the soil matrix.

#### *$\text{NO}_3$ and $\text{NH}_4$ remaining in charcoal fragments after leaching experiment by water extraction*

After the first experiment with whole charcoal fragments detailed above, all columns were extracted using KCl solution, followed by removal and extraction of the fragments themselves. This was carried out to both enable a fertiliser mass

balance calculation as well as indicating what 'plant available' (as described by Bremner 1965) nitrate and ammonium remained in the soil/charcoal mixes.

As previously mentioned, there was a considerable presence of nitrate already present in the soil, and this had to be accounted for when calculating a mass balance as illustrated in the table below. A mean of 170 mg of NO<sub>3</sub> was extracted from the C1 (soil alone) columns as shown in figures 4.3 and 4.4, and a mean of 217 mg was extracted from the C2 columns (soil + 43.4 mg fertiliser i.e. 170 + 43.4 equally roughly the 217 measurement). This figure of 170 mg was therefore subtracted from all treatment columns to negate this interference. This method has potential flaws, and shall be discussed at the end of the chapter.

Table 4.2. 'Plant available' nutrients (mg) left in columns by KCl extraction. 'Sample' is defined by its age (years) and whether it was recovered from aboveground (a) or belowground (u).

sample	after leaching		% of total added		after KCl on column		% of total added	
	NO3	NH4	NO3	NH4	NO3	NH4	NO3	NH4
C1	5.1	0.2	-	-	2.6	10.1	-	-
C2	48.2	0.3	111.1	2.2	1.2	11.2	113.9	91.1
1 u	25.8	0.3	59.5	2.4	5.2	9.6	71.5	78.5
2 u	26.7	0.0	61.6	0.1	7.9	11.0	79.7	87.4
3 a	28.5	0.1	65.6	1.2	17.2	10.4	105.3	83.7
3 u	27.6	0.1	63.6	1.0	5.2	9.9	75.7	79.6
4 a	28.7	0.0	66.0	0.0	2.4	10.5	71.6	83.4
7 a	29.1	0.1	67.1	1.0	12.0	10.4	94.8	83.6
8 a	31.4	0.1	72.2	1.1	15.4	10.1	107.7	81.3
8 u	29.3	0.1	67.6	1.0	3.9	10.2	76.5	82.0
10 a	16.6	-0.1	38.3	-0.6	14.9	10.2	72.5	80.6
10 u	29.1	0.0	66.9	0.2	6.5	10.3	81.8	82.0

Recovery rates of nitrate were deemed to be good as the spiked control gave a result slightly over 100% (although this inflated figure does elude to the general

inaccuracy of all measurements). The treatment columns with charcoal additions showed a nitrate recovery range of between 38 and 72%, which were then increased to between 71 and 100% once the columns had been leached with KCl. These figures further indicate the nitrate retention properties of charcoal fragments in the soil. One would presume that the KCl had removed all remaining ammonium and nitrates from the columns, but further extractions of the removed charcoal fragments themselves revealed residual amounts – see next section.

*'Plant available' nutrients left in charcoal fragments by KCl extraction*

Six sequential extractions using KCl were carried out on samples representing each age of charcoal used in the nutrient leaching experiment. Fragments from the three replicate columns of each treatment were removed, lightly brushed to remove soil debris and then pooled together to give one representative sample. The results are as follows.

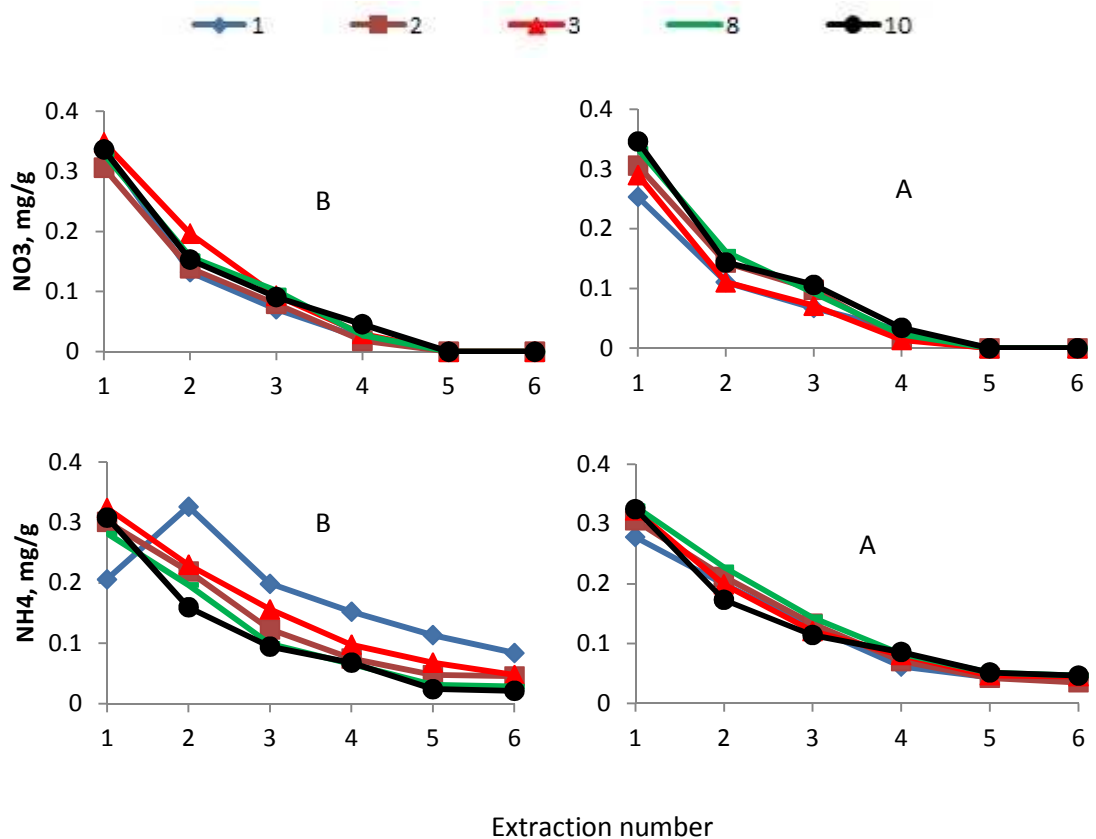


Figure 4.7 Levels of ammonium and nitrate extracted from charcoal fragments with KCl; B denotes the sample was recovered from belowground and A aboveground.

Although there were only small amounts of both ammonium and nitrate present in the extractants, the results show the strength of attraction between charcoal fragments and  $\text{NH}_4\text{NO}_3$ . The fact that it took 6 extractions with a relatively concentrated solution of KCl before levels fell below the limit of quantification are testament to this. Again, there were no statistically significant differences in charcoals of different ages (ANOVA  $P>0.05$ ) or whether they were recovered from above- or belowground ( $P>0.05$ ).

Table 4.3. Ammonium and nitrate (mg) removed from charcoal fragments with KCl. % of total added includes extractants from leaching, column KCl extraction and fragment KCl extraction.

sample	NO <sub>3</sub>	NH <sub>4</sub>	NO <sub>3</sub>	NH <sub>4</sub>
	after KCl on fragments		% of total added	
1 u	0.6	1.1	72.8	87.1
2 u	0.5	0.8	81.0	93.8
3 o	0.5	0.7	106.3	89.6
3 u	0.7	0.9	77.2	86.9
4 o	0.6	0.8	72.9	89.7
7 o	0.5	0.8	95.9	90.0
8 o	0.6	0.9	109.1	88.3
8 u	0.6	0.7	77.9	87.5
10 o	0.6	0.8	74.0	86.9
10 u	0.6	0.7	83.3	87.4

This table shows that all fragments retained a very similar amount of both nitrate and ammonium within themselves despite their differences in age and physico-chemical properties. The mean overall nitrate recovery is 85% and ammonium 89% which compares very well to other soil leaching studies which range between 50% and 90% (Melgar et al 1992; Cahn et al 1993; van Es et al 2002).

