



Application of Fast Pyrolysis Biochar to a Loamy soil - Effects on carbon and nitrogen dynamics and potential for carbon sequestration

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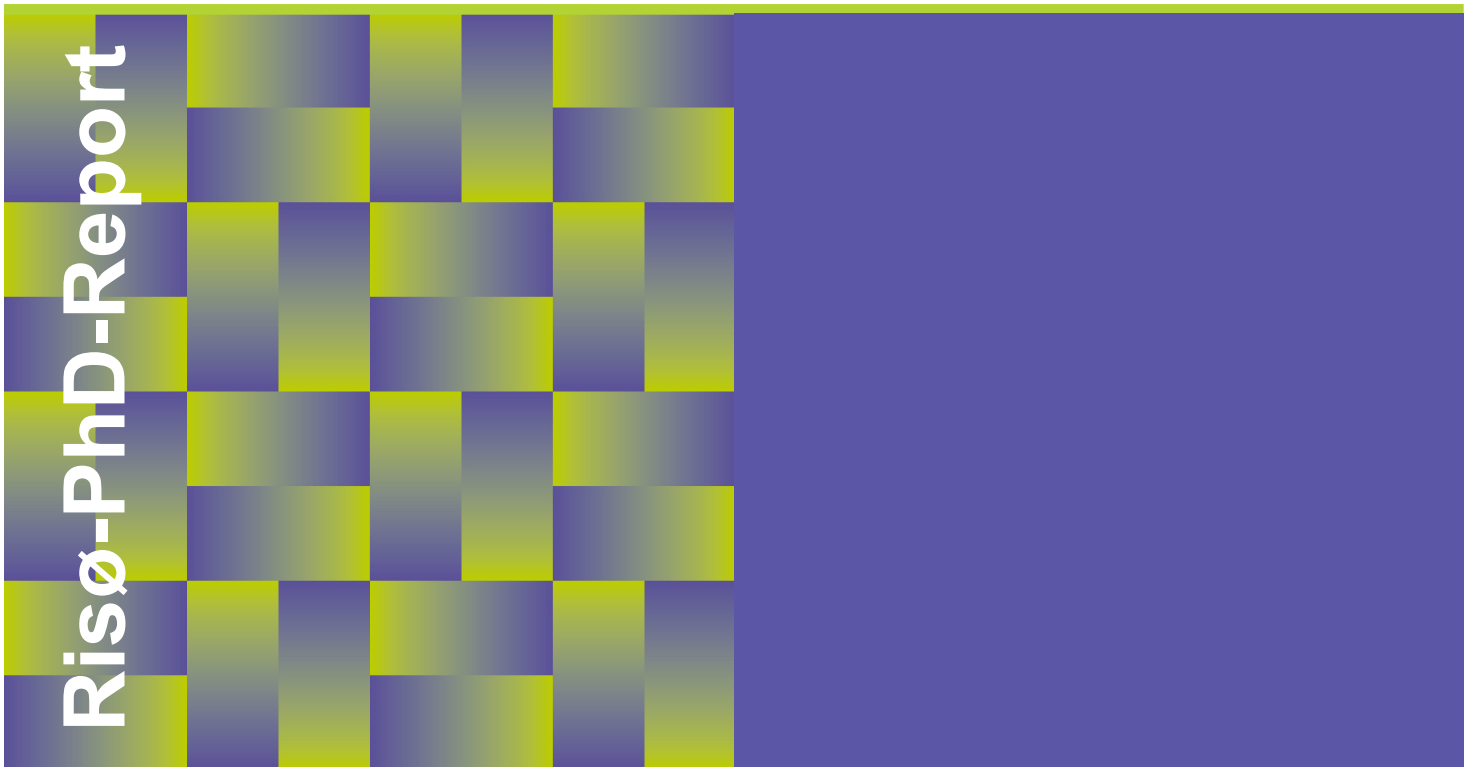
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Application of **Fast Pyrolysis Biochar** to a Loamy soil

- Effects on carbon and nitrogen dynamics and potential for carbon sequestration



Esben W. Bruun
Risø-PhD-78 (EN)
May 2011



APPLICATION OF FAST PYROLYSIS BIOCHAR TO A LOAMY SOIL

- EFFECTS ON CARBON AND NITROGEN DYNAMICS AND
POTENTIAL FOR CARBON SEQUESTRATION

ESBEN WILSON BRUUN

PHD THESIS

Risø-PHD-78 (EN)

BIOSYSTEMS DIVISION

Risø-DTU

MARTS 2011

Bruun, Esben Wilson

Application of Fast Pyrolysis Biochar to a Loamy soil
- Effects on carbon and nitrogen dynamics and potential for
carbon sequestration

Biosystems Division

Abstract:

Thermal decomposition of biomass in an oxygen-free environment (pyrolysis) produces bio-oil, syngas, and char. All three products can be used to generate energy, but an emerging new use of the recalcitrant carbon-rich char (biochar) is to apply it to the soil in order to enhance soil fertility and at the same time mitigate climate change by sequestering carbon in the soil. In general, the inherent physicochemical characteristics of biochars make these materials attractive agronomic soil conditioners. However, different pyrolysis technologies exist, i.e. slow pyrolysis, fast pyrolysis, and full gasification systems, and each of these influence the biochar quality differently. As of yet, there is only limited knowledge on the effect of applying fast pyrolysis biochar (FP-biochar) to soil. This PhD project provides new insights into the short-term impacts of adding FP-biochar to soil on the greenhouse gas (GHG) emissions and on soil carbon and nitrogen dynamics. The FP-biochars investigated in the thesis were generated at different reactor temperatures by fast pyrolysis of wheat straw employing a Pyrolysis Centrifuge Reactor (PCR). The carbohydrate content ranged from more than 35 % in FP-biochars made at a low reactor temperature (475 °C) down to 3 % in FP-biochars made at high temperatures (575 °C). The relative amount of carbohydrates in the FP-biochar was found to be correlated to the short-term degradation rates of the FP-biochars when applied to soil.