#### *Milled charcoal fragments/soil mix*

It has been reported that the size of biochar particles may influence the leaching potential of fertiliser in the soil (Major et al 2009). After soil application, rain

impact, physical disturbance from soil biota and chemical weathering will result in fine biochar particles which can represent a large proportion of the biochar present (Macias-Garcia et al 2004; Nguyen et al 2004).

There is however, still an uncertainty as to how much these different size particles contribute to nutrient retention of soils. This part of the study therefore aims to inform the current state of knowledge by carrying out leaching experiments on both whole and milled fragments of the same sample of known physico-chemical properties.

A ball mill was insufficient, and so a pestle and mortar was used to grind all the samples in to a fine homogenous powder. These powders were mixed thoroughly with soil before application to the leaching columns. Column preparation procedure detailed in section 4.3 was followed and the same treatment regime applied. The results of the subsequent leachate analysis are illustrated below.

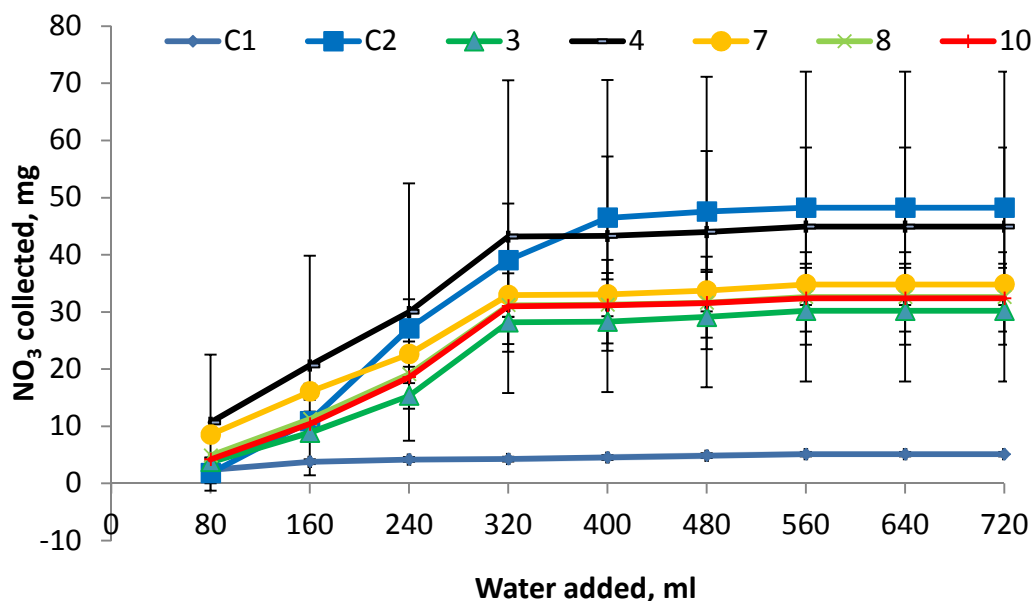


Figure 4.8. Nitrate collected from the various treatments. Milled charcoal recovered from aboveground was used in the charcoal/soil mixtures. The legend describes the age of the charcoal concerned; with C1 being soil alone and C2 soil plus  $\text{NH}_4\text{NO}_3$ . Error bars denote standard deviation around the mean of 3 analyses.

Figure 4.8 shows that all charcoal treatments except that with the 4 year old charcoal (which exhibited an unacceptable variance and whose error bars are the top peaks in the figure) were significantly different to both controls, C1 and C2 ( $P < 0.01$ ). They showed a mean reduction of nitrate in the leachate (when compared to the control C2) of  $28.4 \pm 3.9\%$  when omitting the 4 year old outlier.

There was no significant relationship between the age of charcoal and nitrate reduction in the leachate ( $P > 0.05$ ), similar to the experiment carried out with whole fragments. Interestingly, results begin to plateau around the 5<sup>th</sup> addition (as opposed to the 12<sup>th</sup> in the whole fragment experiment), indicating that milled charcoal retains nitrate for a shorter amount of time than whole charcoal fragments do. This is interesting when considering current explanations for nutrient retention which indicate that the reactive surfaces of biochar are the most likely contributor to nitrate retention (Lehmann et al 2003; Liang et al 2006; Cheng et al 2008). This is discussed in further detail at the end of the chapter.

There is also a vastly reduced overall level of nitrate recovered from this experiment when compared to the previous. As the same soil was re-used for the second experiment, this discrepancy is most likely due to the fact almost all of the soluble nitrate was leached out in the first. The results in this experiment support this hypothesis, as a total  $\text{NO}_3$  recovery of 48.2 mg was obtained from the spiked sample C2 which reflects the combination of the 43.4 mg added as fertiliser and the 5.1 mg detected in the soil alone control, C1.

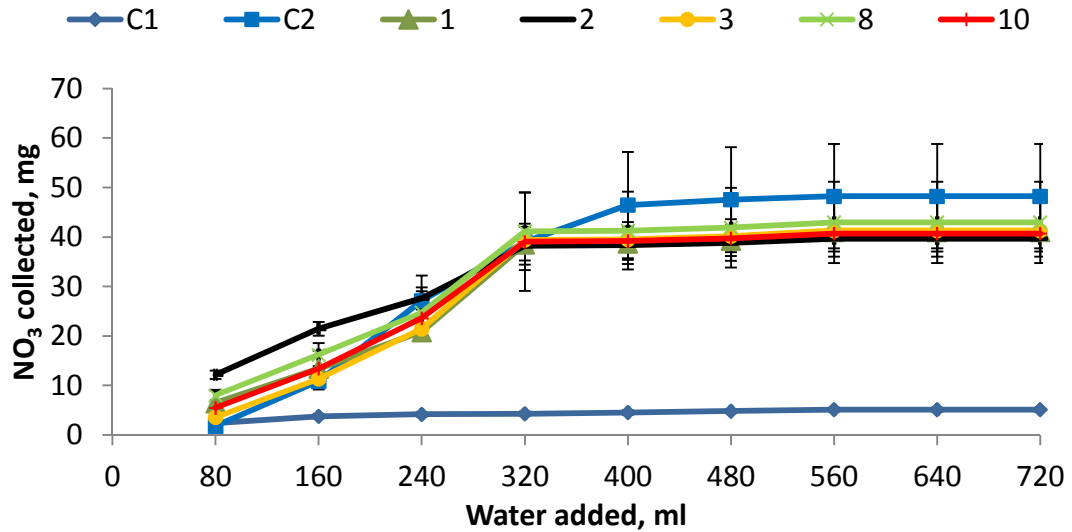


Figure 4.9. Nitrate collected from the various treatments. Milled charcoal recovered from belowground was used in the charcoal/soil mixtures. The legend describes the age of the charcoal concerned; with C1 being soil alone and C2 soil plus  $\text{NH}_4\text{NO}_3$ . Error bars denote standard deviation around the mean of 3 analyses.