Fast and slow pyrolysis of wheat straw resulted in two different biochar types with each their distinct physical structures and porosities, carbohydrate contents, particle sizes, pH values, BET surface areas, and elemental compositions. These different physicochemical properties obviously have different impacts on soil processes, which underscores that results obtained from soil studies using slow pyrolysis biochars (SP-biochar) are not necessarily applicable for FP-biochars. For example, the incorporation of FP-biochar (10 wt%) in a sandy loam soil improved the water holding capacity (WHC) by 32 %, while the SP-biochar reference only increased it moderately. Moreover, soil amendment of FP-biochar caused immobilization of considerable amounts of soil N, whereas SP-biochar resulted in a net mineralization of N after two months of soil incubation. Nitrogen immobilisation can be detrimental to crop yields, as shown in a Barley pot trial in this thesis, but may, on the other hand, constitute an advantage during e.g. fallow periods by preventing N leaching. Moreover, when it comes to the mobility of biochar in soil, FP-biochars acted considerably differently to SP-biochar. FP-biochar contained highly mobile carbon components (nm-scale), which followed the downward movement of water. By contrast, C components from slow pyrolysis biochar were retained in the topsoil.

In summary, the research of this thesis shows that, compared to its more inert 'traditional biochar counter-part' made by slow pyrolysis, FP-biochar, in a number of ways, acts more like the original organic matter feedstock when added to soil. Yet, on the longer term the effects are likely a transient phenomenon, as the labile part is used up after a few months, leaving a much more recalcitrant FP-biochar. It is still too early to recommend - or discourage - FP-biochar for agronomic use, since field trials are needed in order to verify potential benefits or drawbacks on soil fertility and crop yields. However, this thesis has improved the mechanistic understanding of the effects of applying FP-biochar to soil, and shows that wheat-straw FP-biochar has properties beneficial for agricultural soil, e.g. it improves soil WHC, adds minerals, enhances microbial activity/biomass, and increases the N and C turnover dynamics.

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Contents

Preface	3
1 Introduction	4
1.1 Stabilisation of plant-captured carbon in biochar	4
1.2 Pyrolysis.....	5
1.3 Impacts of biochar on soil.....	6
1.4 Objectives.....	7
1.5 The Biochar project.....	7
2 Background	8
2.1 Historical perspective.....	8
2.2 Emerging awareness of biochar	8
3 Biochar production	9
3.1 Pyrolysis.....	9
3.2 Methods of pyrolysis.....	10
3.3 Slow Pyrolysis.....	10
3.4 Fast Pyrolysis	11
3.5 Gasification	13
3.6 Biomass feedstock.....	14
4 Physicochemical biochar properties (as influenced by pyrolysis)	15
4.1 Structural and chemical composition	15
4.2 Porosity and Surface area.....	18
4.3 Particle size distribution.....	19
5 Impact of biochar on soil	20
5.1 Influence of biochar on soil structure.....	20
5.2 Addition of minerals and organic matter in the form of biochar.....	21
5.3 Influence of biochar on water retention in soil	22
5.4 Influence of biochar on nutrient retention in soil.....	23
5.5 Influence of biochar on soil fertility and crop production.....	25
5.6 Application strategies.....	28
5.7 Impact of biochar on greenhouse gas emission.....	28

6	Synthesis	29
6.1	Impacts of fast pyrolysis on biochar characteristics.....	30
6.2	Impacts of fast pyrolysis biochar in soil	30
6.3	Impact of fast pyrolysis temperature on the overall carbon abatement.....	33
7	Critical reflections	33
8	Outlook	34
9	References	35
10	Appendices	41
Paper 1	Influence of fast pyrolysis temperature on biochar labile fraction and short-term carbon loss in a loamy soil.....	43
Paper 2	Effects of slow and fast pyrolysis biochar on soil C and N turnover dynamics.....	59
Paper 3	Application of biochar to soil and N ₂ O emissions: potential effects of blending fast-pyrolysis biochar with anaerobically digested slurry	77
Paper 4	Biochar mobility and effects on nitrogen leaching in repacked sandy soil ...	93

Preface

This PhD thesis is submitted as partial fulfilment of the requirements for the degree of the Philosophiae Doctor (PhD) at the National laboratory of Renewable Energy, Technical University of Denmark (Risø-DTU).

The thesis is based on four papers, of which one has been published and the remaining three submitted for publication. All four papers appear as appendices and will in the following be referred to by the numbers given below.

1. Bruun EW, Hauggaard-Nielsen H, Ibrahim N, Egsgaard H, Ambus P, Jensen PA, and Dam-Johansen K. Influence of fast pyrolysis temperature on biochar labile fraction and short-term carbon loss in a loamy soil. *Biomass & Bioenergy* 35: 1182-1189
2. Bruun EW, Ambus P, Egsgaard H, and Hauggaard-Nielsen H. Effects of slow and fast pyrolysis biochar on soil C and N turnover dynamics. Submitted to *Soil Biology & Biochemistry*
3. Bruun EW, D. Müller-Stöver, P. Ambus, and H. Hauggaard-Nielsen. Biochar soil application and N₂O emissions – potential effects of blending biochar with anaerobically digested slurry. *European Journal of Soil Science*, accepted for publication
4. Bruun EW, Petersen C, Hauggaard-Nielsen H, and Strobel BW. Biochar mobility and effects on nitrogen leaching in repacked sandy soil. Submitted to *American Journal of Soil Science*

During the course of the project I had my work base at the Biosystems Division at Risø National laboratory and a minor period at the Department of Basic Sciences and Environment, Environmental Chemistry and Physics, University of Copenhagen.

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1 Introduction

1.1 Stabilisation of plant-captured carbon in biochar

Soils worldwide contain around twice as much carbon (C) (1500 Gt) as the atmosphere (760 Gt), and three times the amount found in vegetation (560 Gt), and hence constitute an enormous C reservoir (Batjes, 1996; Lal, 2004). While poor agricultural management can have serious consequences by dramatically speeding up the release of CO₂ emissions from soil, other practices can increase the soil C stock considerably, and thereby mitigate climate change (Schils, et al. 2008). One interesting abatement strategy is to sequester carbon in soil by means of charred biomass (biochar) (Laird, 2008; Lehmann, et al., 2006). The mechanism behind biochar C sequestration in soil is relatively straightforward. Organic matter is thermally decomposed in an oxygen depleted atmosphere (pyrolysis) and modified to form structures that are much more resistant to biological and chemical degradation as compared to the original feedstock. Thus, by stabilizing plant-captured carbon as biochar and sequestering it on a long term basis in the soil, application of biochar is a way to withdraw CO₂ from the atmosphere. Taking also the pyrolysis energy products - bio-oil and syngas - into account, the whole process becomes ‘carbon-negative’, as illustrated by the example in Figure 1, where a net withdrawal from the atmosphere of 12 % C is obtained.