Figure 4.9 shows that all charcoal treatments resulted in a total collected  $\text{NO}_3$  significantly different to both controls, C1 and C2 ( $P < 0.01$ ). They showed a mean reduction of nitrate in the leachate (when compared to the control C2) of  $14.7 \pm 2.5\%$ .

There was no significant relationship between the age of charcoal and nitrate reduction in the leachate ( $P > 0.05$ ), similar to the results obtained from the aboveground samples. Interestingly, the belowground samples as shown in figure 4.9 exhibit a much narrower range of results and a lower mean % nitrate reduction in the leachate when compared to the aboveground samples. Comparisons between belowground and aboveground samples are discussed in the next section.

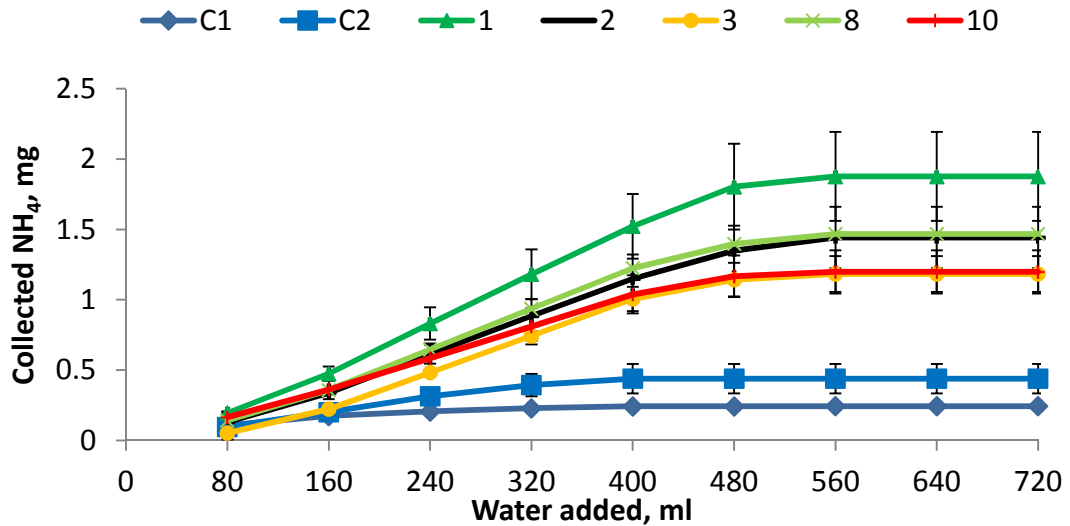


Figure 4.10. Ammonium collected from belowground milled charcoal/soil mixtures. The legend describes the age of the charcoal concerned; with C1 being soil alone and C2 soil plus NH<sub>4</sub>NO<sub>3</sub>.

Figure 4.10 above depicts a different story to that of nitrate – all treatment samples leached more ammonium than the controls. This would suggest that by milling the charcoal, ammonium is released and susceptible to leaching. This is also reflected in the fact that mean recovery of ammonium from columns with whole fragments was 8.5% as opposed to the milled charcoal/soil mixtures which yielded a greater 10.7% recovery.

### Comparisons

The following figures and tables compile all the results in order to determine the potential differences in nutrient retention for samples of different age, porosity, O:C and whether they were recovered from under- or aboveground.

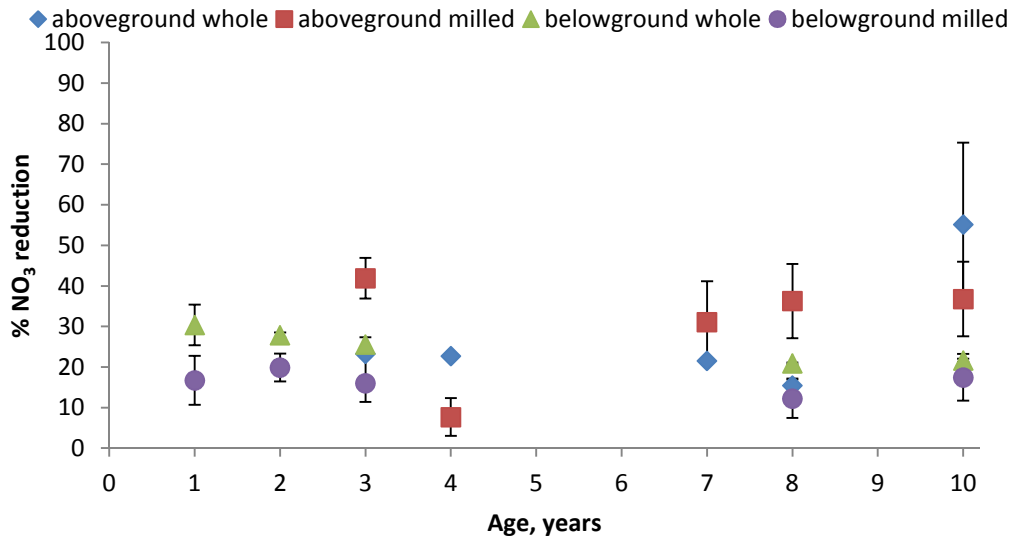


Figure 4.11. Relationship between age and % nitrate reduction in the leachate. Error bars denote standard deviation from the mean of triplicate results.

% NO<sub>3</sub> reduction was calculated from the proportion of nitrate in the leachate compared to that found in the spiked control leachate, C2. The background NO<sub>3</sub> was also accounted for, as explained previously. Regression analysis reveals that there is no statistically significant relationship between age of charcoal and level of nitrate reduction in the leachate ( $P > 0.05$ ). The 10 year old aboveground whole fragment sample was deemed an outlier due to unacceptable variance (mean of  $49.7 \pm 31.1$ ) and was not included in statistical analysis.

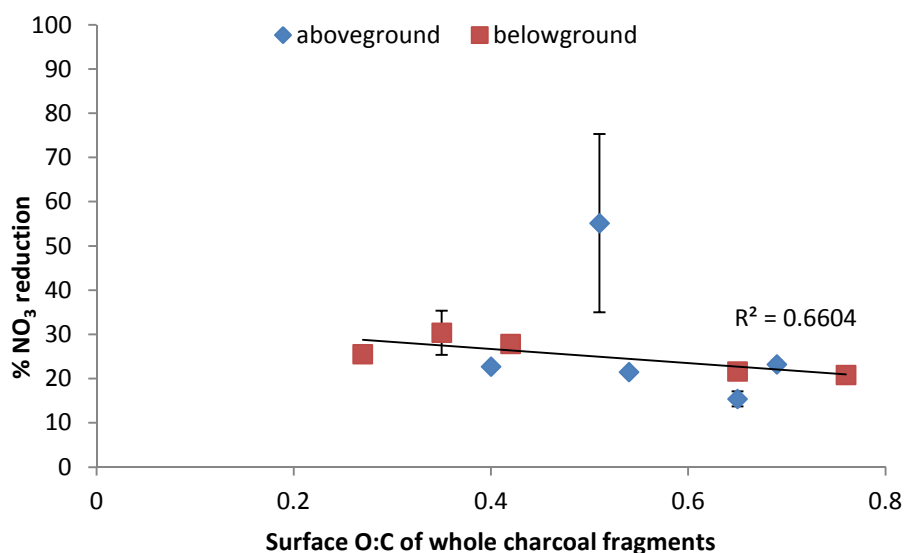


Figure 4.12. Relationship between surface O:C of whole charcoal fragments and nitrate reduction in the leachate. Error bars denote standard deviation from the mean of triplicate results. The clear outlier was not included in the trend line.

With the exception of the 10 year old whole sample (due to its unacceptably high standard deviation around the mean), regression analysis on the results in figure 4.12 could suggest that there is a relationship between fragment surface O:C and nitrate retention as the  $R^2$  value is reasonably high. One might expect an increasing O:C to result in a slight decrease in nitrate reduction, which would fit the argument put forward by Lehmann et al (2003) in their biochar-amended pot experiments. They state that biochar displays a high cation exchange capacity, and that its application to soil would contribute to negative charge thereby repelling the similarly charged  $\text{NO}_3^-$  ion. However, one could also interpret the regression line as being almost horizontal, signifying that there is no relationship between O:C and % $\text{NO}_3$  retention whatsoever.

Additionally, there is no significant difference between above- and belowground samples with relationship to % nitrate reduction in the leachate.

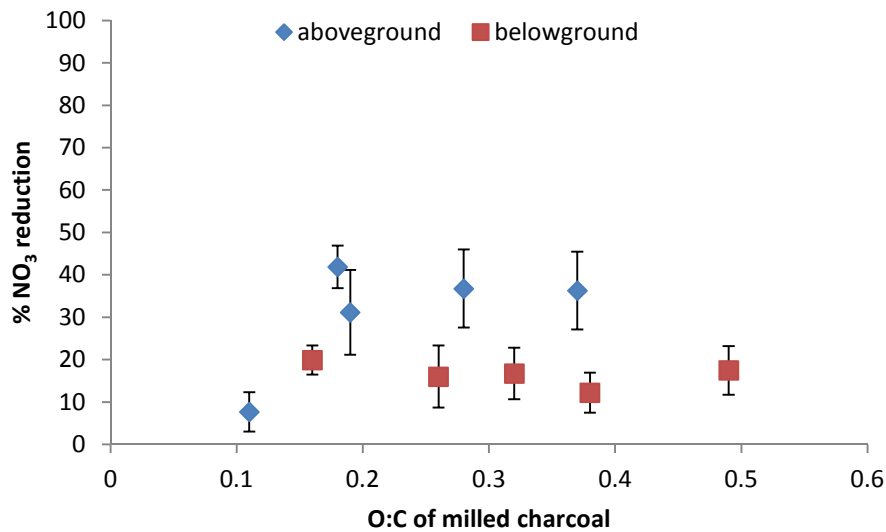


Figure 4.13. Relationship between O:C of milled charcoal and nitrate reduction in the leachate. Error bars denote standard deviation from the mean of triplicate results.

ANOVA of the results shown in figure 4.13 above shows that there is no statistically significant relationship between O:C of milled charcoal and % nitrate reduction in the leachate ( $P > 0.05$ ). Milling reduces the variability of results within triplicate analyses when compared to whole fragments, as is to be expected due to the greater homogeneity of the treatment material. Interestingly, the aboveground samples exhibit a higher level of nitrate reduction which is to be discussed at the end of this chapter.

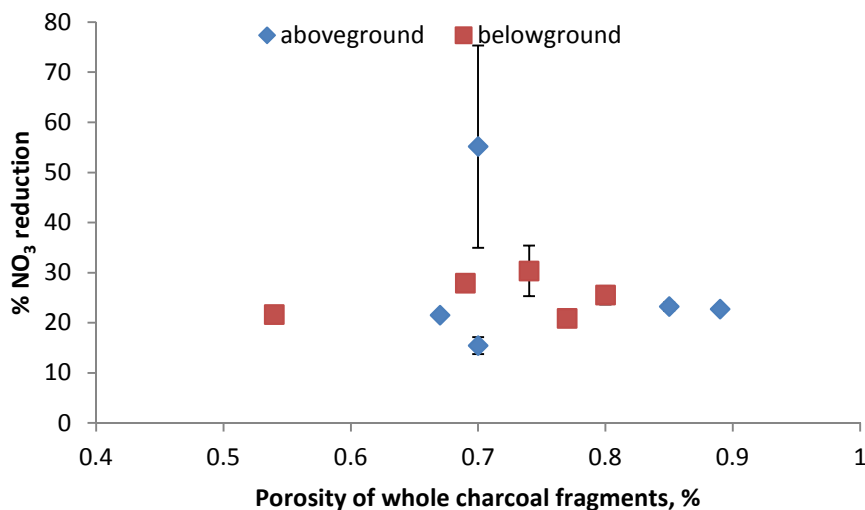


Figure 4.14. Relationship between porosity of charcoal fragments and nitrate reduction in the leachate. Error bars denote standard deviation around the mean of triplicate results.

ANOVA of results shown in figure 4.13 shows that there is no statistically significant relationship between porosity and nitrate reduction in the leachate ( $P>0.05$ ). The clear 10 year old outlier mentioned before was not included in any statistical analysis. There is also no relationship between porosity and whether the sample was recovered from above- or belowground (t-test,  $P>0.05$ ). This shows that this experiment could not detect any influence of porosity on the capacity of a charcoal fragment as a nutrient retainer.

Soil porosity is critical at determining the rate at which rain can infiltrate and carry nutrients away from the surface layer, and it has been shown that amounts of leached nitrates are greater in coarser-textured soil (Melgar et al 1992; van Es et al 2002). This would suggest that finely porous biochar would have an effect on leaching, and changing levels of porosity could exhibit a measurable effect on leaching rate.

This is however not the case in this experiment. Perhaps confounding variables are masking the effect of porosity, or, which is more likely, the pores within the charcoal fragments are 'sealed off' and not readily accessible to water in short-term laboratory experiments. The reported hydrophobic nature of unweathered charcoal (Lebo et al 2003; Bornemann et al 2007) could also negate any proposed mechanism of charcoal porosity's relationship with water/nutrient retention.

Table 4.4. Summary of charcoal properties and their influence on nitrate reduction in the leachate.

age, years	W/M	A/B	O:C	Porosity	% nitrate reduction
1	W	B	0.35 ± 0.08	0.74 ± 0.03	30.4 ± 5.0
1	M	B	0.32 ± 0.00	-	16.7 ± 6.1
2	W	B	0.42 ± 0.09	0.78 ± 0.02	27.8 ± 0.7
2	M	B	0.16 ± 0.00	-	19.9 ± 3.4
3	W	A	0.69 ± 0.14	0.85 ± 0.02	23.2 ± 0.8
3	M	A	0.18 ± 0.00	-	41.9 ± 5.0
3	W	B	0.27 ± 0.01	0.80 ± 0.02	25.5 ± 1.8
3	M	B	0.26 ± 0.01	-	16.0 ± 7.3
4	W	A	0.4 ± 0.16	0.89 ± 0.01	22.7 ± 0.2
4	M	A	0.11 ± 0.01	-	7.7 ± 4.6
7	W	A	0.54 ± 0.11	0.67 ± 0.03	21.5 ± 0.5
7	M	A	0.19 ± 0.00	-	31.1 ± 10.0
8	W	A	0.65 ± 0.27	0.70 ± 0.02	15.4 ± 1.7
8	M	A	0.37 ± 0.02	-	36.2 ± 9.1
8	W	B	0.76 ± 0.20	0.77 ± 0.01	20.9 ± 0.2
8	M	B	0.38 ± 0.02	-	12.2 ± 4.7
10	W	A	0.51 ± 0.14	0.7 ± 0.02	49.8 ± 31.1
10	M	A	0.28 ± 0.01	-	55.2 ± 20.2
10	W	B	0.65 ± 0.17	0.54 ± 0.05	21.7 ± 0.4
10	M	B	0.49 ± 0.04	-	17.5 ± 5.8

Table 4.2 above shows a mean nitrate reduction for aboveground whole charcoal fragments of 27.6%, with belowground being 25.3%. Whereas for milled samples, reduction is 30.7% for aboveground and 16.5% for belowground. The significance of these comparisons and their potential flaws are discussed in the next section.