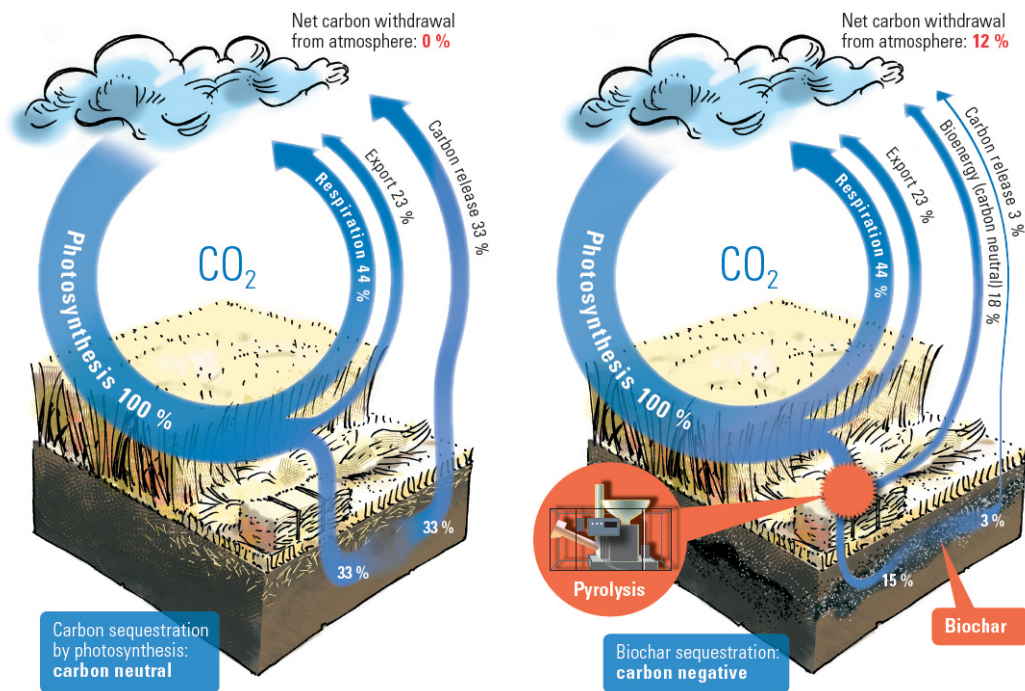


Figure 1. Principle behind C sequestration with biochar soil application compared to a normal agricultural system. ‘Export’ denotes removal of grain. Wheat carbon cycle is based on Aubinet et al. (2009). Biochar C loss from soil is based on paper 1 using fast pyrolysis biochar made at 500 °C. Copyright E.W. Bruun, Risø-DTU.

In this thesis, biochar is defined as ‘charred organic matter produced and applied to soil in a deliberate manner, with the intent to sequester carbon and improve soil properties’ (based on Joseph and Lehmann 2009). In a broad sense, biochar is just another word for charcoal used for barbecue, heating, iron production etc., with the only difference being functional intentions with the materials. However, although physicochemically being the same material, the distinction between charcoal and biochar is important. The use of the term ‘biochar’ implies that effort has been made to ensure that the biochar product is stable, improves soil quality, and does not impose environmental or health risks when applied to soils.

The great C sequestration potential of biochar, together with biochar’s apparent ability to improve soil quality, as well as the pyrolysis energy products (bio-oil and syngas) make the pyrolysis technology a highly interesting concept - a potential ‘Win-Win-Win Scenario’, as suggested by Laird (2008). However, biochar is not just one uniform material, but is formed by the original feedstock’s physicochemical characteristics and the pyrolysis settings. Biochar as a mean for carbon sequestration in soil is a relatively new research field, and studies constantly add knowledge to this already highly complex research area. Research reveals e.g. that, depending on pyrolysis type and temperature settings, some biochar types may on the short-term be considerably more degradable than others, or have much larger specific surface areas (Baldock and Smernik, 2002; Bruun, et al., 2008; Zimmerman, 2010; Downie, et al., 2009). Obviously, the effect of biochar incorporation is also influenced by soil type and other environmental conditions. Biochar can be applied to a multitude of soils within various climates and agricultural systems, which implicate that one biochar type may improve nutrient retention and crop yields in one system, but not in another. It is therefore a highly diverse picture of the potential biochar benefits and drawbacks one gets when reviewing the literature (see e.g. Atkinson, et al., 2010; Lehmann, et al., 2009; Verheijen, et al., 2010).

1.2 Pyrolysis

Biochar is made by pyrolysis (‘pyro’ in Greek means fire, while ‘lysis’ means breaking down into constituent parts). During pyrolysis, the organic matter is heated up to 300-600 °C in an oxygen depleted atmosphere and transformed into three different components: bio-oil, syngas, and biochar. Bio-oil yields can be maximised by fast heating pyrolysis (FP) processes, whereas slow heating pyrolysis (SP) maximises biochar yields. Despite that SP processes can be considered the most suitable technology for biochar production (Mašek and Brownsort, 2010; Verheijen, et al., 2010), FP seems an equally important technology for the supply of biochar. The production of fossil fuels (especially oil and gas) is expected to decline over the next decades to come (Denman, et al. 2007), which will inevitably push the development in the direction of increased use of renewable energy, including bioenergy. It is therefore reasonable to expect that FP processes, optimised for bio-oil production, will hold an increased market interest in the near future, and that the FP ‘biochar residue’ will be marketed alongside SP-biochar. Slow and fast pyrolysis result in biochars with different physicochemical qualities, which in turn may cause varying effects in soil (Brewer, et al., 2009). A fast pyrolysis process at low temperatures or with large feedstock particles may e.g. result in incompletely pyrolysed biomass. In contrast, the longer particle retention time in the pyrolysis unit in SP

processes creates a more completely pyrolysed inert biochar-product with less volatile C-substrate. The specific biochars studied in this thesis was produced by fast pyrolysis using a pilot scale Pyrolysis Centrifuge Reactor (PCR) (described in chapter 2).