#### 4.5 Conclusions

This investigation set out to explore the relationship between the properties of charcoal and its ability to retain nutrients in a soil column experiment. It has been shown that there is no statistically significant relationship between any of the properties mentioned in this chapter. Neither age, porosity nor O:C had any

discernible effect in this experiment. If it were to be of any interest, then charcoal produced under controlled conditions with the resultantly more homogenous properties would be a better substitute if any relationship were to be quantified.

It can be argued that the presence of both whole and milled fragments reduces both the leaching rate and total amount of nitrate present in the leachate from this column experiment. However, a major obstacle in proving this argument is the omission of an important control experiment. An additional set of control columns containing charcoal and soil alone without any fertiliser added would be required to comprehensively validate arguments regarding fertiliser retention in this experiment.

Another confounding factor is the difference between the soil used in the whole fragment experiment and the soil used in the milled charcoal experiment. Although the same soil was re-used for the second experiment (due to the limited amount brought back from Ghana), it had undergone changes and exhibited different blank control results in the two experiments. It was apparent that the soil originally contained a large amount of soluble nitrate which was eluted during the first experiment and subsequent KCl extractions. This was dealt with by subtracting the 'background' level of nitrate away from all treatment results in the first experiment, thereby resulting in a further uncertainty in the final outcome.

As was previously mentioned, every effort was made to ensure water percolated through all the treatment columns at an equal rate. Studies have shown that leaching losses are significantly affected by infiltration rates (Melgar et al 1992; Renck & Lehmann 2004; van Es et al 2006). However, observations made during the experiment showed that although infiltration rates were similar at the beginning, they then began to differ over time. A possible explanation for this was the relatively small bore of columns used which could have a propensity to clog as smaller particles settle into layers. Again, more available soil would have allowed a greater bore of leaching column.

It is uncertain whether charcoal recovered from aboveground reduces NO<sub>3</sub> leaching more than belowground samples as the figures suggest. There is too much variation in results to say with confidence (% nitrate reduction figures show a mean relative standard deviation of 8.3%), but perhaps the charcoal belowground becomes clogged with mineral matter and decreases its ability to retain nutrients in its porous and chemically active structure.

To conclude, this study did not succeed in quantifying the relationship between physico-chemical properties of biochar and its ability to retain nutrients. What it did show however, was that the nutrient retentive capacity of charcoal potentially remains unchanged after 10 years residence time in the soil.

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## **5. Discussion**

This chapter will discuss the significance of the findings of previous experimental chapters with regards to the subsistence farming practices of the study area in Ghana. This study area was originally chosen due to the reported use of biochar in subsistence agriculture (Sohi & Yeboah 2009). A traditional established use of biochar to maintain soil fertility in subsistence agriculture with no external inputs had been described. Based on verbal information, the authors report that one particular farmer has been carrying out a labour-intensive regime of slash-and-char for 20 years. However, having spent a few weeks living and working with this farmer and members of her family, it became apparent that no such work had ever been carried out. Along with other farmers in the region, the farmer practices slash-and-burn rotational agriculture, with no purposeful production of charred material as had been previously described. Instead, charcoal residues from previous production sites were sampled and analysed with the overall aim of assessing their potential benefits to local agriculture.

### **5.1 Ghanaian agriculture**

Unless otherwise cited, the following section contains information gathered from the Ministry of Food and Agriculture (MOFA) in Wenchi District, correspondence with agricultural extension officers in Wenchi and time spent with local farmers.

While the decisions of a farmer in technologically advanced countries may not be unduly influenced by the physical attributes of land, the ecological factor is a dominant factor in Ghanaian society. Two broad systems of small-scale farming may be distinguished in Ghana based on this criterion. These are the bush fallow system and permanent tillage. The latter may be based on the application of compost,

manure, and fertilizers to restore soil fertility or on tree cropping. The two systems are subdivided on the basis of land tenure which largely determines field patterns and the intensity of cultivation in terms of capital inputs. In parts of northern Ghana each farming unit combines permanent tillage of the area immediately around its compound house with bush fallowing at some distance from the settlement in much the same way as the well-known infield-outfield system (Benneh 1973).

Tropical forests constitute a prime example of the challenges of sustainable development. They produce diverse goods and services including those of tangible and immediate value such as timber, medicinal plants, fruit, etc.; those that arise indirectly through ecological systems, such as nutrient cycling, water conservation, and carbon storage; the option value of future uses of the forests; and the intangible existence values of forest biodiversity and landscape. For those who live and work in tropical forests, the returns to cutting forests for commercial timber, or to converting forest into cattle pasture or tree crop plantation, are often financially attractive, tangible, accrue to the landholder or occupier and generate returns within a few years of the initial investment. In contrast, when forest is degraded or cleared, the loss of environmental services may in large part fall on those current and future generations who neither live in forests nor own them. Without strong and effective countervailing regulation or incentives, those living and working in the forests here and now will thus tend to cut the forests back.

#### *Agricultural research in Ghana*

Agricultural research and development (R&D) spending in Ghana more than doubled during 2000–08, largely as a result of rising salary costs at the agencies under the Council for Scientific and Industrial Research (CSIR) and increased funding for the Cocoa Research Institute of Ghana (CRIG) following the country's boost in cocoa production.

- Agricultural research staff also showed steady growth throughout this period, albeit at a much slower rate than expenditures.
- The higher education sector is playing an increasingly important role in Ghana's agricultural R&D.
- Non-profit and for profit private companies, although involved in some collaboration with CSIR and the higher education agencies, continue to have minimal involvement in agricultural R&D in Ghana.
- During 2000–08, Ghana's agricultural research was primarily funded through the government and a number of donor and loan-funded projects. Although the government legislated more than a decade ago that the CSIR agencies should derive 30 percent of their budget from private sources, only the Oil Palm Research Institute (OPRI) has come close to reaching this commercialisation target (Flaherty et al 2010).

Carbonised materials are formally authorised for use as soil amendments in Japan, which uses 27% of its national charcoal production (50,835t) for purposes other than fuel, more than 30% of which is used in agriculture (Okimori et al 2003).

Oxisols are often used for tropical crops such as cocoa and rubber. In some cases, rice is grown on them. Permanent cropping of oxisols in low-income areas is very difficult because of low cation exchange capacities and high phosphorus fixation on iron and aluminium oxides (ligand exchange mechanism; inner sphere complex with phosphate). However, many oxisols can be cultivated over a wide range of moisture conditions. On this account, oxisols are intensively exploited for agriculture in some regions which have enough wealth to support modern agricultural practices (including regular additions of lime and fertiliser). A recent example of exploitation by modern methods involves the growing of soybeans in Brazil.

## 5.2 Biochar in Ghanaian agriculture

The reported use of biochar In Ghana is described as an example of traditional, established use of biochar to maintain soil fertility in subsistence agriculture with no external inputs. The dual purpose is to maintain higher crop yield, and attain sustainability of soil use. The strategy is economic without any energy capture, and informal production methods are used. The techniques practiced in this example have evolved in the environment, over the long term: the knowledge is indigenous and established. The barriers to its wider use are socio-economic, as is the barrier to technological development of the traditional practices.

Asuano (7°35'N, 2°05'W) is a small village with a total population of about 760. It lies just 20km east of the Ivory Coast border at Sampa, and north to south halfway between Ghana's northern and southern margins. Farmers work here with scientists from Ghana's Soil Research Institute to test and evaluate soil management options. Despite lying on one of the few untarred roads connecting Ghana and Ivory Coast, the distance to the nearest town and the absence of motorised transport limits access to markets for farm products. The climate in this part of Ghana is characterised by a bimodal rainfall pattern (1271mm, mean annual temperature 26°C). The natural vegetation is 'transitional' forest contrasting with dense 'rain' forest to the south and savannah in the north. Satellite images reveal, however, a predominance of secondary forest that is heavily encroached by agriculture. A few tens of kilometres to the south the landscape is characterised by unbroken farmland and more organised agricultural activity.

Soil texture is predominantly sandy, and the topography undulating. The village has a total of 270 farmers, all of whom participate in an organised democratic cooperative. According to the cooperative's leader three-quarters of crop production is for domestic consumption – maize, plantain and coco-yam – with cashew and cocoa providing the main cash crops. Two crops are grown each year to coincide with the rainy seasons. Diminishing soil fertility and the land division are

key challenges facing agriculture here. Outlying plots may be as far as 10km from habitation, and extend to the ultimate boundaries in secondary forest that are defined (as is traditional) by local streams. Average landholding is 1ha and individual fragmented plots may be as small as 0.5ha. The use of chemical fertilisers is limited and, owing to tsetse-borne disease, livestock plays a minimum role in the farming systems.

### *Faustina Addai*

The following information was provided by Sohi & Yeboah (2009) prior to undertaking this work. They state that Faustina Addai is among those with the largest landholding in the village, totalling 5ha; the following is based on her verbal information. Since all farming is performed with hand tools, continuous cultivation of such area is not possible: at any point in time half of her land holding is in cropping and the other half is undergoing short-term regeneration to secondary forest. Every five years on average the management is switched and regenerated vegetation 'partially burned' to enhance soil fertility for subsequent cropping. Her charring procedure is labour intensive: slashed vegetation is piled up, covered with soil, and ignited. The charred product is then spread across entire plots. She emphasizes that she could farm the amended soils for as long as she wished; the switch between forest regeneration and agriculture is not a response to declining productivity, but due to the need to protect her extensive landholding from other farmers. The motive for repeated charring rather than simple one-off slash-and-char is not the maintenance of the benefits, but to gradually build them.

Faustina has reportedly been practicing her rotational slash-and-char regime for 20 years. She considers that her yields exceed those achieved on other farmers land by 100%. She augments these periodic inputs of biochar with annual charring of crop residues according to a similar protocol. Her perception is that the underlying mechanism for the effects she sees is entirely physical, citing two factors: enhanced

rainwater infiltration, and enhanced soil moisture retention. In drought-susceptible sandy soils – prevalent in most parts of Ghana – crop performance is considerably governed by the timing and extent of rainfall, and its effects on crop establishment and maturation. However, it is doubtful that productivity could be sustainably enhanced if there were not some benefit in terms of nutrient retention perhaps concomitant, or perhaps resulting from control of nutrient release from other added organic matter to the growing crop.

With such a dramatic and demonstrable reported impact on crop productivity it is on the face of it surprising that Faustina's management practices have not been progressively adopted, and that the dominant land clearance practice remains open burning. Rather, the constraints to uptake are socioeconomic. Previous conversations within the village suggest that farmer time horizons are diminished by the expectation that children will not continue in agriculture, due to the very low cash income. More fundamentally, much land in the village is rented under informal and extremely short-term arrangements of one or two years. The land tenure situation makes investment in the soil unattractive. However, given the typical land rental rates of US\$20 ha<sup>-1</sup> yr<sup>-1</sup>, the comparatively large returns available from engagement in the C offsetting market should radically impact the uptake of biochar, given that there is no requirement to physically transport the commodity to market (though verification procedures would need to be defined). The possibility of a formal, village-wide engagement in the C offsetting market that would also enhance soil fertility is constrained by the size, accessibility, distribution and distance of farm plots from habitation. Specifically, moving feedstock – abundant elephant grass and *Leucaena* spp were identified in addition to crop residues – to some centralised, formal production facility such as a kiln and similarly the return of the biochar would demand scarce labour resources.

However, concentrating on land closest to the village, where soil fertility has also declined the most, could ease this challenge. Substituting slash-and-char for slash-

and-burn in initial clearance of forest could provide baseline benefit and enduring improvement in crop production, although such additions would not be tradable.

The reported practice of slash and char agriculture outlined above had been described and based on this information, the PhD had been designed. I subsequently spent several weeks living and working with 'Madame Fausti' and her extended family to properly investigate this practice.

In contrast to that described above, I found no evidence of such practice. She simply practices shifting slash and burn agriculture, and has done her whole life. When I asked about this apparent discrepancy, it was stated that there must have been some 'misunderstanding' during translation. Further confirmation was given by the Director of the Wenchi branch of the Ministry of Food and Agriculture (MOFA) who stated that he knows of no such practice in his municipality or any other.

### **5.3 Agriculture in Wenchi District, Brong Ahafo region**

#### *Land Tenure System*

Land acquisition is not difficult in this district. About 81% of all farmers acquire their land through inheritance or are farming on family lands. The rest who have various forms of shared tenancy arrangements are mostly settler farmers.

#### *Farm size and major crops*

The farmers work on relatively large size farms, especially those growing maize and yams. Farm sizes range from 1 acre to 10 acres and above. From Table 5.1 below, just 6.3% of the farmers work on farms below 5 acres and as much as 84.4% work on between 5-10 acres. The major crops grown are maize, yam and tomatoes. Root crops such as cassava and cocoayam are grown extensively. Plantain is also one of the major crops grown.

Table 5.1. Farm sizes in Wenchi District.

Acres	Number	%
0-5	2	6.3
5-10	27	84.4
10+	3	9.3
Total	32	100

#### *Production levels*

Total averages under cultivation for the major crops have increased steadily over the years. Yam covers the highest land space of 199,752 hectares as of 2010. In terms of yield estimates cassava yields are the highest with 21 tons/hectare, and yielded 199,920 tons in 2010 alongside 115,584 tons of yam. Cowpea was the least produced with 2,300 tons in 2010.

#### *Access to funds and credit*

From MOFA survey in 2010, 76.6% have no access to formal financial credit and rely on family/friends for financial assistance. Financial institutions find it difficult to deal with traditional farmers because of their unreliable production patterns and levels. Access to funds and credit is therefore limited to few farmers who are described as being resource-poor and lack the requisite capital to expand their farms.

The government-funded projects in the area of food crop production and cashew farm development have been limited to 20% of farmers in the district since 2001 (MOFA 2011). Support to farmers also takes the form of input supply with direct cash support at times to on-farm labour. Repayment of such government loans has however been discouraging with a recovery rate being 87% in 2003; 50% in 2004 and 2005; and just 31.6% for 2005. There is a need to link farmers (viable groups) to micro finance institutions and project credit lines or donor support funds.

### *Access to farming inputs*

Access to farming inputs can be said to be difficult, with all the supply points located at Wenchi town. It has been suggested that there is the need to attract 'big time dealers' to offer the required adequate services and farm inputs to farmers. Their products are cheaper and are able to respond quickly to farmers' demands.