1.3 Impacts of biochar on soil

In addition to holding considerable carbon sequestration potential, biochar has been shown to improve soil quality and crop yields (discussed in chapter 5). The positive effects have mainly been attributed to biochar's ability to absorb plant nutrients (Chan, et al., 2007; Glaser, et al., 2002; Steiner, et al., 2008a) and to increase soil water holding capacity (Brockhoff, et al., 2010; Pietikainen, et al., 2000). Other studies have shown that the application of biochar together with fertilizer (NH_4^+) increases crop yields as compared to pure fertilizer application (Chan, et al., 2007; Steiner, et al., 2008b). However, the majority of these biochar-studies have been conducted on highly weathered infertile tropical soils and generally for very limited time periods, i.e. 1-2 year (Kolb, et al., 2009). In order to obtain a general evaluation of biochar soil application, studies conducted on other soil types and in other climatic zones, e.g. on fertile soils in temperate regions like Denmark, are highly required. Moreover, laboratory studies have shown that biochar amendment to soil is able to reduce emissions of the potent greenhouse gases methane (CH_4) (Spokas, et al., 2009) and nitrous oxide (N_2O) (Singh, et al., 2010; Spokas, et al., 2009; Yanai, et al., 2007), although further research is needed in order to verify these results. Several characteristics of biochar potentially influence its effects on soil quality, including its labile fractions, porosity, density, particle size, mineral content, residual oils and tars, and surface chemistry and sorption properties (Downie, et al., 2009).

Lead by a relatively limited number of scientists, the scientific attention has resulted in an increasing body of biochar publications, which have provided a growing knowledge pool about biochar and the pyrolysis process in general. To get an overview of the number of slow vs. fast pyrolysis biochar studies, a literature review of papers published between 2004 and 2011 was conducted as part of the thesis research, using the Web of Knowledge (26.01.2011). Out of 170 papers containing the word 'biochar', 92 papers specified the pyrolysis conditions. Of those, 81 % were 'slow' pyrolysis studies, while fast pyrolysis studies made up the remainder. Twenty-nine studies (lab and field) dealt with the effect of applying biochar to soil. Only one of these soil studies used fast pyrolysis biochar (Spokas, et al., 2009).

This thesis seeks to diminish the obvious research gap regarding the effect of applying FP-biochars to soil.

1.4 Objectives

The overall objective of this thesis has been to study the short-term effects of soil application of fast pyrolysis biochar on microbial activity and soil nutrient dynamics, including potential GHG emissions (CO₂ and N₂O). In order to address this, four major research activities were conducted, which are enclosed in this thesis as paper 1-4. The specific objectives for each paper were:

1. to study the influence of fast pyrolysis temperature settings on the CO₂ emissions from biochar amended soil and to determine the net CO₂ mitigation combining biochar-C sequestration and bio-oil fossil fuel substitution.
2. to study the short-term biochar stability in soil in relation to microbial biomass and C and N turnover, comparing FP biochar with a SP-biochar as reference.
3. to study the GHG emissions and soil C and N turnover dynamics after soil incorporation of different concentrations of biochar alone as compared to biochar blended with anaerobically digested slurry.
4. to study nitrogen leaching after the application of N-fertilizer to soil amended with FP biochar, including potential downward movements of biochar particles in a repacked sandy soil.

Six types of freshly made biochars were used in the experiments: five FP-biochars made at different temperatures (475 to 575 °C) and a reference SP-biochar produced at 525 °C. Wheat straw was used as pyrolysis feedstock, representing a valuable lignocellulosic agricultural crop residue.

1.5 The Biochar project

The PhD was an integrated part of the project: Sustainable Co-Production of Pyrolysis Bio-Oil for Fuel and Biochar for Carbon Sequestration from Bioresidues (Acronym: BioChar) funded by DTU globalization money involving Risø-DTU and DTU Chemical Engineering and Biochemical Engineering.

The overall objective of the interdisciplinary project was to upscale and optimise a new fast pyrolysis (PCR) unit for co-production of bio-oil and biochar. The effect of the project in society would be the provision of a new decentralised biomass conversion technology able to produce biofuels, which can offset GHG emissions from fossil energy use, and provide biochar, which can be used for soil C storage and improvement of soil fertility, as described above. The up-scaling process of the pyrolysis unit is currently delayed. Further information about this pyrolysis unit can be obtained in Bech (2008).

2 Background

The following background chapters provide a theoretical background for the pyrolysis process, its influence on the biochar characteristics, and the effects of biochar soil application on the short-term C and N dynamics, crop yields and GHGs emissions. Additional data from own research which is not otherwise included in the enclosed papers will be presented in these chapters. Following the more specific theoretical chapters, a synthesis chapter is provided to summarise the main results of the four papers and discuss them in relation to other studies on fast pyrolysis biochar. A set of reflections that has arisen throughout the three-year duration of the PhD project are presented in a chapter titled “critical reflections”, while a short ‘outlook’ chapter finishes this background.

2.1 Historical perspective

The scientific attention towards biochar originates from the research in charcoal amended anthropogenic soils situated close to current or historical settlements in the Amazon region and estimated to cover an area of 500 km² (Smith, 1980). These soils were modified by the native people, as far back as 10,000 year BP (Verheijen, et al., 2010), and are today highly fertile soils, which are sold locally under the name ‘Terra Preta’. The distinguishing feature of these soils compared to other anthropogenic soils e.g. in Europe is their high fraction of charcoal (up to 50 t C ha⁻¹) (Glaser, et al., 2002). It is assumed that the charcoal was deliberately made and applied as a soil conditioner to the otherwise poor soils by the native population, rather than just charred residues remaining after slash and burn practices. Many parallels have been drawn between the charcoal amended Terra Preta soils and the use of biochar as a soil conditioner and a mean for C sequestration. For example, Terra Preta soils are used to document the stability of charred organic matter in soil, which in some studies has been ¹³C dated to up 7000 years (Lehmann, et al., 2009). Yet, there are important differences between Terra Preta soils and present biochar application: Today biochar will typically be applied in large quantities and often to soils already receiving high amounts of organic and synthetic fertilizers. Also, the biochar feedstock, the pyrolysis conditions, and the biochar quality are likely different from the charcoal applied in ancient times. Terra Preta soils received small amounts of charcoal (and other organic material) repeatedly over a long period of time, and hence the soil microbial community has adapted to the input. The charcoal in the Terra Preta soils has been altered by biotic and abiotic oxidation processes over centuries.