### *Disease and pests*

Disease and pest problems could be rated as average for Ghana with the occasional outbreak e.g. armyworms. Disease and pest control problems have come about as the result of the changing ecology due to the intensive use of land and unsustainable cultural practices. Resistant pests and diseases of crops have become endemic for grains, legumes, tubers and tree crops, especially as a result of misuse of agro-chemicals. However, public campaigns set-up by central government have not matched the ever-growing needs and complexity of the problems. Local support from the public and civil society organisations to partner the District Assembly is a panacea to the problem if the effort to improve agriculture to reduce poverty would be realised.

### *Soil fertility and productivity*

Soil fertility and productivity have reduced considerably with resultant declining crop yields. The major contributing factor has been the rampant and indiscriminate bushfires, which have limited the restoration of soil fertility on most lands (Asuano being an exception, where the local chief has outlawed slash-and-burn practices).

Soil management and land conservation schemes must be introduced. Without support, a lot of land and water management practices are beyond the reach of individual farmers. In order to solve the problem there is a need to adopt comprehensive land use plans for all land based activities.

Storage and post-harvest management problems have resulted in high losses in roots, tubers and cereals. The absence of storage facilities and value addition to produce has been identified as the major factors responsible for the problem. Local methods of storage have contributed to the loss of grain quality and value for which more improved methods of storage/preservation are necessary. Investors could be encouraged to take up the defunct Ghana food distribution storage and drying facilities located at Wenchi for mass storage of grains and cereals. The capacity is 30,000 mini bags of maize and this facility should not be left to decay.

Processing of agricultural produce is limited and some people within MOFA feel the need to encourage more processing through credit provision. They state that transportation has been limited by the bad nature of the roads which has contributed greatly to high post-harvest losses and low farm incomes. Also, marketing of agricultural produce has been slow due to limited availability of capital. Additionally, a lack of business orientation and unstable producer price for farm produce has not helped much. They therefore argue the need for improved access to credit facilities so that farmers could market their goods with less difficulty.

#### *Sources of labour*

Hired labour is the dominant source of labour for farming in this district. From the latest survey (MOFA 2011), 78.1% of all labour employed on the farm is hired, 15.6% family and 6.3% reciprocal labour.

#### *Farm technology*

Around 74% of farmers use rudimentary methods such as cut, slash and burn. Tools such as machetes and hoes are the major farm implements, and just 6% use tractors to plough the fields. Only a few apply fungicides, herbicides and pesticides but this number is rapidly growing. In terms of storage, 19% store their excess produce in kitchens and 81% use traditional barns. This limits the quantity that can be stored, and as such large quantities of produce are sold at low prices at harvest. In terms of

transportation, 69% transport their produce by hand and the rest use tractors and pick-up trucks to get their produce to the point of sale.

#### *Agricultural extension service*

Services being provided by the extension staff include: education on good methods of farming; introduction to new planting materials e.g. maize, sorghum and cassava; and increased technical know-how. However, the extension service officer to farmer ratio is 1:1000, and poor road conditions and the expansive nature of the district make it difficult for officers to reach out to more farmers. It is therefore not surprising that as much as 75% of the farmers do not receive any technical support from the extension service department. There are also very few veterinary services for the livestock farmers.

#### *Post-harvest situation*

Post-harvest loss is a critical problem facing agricultural development in the district. The rate and magnitude of post-harvest losses occur during harvesting, transportation, processing and finally storage. The district does not have adequate storage structures and processing machines for handling farm produce which flood the market during the main harvest season, thereby bringing down prices. For example, there is only one central point silo for maize storage in Wenchi town, which has been deemed to be woefully inadequate. Post-harvest losses are conservatively estimated between 15% and 30% for both perishables and non-perishables of which the former is generally higher.

### **5.4 Potential biochar feedstocks**

This section describes potential biochar feedstocks that were observed whilst visiting smallholding subsistence farms. Selection criteria for their suitability were founded on two main principles: they needed to be available immediately on site as

transport of material from one place to another was prohibitively labour and time intensive; and they were not used for any other valuable purpose e.g. wood used for cooking.

The first and most obvious feedstock was the regrowth of plants and trees on fallow lands. After being left for anything between 3 and 10 years and during the dry season, dense undergrowth and numerous small trees up to 3m high were slashed with machetes, left to dry for several days then set on fire. Despite providing an influx of nutrients to the soil, the effect is short-lived as heavy rains rapidly leach the soil of its fertility.

By piling up the slashed material and smothering with soil, this plant material could relatively easily be charred and then spread in the immediate vicinity. This involves hard physical labour with hoes which would be carried out anyway to provide the 'hillocks' used in yam cultivation (see plate 5.1 below). The only extra physical effort would be the piling of cut plant material in the first place.

Plate 5.1. Soil is mounded into small 'hillocks' for yam planting.



Another potential source of charring material are the cocoa pods found discarded in heaps below cocoa trees after harvesting (see plate 5.2). These are left to decompose, providing valuable compost to the trees, but a proportion could also be charred and easily top spread below the trees.

Plate 5.2. Cocoa pods left to decompose under the cocoa trees



Overall, the subsistence farmers were very aware of how good fire was to their lands, but were not aware that charcoal could act as a sponge in the soil, retaining both nutrients and water. At least then, farmers would potentially be amenable to adopting slash and char as opposed to slash and burn if they were to trial the method and see visible improvements to the productivity of their crops.

The main obstacle to adopting this method of agriculture however, was the labour involved. Most farmers have second jobs in town e.g. waitresses or shopworkers, and are reluctant to take on any more work. Second to this was the difficulty in transport of any material across the rough terrain of the farmlands.

## 5.5 References

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## **6. RESEARCH LIMITATIONS, SUGGESTED IMPROVEMENTS AND RECOMMENDATIONS FOR FURTHER WORK**

To start this discussion chapter off, it is worth talking about the difficulties and challenges faced whilst conducting fieldwork in Ghana. For whatever reason, the indigenous practice of slash and char in the Wenchi District was incorrectly reported and led to the planning and commencement of this PhD. The feeling of not quite knowing what the truth was remained with me and proved to be quite challenging on numerous separate occasions throughout my stay there. I eventually learnt not to ask yes/no questions when I was there, as quite often I got the feeling that people did not want to come across as being contrary and thereby avoided answering 'no' to many questions. The cultural difference in conducting conversation on an official capacity was certainly an eye-opener. To give an example, I was talking with one farmer asking him about his charcoal production sites and how old they were. When I asked if he had any that were 5 years old, he replied 'yes' and showed me where. The same applied for any age of site that I requested. On a second visit I asked the same questions but was taken to different sites. I thereby had to change my approach and spent weeks travelling to many different farms until I could acquire reliable and reproducible information regarding the collection of samples for analysis.

### *Charcoal*

Although this study originally set out to investigate the stability and sustainability of biochar in Ghanaian subsistence agriculture, for reasons stated before, charcoal from previous production sites was chosen for investigation. This was not an ideal scenario, but the best option on offer. There was an abundance of charred material in agricultural fields from previous burns, but it was impossible to determine its age and therefore useless in investigating the stability of the carbon in the soil.

The charcoal itself came from three species of hardwood tree – known locally as Srono, Kande and Senya. There were originally concerns that different species of tree would produce charcoal with different properties and interfere with any

meaningful conclusions, but thankfully preliminary statistical analysis revealed that there were no significant inter-species differences.