2.2 Emerging awareness of biochar

Although the practice of charcoal application for soil fertility building is thought to be several thousand years old, the research in biochar for C sequestration is relatively new, emerging with the rising scientific and political awareness of climate change. The concept of using biochar for carbon sequestration and soil fertility building has been receiving increasing attention politically, scientifically, and in the popular media, although the term ‘biochar’ is far from being generally known. In the popular media, biochar is often described as a bit of a miracle cure, see e.g. Al Gore’s book ‘Our Choice: A Plan to Solve the Climate Crisis’ or James Lovelock’s article in the Guardian (Lovelock 2009), or, for quite the opposite view, e.g. “Biochar for Climate Change Mitigation: Fact or Fiction?”

from the organisation Biofuel Watch (Ernsting, et al., 2009). The increasing attention is also reflected in the growing numbers of biochar initiatives, which support and promote the use of biochar, e.g. The International Biochar Initiative (IBI, 2006), Terra – The Earth Renewal and Restoration Alliance (TERRA, 2009), the CarbonZero Project (CarbonZero, 2009), Biochar Carbon Sequestration (BCS, 2006), and The Biochar Fund (BiocharFund, 2008). Commercial initiatives are also slowly growing in numbers, and ‘old’ companies like Dynamotive (Dynamotive, 1991), Eprida (Eprida, 2002), and Best Energies, Inc (Best, 2006) are no longer alone on the market. The research on, and public attention towards, biochar has been especially large in Australia, but also in the United Kingdom and the United States, where biochar research centres e.g. have recently been opened.

3 Biochar production

3.1 Pyrolysis

The pyrolysis of biomass is a very old technology, which is still relevant within energy production and conversion of biomass (Antal and Gronli, 2003; Demirbas and Arin, 2002). Charcoal has been produced from pyrolysis of (woody) biomass for thousands of years, and recently the technology has also become interesting for use in the production of biochar (Laird, et al., 2009). The main purpose of charcoal making is to use it for fuel, in cooking and iron production, or as active coal. The requirements for charcoal (e.g. good combustion and minimal impurities) are different from the requirements for biochar, the making of which aims at high stability, positive effects on soil properties, e.g. high cation exchange capacity (CEC), and high surface area (Mašek and Brownsort, 2010).

Pyrolysis is, as mentioned in the introduction, a thermal conversion process in which organic material is converted into carbon rich solids and volatile matter in an oxygen depleted atmosphere (Bridgwater, et al., 1999). The charcoal solid, termed biochar, if deliberately made for soil application, is generally of high carbon content, up to 50 % of the original plant-carbon. The high content of carbon remaining in the biochar is preserved despite the relatively high process temperatures, because oxygen is unavailable for further reaction. The inert atmosphere is created by using an inert sweep gas, which prevents complete oxygenation/combustion of the biomass during the process. The volatiles that leave the biomass during the pyrolysis can be partly condensed to give a liquid fraction, commonly termed bio-oil (Mohan, et al., 2006), which can be combusted in a suitable boiler for heat and energy production. Bio-oil consists of water and a long range of organic compounds, such as CH_3OH (methanol), $\text{C}_3\text{H}_6\text{O}$ (acetone), and $\text{C}_6\text{H}_5\text{OH}$ (phenols) (Yaman, 2004). The remaining mixture of so-called ‘non-condensable’ gases, termed syngas (from synthesis gas), consists primarily of a mixture of H_2 and CO , but contains also CH_4 , CO_2 , H_2O , and several low-molecular-weight volatile organic compounds (Laird, et al., 2009; Yanik, et al., 2007). The process of pyrolysis requires energy, but the decomposition of the biomass releases enough energy-rich syngases to drive this reaction and still give a net energy output (Bridgwater and Peacocke, 2000). The liquid product, bio-oil, has the advantage relative to biomass used for energy that it can be easily stored, transported, and handled for the production of heat, power, and chemicals. However, as a fuel it has some undesirable characteristics, i.e. a low heating

value, due to the water content and highly oxygenated compounds, a tendency towards phase separation, and an organic acid component, which will corrode a normal diesel engine rapidly (Bridgwater, 1999; Mohan, et al., 2006).

Pyrolysis reactor characteristics, peak process temperature, heating rate, and feedstock quality (e.g. particle size and water content) strongly influence the proportion and quality of the pyrolysis products. In general, higher pyrolysis temperatures result in lower biochar yields (but higher output of gas) with less original structures and chemical components remaining (Figure 2). Biochar characteristics such as elemental composition, porosity, particle and pore sizes, and fractions of easily degradable hydrocarbons are also highly influenced by the above parameters (discussed in chapter 4) (Antal and Gronli, 2003; Downie, et al., 2009).

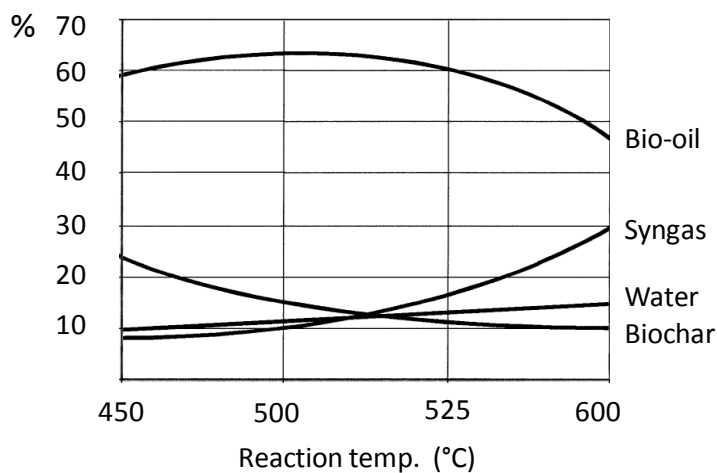


Figure 2. Typical yields from fast pyrolysis of wood, wt% on dry feed basis. Adapted from Bridgwater et al. (1999).

3.2 Methods of pyrolysis

The general process for pyrolysis of biomass is always the same, namely thermochemical decomposition of biomass in the absence of oxygen. However, different methodologies exist, and pyrolysis can be divided into three basic subcategories: slow pyrolysis, fast pyrolysis, and full gasification. These systems are all briefly introduced below. A very fast pyrolysis process is sometimes referred to as a ‘flash pyrolysis’ (Demirbas and Arin, 2002), and this distinction was originally of some importance, but has by now largely disappeared. Today, the term ‘flash’ is gradually being replaced by a more generalised definition for fast pyrolysis (Peacocke and Joseph 2009).

3.3 Slow Pyrolysis

Slow pyrolysis can be categorised as a rather low-tech and robust technology which has been optimised for biochar production. Historically, slow pyrolysis of woody biomass in traditional kilns has been the most widespread application for charcoal production (Antal and Gronli, 2003). Liquid and gas products are in some process designs allowed to escape

as smoke with consequent environmental pollution. Compared to fast pyrolysis, slow pyrolysis uses slower heating rates (ranging from 0.01 °C s⁻¹ to up to 10 °C s⁻¹, Peacocke and Joseph 2009), relatively long solid and vapour residence times (minutes to hours), and usually lower temperatures. Typical ranges for key process variables and product yields of slow and fast pyrolysis processes compared to the PCR product yields are shown in Table 1. Modern slow pyrolysis often takes place in continuous reactors, e.g. drum pyrolysers, rotary kilns, or screw pyrolysers (Brown, 2009). These plants, which, besides charcoal, collect bio-oil and syngas, are highly energy efficient compared to traditional kilns. In modern slow pyrolysis, the syngases from the process are usually burned in an external heat supply to keep the reaction going, as this is technically fairly simple and suitable for the long retention times.

Due to the long history of slow pyrolysis, modern slow pyrolysis technologies have a well-established commercial basis, although there is, as yet, little commercial use with biomass in biochar production. BEST Energies (Downie et al, 2007) and Pro-Natura's Pyro-6 and Pyro-7 technology (Pro-Natura, 2008) are examples of companies using slow pyrolysis technology.

Table 1. Pyrolysis process control and yield ranges. Based on a review of over 30 literature sources (Brownsort, 2009). Adapted from Ondrej Masek and Brownsort (2009).

Process		Slow pyrolysis	Fast pyrolysis	Pyrolysis Centrifuge Reactor (PCR)
Temperature (°C)	Range	250-750	400-750	475, 500, 525, 550, 575
	Typical	350-400	450-550	
Residence time	Range	mins-days	ms-s	~1 s
	Typical	2-30 mins	1-5 s	
<i>Yield (wt% of DM)</i>				
Biochar	Range	2-60	0-50	23(575°C) - 48(475°C)
	Typical	25-35	10-25	
Bio-oil	Range	0-60	10-80	46(475°C) - 58(525°C)
	Typical	20-50	50-70	
Syngas	Range	0-60	5-60	5(475°C) - 15(575°C)
	Typical	20-50	10-30	

3.4 Fast Pyrolysis

Fast pyrolysis plants use high-tech continuous processes designed to give a large fraction of liquid product (Yanik, et al., 2007). Fast pyrolysis converts biomass to products in a few seconds, using high heating rates (> 200 °C s⁻¹), short solid and vapour residence times (< 5 s), and temperatures typically around 500 °C (Table 1). To secure the instant conversion of the feedstock particles, feedstock must be dried to < 10 wt% water, and particles must be ground to < 2 mm to avoid significant diffusion barriers and temperature gradients in the particles during the heating process (Maschio, et al., 1992;

Verheijen, et al., 2010). Drying of the feedstock is, moreover, necessary in order to avoid too large fractions of water in the bio-oil product (Bridgwater and Peacocke, 2000). Relative to slow pyrolysis processes, the preparation of the feedstock, as well as the more advanced design, implies extra costs associated with the operation of fast pyrolysis. However, the larger yield of bio-oil provides an economical advantage.

During pyrolysis of lignocellulosic biomass, biochar is formed in two general reaction pathways. The main pathway occurs by de-volatilization of the biomass leaving behind a carbonaceous residue (primary biochar). The second pathway begins at higher temperatures (typically above 500-550 °C), where organic vapours (tars) decompose on the residue surface to form coke (secondary biochar) (Brown, 2009). The secondary reaction occurs at the cost of condensable volatiles and becomes increasingly important with rising temperature up to 700-800 °C. Therefore, for any given feedstock, there is an optimal operating temperature for the maximisation of liquid product yield in fast pyrolysis processes (Figure 2). The residence time is also essential in fast pyrolysis plants maximising bio-oil production. The vapour residence time in particular has to be short (preferably around one second) to minimise secondary reactions (Bridgwater, et al., 1999).

The fast pyrolysis technology is a lot more advanced than the technology in most slow pyrolysis plants and the specific approach varies a lot from one plant to another: Fluidised beds (feedstock is blown into a bed of heated sand, and mixed instantly), ablative reactors (feedstock is pressured against a heated metal disc in fast rotation), twin screw reactors (two parallel screws rotate at high speed, transporting and mixing heated sand and biomass), and Pyrolysis Centrifuge Reactors (PCR) (feedstock is blown into a heated centrifuge at high speed), which is used in the current report, are examples of different kinds of fast pyrolysis reactors. For additional examples see Bridgwater et al. (1999). Currently there are a small number of well-established commercial companies using fast pyrolysis technology, for example Eprida, Dynamotive, and Ensyn (see e.g. www.eprida.com; www.dynamotive.com; www.ensyn.com). A small mobile plant (on a truck) has also been developed by the Australian company BiG to meet the need for onsite biochar production (<http://www.bigchar.com.au>).