A barrier to overcome was the overall heterogeneity of the charcoal fragments themselves. Due to the uncontrolled nature of its production as described in chapter 2, there was a wide range of XPS results obtained from samples collected from the same site. Differences in temperature and oxygen supply throughout the smouldering pile of wood would naturally create chars of different textures and with different chemical properties. The part of the tree that had been charred also affected the properties of the charcoal – it was noted that some fragments were very friable and heavily oxidised whilst others were hard, shiny and had very low O:C ratios on their surface. It was therefore very time-consuming and in reality a rather subjective exercise in selecting appropriately representative samples for analysis. Great care was taken to apply the same selection criteria to all samples, but nevertheless a more controlled and homogenous sample stock would have been much more desirable.

Sample preparation of the chosen fragments also posed a challenge as some were encrusted in soil matter while others were relatively clean. The soil and sand needed to be removed to allow XPS analysis of the charcoal surface, and with this some of the carbon itself was inevitably removed. This was especially pertinent when considering the importance of surface analysis with XPS.

There was also the uncertainty of how long a particular charcoal surface had been exposed to the elements. A fragment is found from a site proved to have been 10 years old, but what's to say that the fragment hadn't fractured six years ago and the subsequently analysed surface has only been exposed for four years rather than the assumed 10? This was in part overcome by only selecting fragments that were clearly whole branches, with the still-intact tree rings indicating where the 'oldest' surface would be. Nevertheless, this was an uncertainty that could possibly negate any conclusions made concerning the change of charcoal over time. As it turns out, this study reports that the change detected over time has no significant effect on its

water or nutrient retention properties, and so there is no argument to be argued against.

The fact that it was so time-consuming preparing the charcoal fragments was a huge hindrance. Fragments selected for the soil leaching experiments needed to constitute the same mass and volume for each individual column. This was simply not practicable, and indeed there was not an adequate cache of samples for sites of 5 and 6 years old – leaving a gap in the 10 year chronosequence.

The roughly 1 cm<sup>3</sup> fragments of charcoal selected for the leaching experiments also only had one side analysed by XPS. It was not possible to analyse every face of the fragment, and so a large assumption had to be made. In retrospect, it was not an achievable goal to quantify the relationship between surface properties of the charcoal and its ability to retain nutrients.

### *XPS*

XPS has been used in several studies to determine the O:C as a proxy for oxidation and thereby weathering or stability. It is normally used however for the analysis of relatively pure substances e.g. the surface of important metal components in machinery. In this study, it was far from simple to use the method on samples recovered from natural soil. Natural components in the soil interfered with results to such an extent that roughly 30% of analyses were rejected due to failures in selection criteria.

The obstacles were many: the presence of minerals shifted and distorted peaks beyond identification; when the presence of a sufficient quantity of minerals was present but the peaks were acceptable, a rough calculation had to be made to account for the oxygen present in minerals such as aluminosilicates which is clearly not ideal; the charcoal surface itself often became ionised under bombardment from the Xray source, distorting peaks out of the acceptable range; and fragments with any sizeable (but hidden) air pockets within them caused the machine to go

into emergency shutdown procedures due to vacuum failure (leaving it inoperable for two days).

Overall, XPS was a very laborious and time-consuming method to look at a substance such as field-retrieved charcoal which contains such a wide range of potentially interfering substances.

#### *Leaching column apparatus*

The apparatus shown in plate 3.1 was handmade from plumbing material and scrap wood, and was deemed to have performed quite well when considering the high recovery from the spiked soil samples. Great care was taken to create a uniform water infiltration rate across all of the columns, and at the start of the experiment the observed leaching rates were satisfactorily uniform. However, as the experiment progressed, the infiltration rates began to differ. In a few cases results from individual columns had to be rejected due to an agonisingly slow infiltration rate or in two cases, a complete blockage.

Columns with a diameter of just 5cm were used, and this was deemed to be one of the contributing factors to a varying infiltration rate. Other studies use larger columns with a diameter of around 10-15cm, with the general rule being the larger the better. Unfortunately there was just not enough soil brought back from Ghana to accommodate such size columns. As a result, it is hypothesised that the columns were just too narrow to allow unhindered flow, and possibly began to silt up at the bottom as the experiment wore on. This would undoubtedly affect the results, but in which way is not clear.

#### *Nutrient retention*

This experiment led to one crucial conclusion that even after 10 years of residence in the soil, charcoal still maintains its ability to retain plant available ammonium nitrate better than soil alone would. On average, 35% of the nitrate applied was retained by charcoal/soil mixtures after 12 successive 'downpour events' and was

plant available. This amount of water added roughly mimics half of an entire rainy season in the months of April to July in central Ghana.

It would be of great interest whether the same applies for a whole suite of micro- and macronutrients. Phosphate, potassium, magnesium and calcium to name just a few. This experiment would have been greatly enhanced by the ability to monitor these additional nutrients to get a more complete picture of biochar's soil enhancement properties.

In addition, it would have been perfectly feasible to grow seedlings in each leaching column, and to measure plant growth, leaf area, nutrient uptake of radioisotopes and root mass etc. Again, this would improve the experiment by introducing as many natural processes into the laboratory as possible. It would also be advantageous to use 'alive' soil with all its associated flora and fauna to introduce as many factors involved in nutrient cycling as possible.

### *Conclusion*

The first objective in this investigation was to describe the effect of varying levels of biochar on soil hydrology. This was achieved as the study described in detail the water retention properties of charcoal and soil mixtures. As stated in section 1.4.1, two hypotheses were tested: a) Biochar affects the water retention characteristic of a sandy/clay soil; and b) The level of biochar addition affects the water retention characteristic of a sandy/clay soil. It was found that Biochar did indeed affect the water release characteristic of both soil types. Up to a level of 10% (by weight) addition, biochar significantly increased the water holding capacity, but no significant differences were found between the different levels of treatment. The information gained is of great interest to agronomists who investigate drought stress on crops, and need to know how a soil responds to an ever increasing level of dehydration. It is of particular importance to agricultural practices in hot parts of the world where rainfall can be erratic and sometimes unreliable.

The second objective was to observe and describe changes in surface chemistry of biochar over time, and the following hypothesis was tested: c) exposure to the soil causes changes in biochar surface chemistry over time. This hypothesis was rejected as no significant difference between charcoal fragments of different ages was found. This would imply that during its first 10 years of residence in the soil, the charcoal retains its original surface chemistry. Therefore, the aforementioned beneficial properties of such a soil amendment could be present for a considerable amount of time – essential information for a farmer considering investing in such a practice.

The third objective was to assess the mobility of fertiliser in different soil/biochar mixes, and the following hypotheses were tested: d) exposure to the soil causes changes in biochar porosity over time; e) addition of biochar affects the nutrient retention capacity of soil; f) biochar surface chemistry affects the nutrient retention capacity of soil/biochar mixes; and g) biochar porosity affects the nutrient retention capacity of soil/biochar mixes. Hypothesis (e) was supported by this research, as additions of biochar significantly increased the nutrient retention capacity of the soil. Hypotheses (d),(f) & (g) however, were all rejected as no significant relationship was found between age and porosity, indicating that physical breakdown of charcoal fragments was not a significant factor over 10 years of exposure to the soil. There was also no significant relationship between either surface chemistry or porosity with regards to nutrient retention.

These findings support theories in the current literature that biochar increases both water and nutrient retention, but however did not succeed in quantifying any relationships therein. As discussed before, this was most likely due to the heterogenous nature of the test material. In conclusion, charcoal can be an easily available soil amendment material for subsistence farmers living off sandy, nutrient depleted soils. This study does not intend to support the use of biochar as a geoengineering style method of carbon sequestration, but instead highlights its value as both a nutrient and water retainer in degraded soils.

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