The goal of the present PhD dissertation was to study soil application of biochars made specifically by fast pyrolysis of the PCR type. The PCR used for this purpose was a small stationary pilot plant, which was developed to characterize and test wheat straw bio-oil as a liquid fuel and characteristics of biochar under different pyrolysis reactor settings. The PCR set-up consists of a screw type feeder, an electrically heated ablative centrifuge reactor, a cyclone used for biochar collection, a condenser, and a coalescer used for bio-oil collection. The reaction takes place at the inner surface of the heated reactor at temperatures in the range 450-600 °C, into which small particles are twirled by high-speed centrifugal powers. A conceptual diagram and short technical explanation are provided in paper 1: figure 1, while a detailed description of the PCR and its operation can be obtained in Bech (2008).

The product yield distribution range for the five reactor temperatures (475, 500, 525, 550, 575 °C) used to produce the biochar is given in Table 1. It is evident that less bio-oil and higher biochar yields were obtained from the FP PCR equipment compared to typical

values for other FP systems. Of the five temperatures tested, the optimum temperature for maximised bio-oil yield was around 525 °C, independent of the feedstock moisture content, while the low temperature (475 °C) yielded the largest amount of char (paper 1). Fast pyrolysis of wood shows approximately the same behaviour (Figure 2).

Scanning Electron Microscope (SEM) images of parent wheat straw and the produced SP- and FP-biochars are shown in Figure 3 below. The images illustrate the large impact which the two pyrolysis technologies had on the original feedstock particle size and other structural characteristics. Overall plant structure was clearly visible in the SP-biochar, while FP-biochar particles were much finer with large macropores and less visible resemblance to the parent straw material.

3.5 Gasification

Gasification is a thermo-chemical conversion technology, in which the widespread aim is to turn the complete organic fraction of the biomass into gases and thus avoid the production of char and bio-oil. The process of converting highly carbonaceous compounds into gas is a highly endothermic reaction, and therefore it requires heat to facilitate this step in the process. This heat is usually supplied through a partial combustion of the biomass or char creating temperatures from 600 °C to as much as 1300 °C depending on the process design. Although designed to produce gas, some gasifiers can also produce reasonable yields of char under specific settings, and have been proposed as an alternative biochar production pathway (Brown, 2009).

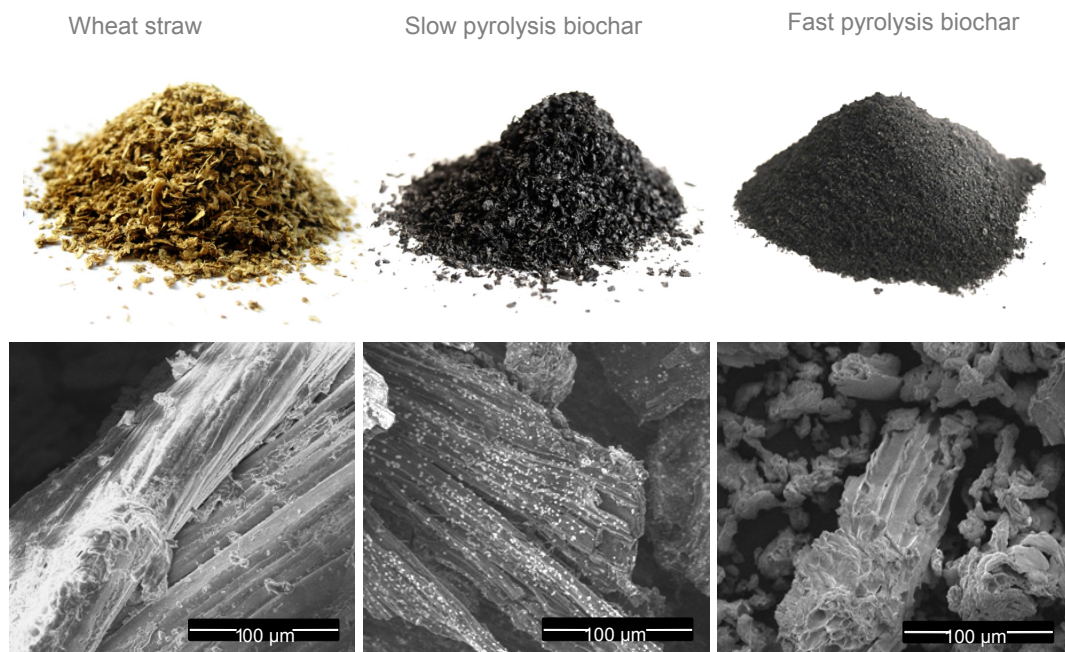


Figure 3. Above: Images of the wheat straw feedstock, slow pyrolysis biochar, and fast pyrolysis biochar, studied in this thesis (left to right). Copyright T. Thomsen. **Below:** Scanning electron microscopy (SEM) images of the above wheat straw, slow pyrolysis biochar, and fast pyrolysis biochar (pictures from LightSmyth Technologies Inc).

3.6 Biomass feedstock

Due to the robustness of the pyrolysis process, almost any organic material can be pyrolysed - from forestry by-products and various crop residues to animal manures (Demirbas and Arin, 2002; Roberts, et al., 2010; Yaman, 2004). Organic waste e.g. household waste, urban yard wastes, industrial by-products, or sewage sludge can also be used as feedstock in pyrolysis, but here cautions should be taken, as some constituents (e.g. heavy metals) may contaminate the biochar product. The specific feedstock characteristics significantly alter the physicochemical quality of the biochar produced as well as the composition and quantity of the ash component. Thus, soil application of biochars made from different feedstocks may result in different impact patterns on crop yields, soil nutrient dynamics, and biochar stabilities. Wheat straw was employed as feedstock for the FP-biochars used in the experiments of this thesis.

For the sake of the economic feasibility of the pyrolysis process, it is usually important that the applied feedstocks are relatively cheap and easily achievable. Wheat straw represents an abundant and valuable feedstock source, used in other energy technologies as well (Yaman, 2004). Compared to fast pyrolysis of wood, straw provides lower yields of bio-oil, but higher yields of biochar (Hamer, et al., 2004). It has a relatively high ash fraction compared to most other biomass feedstocks, which can cause problems for conventional combustion equipment, but which is normally not a problem in pyrolysis processes (Scheller and Joergensen, 2008).

As a lignocellulosic feedstock, wheat straw is mainly composed of cellulose, hemicelluloses, and lignin, along with smaller fractions of inorganic materials (ash), organic extractives, and water (Brown, 2009; Yaman, 2004). These fractions display distinctive thermal decomposition behaviours, which depend upon heating rates and highest treatment temperatures (HTT) used in the pyrolysis process. Higher heating rates require higher temperatures to initiate pyrolysis (Brown, 2009). Consequently, biochar produced by fast pyrolysis at higher reactor temperatures may contain unconverted cellulose and hemicellulose fractions, while biochars produced by slow pyrolysis at similar temperatures may be fully pyrolysed.

Cellulose is composed of repeating units of glucose of up to several thousand (Brown, 2009). During pyrolysis, the cellulose fraction depolymerises, and the number of glucose units bound together decrease continuously. When the polymers are degraded to very small molecules with around eight compounded units, the fractions become volatile and evaporate from the solid mass (Overend, 2004). Cellulose degradation occurs between 315-400 °C, although high heating rates may require higher reactor temperatures, as noted. The final product range normally contains biochar, CO₂, H₂O, CO, CH₄, other volatiles, and a range of condensable gases and/or tars (Brown, 2009).

Hemicellulose is a more complex and much smaller polysaccharide than cellulose. Contrary to cellulose, hemicellulose is branched and consists of a large variety of sugar monomers, such as xylose, mannose, and galactose. The more amorphous structure lowers the chemical and thermal stability, causing hemicelluloses to decompose at lower temperatures than cellulose (220-315 °C) (Brown, 2009). The decomposition of hemicelluloses yields more volatiles, less tars, and less chars than the decomposition of cellulose.

Lignin is the largest non-carbohydrate fraction of lignocellulosic material, and differs in many ways from both cellulose and hemicelluloses. Lignin has a highly amorphous structure, and the individual units can link in many different ways. Unlike cellulose and hemicelluloses, lignin cannot be depolymerized back to its original monomers (Overend, 2004). The pyrolysis of lignin yields more char than the other fractions and produces a pyrolygneous acid, which typically consists of methanol, acetic acid, acetone, water, and a tar fraction (Brown, 2009; Mohan, et al., 2006).

4 Physicochemical biochar properties (as influenced by pyrolysis)

4.1 Structural and chemical composition

Biochar has a highly heterogeneous composition, which contains both stable and more labile components, and carbon, volatile compounds, mineral content (ash), and moisture are generally considered the most important constituents (Antal and Gronli, 2003).

Biochar is first and foremost characterized by its high organic C content, which mainly comprises conjugated aromatic compounds of six C atoms linked together in rings. The condensed aromatic nature of biochar is what makes it so stable in the environment. The biochar structure is essentially amorphous, but may contain crystalline structures locally of highly ordered grapheme sheets (Downie, et al., 2009). With increasing pyrolysis reactor temperatures, the carbon structure becomes increasingly ordered until, at very high temperatures (>2000 °C), the biomass is eventually converted to graphite, with ring-layers systematically stacked on top of each other (Downie, et al., 2009).

The total carbon content of biochar varies considerably depending on feedstock and may range from 400 g kg⁻¹ up to 900 g kg⁻¹ (Antal and Gronli, 2003; Chan and Xu, 2009; Gaskin, et al., 2010). The highest C contents are obtained from hard-wood feedstocks pyrolysed at high temperatures, while manures generate biochars with low C contents. Relative to woody biomasses, nutrient-rich manures contain more minerals, which end up in the biochar, and thus decreases the C proportion. For example, biochars produced from pine chips in a study by Gaskin et al. (2010) had a C content of 817 g kg⁻¹ when produced by SP at 500 °C, while poultry litter ended up with 399 g kg⁻¹. A low total C content could also indicate that part of the original plant structures remain in the biochar in the form of carbohydrates (cellulose and hemicellulose). Depending on the pyrolysis conditions, biochar may contain from none to relatively large fractions of labile carbohydrates (as already mentioned in the introduction). This may especially be true for fast pyrolysis processes performed at low temperatures and/or with large feedstock particles, which, due to the very fast residence time, may result in incompletely pyrolysed biomass. Yet, fast pyrolysis processes do not necessarily result in high contents of labile biochar fractions. For example, none of the FP-biochars used in a study by Brewer et al. (2009) contained detectable amounts of only partially pyrolysed biomass. The FP-biochars made by the PCR unit in the present PhD study all contained carbohydrate fractions (Figure 4, Table 2). As shown in Figure 4 the fractions decreased exponentially

by a first order reaction with increasing reactor temperature.

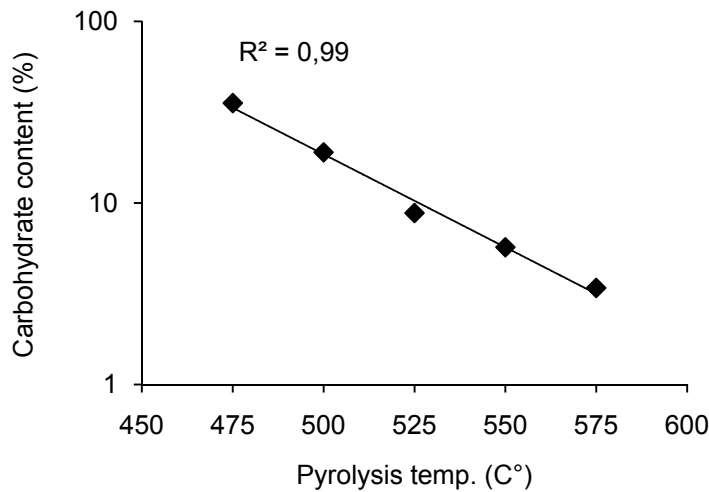


Figure 4. Carbohydrate content (cellulose plus hemicellulose) plotted against the reactor temperature of the PCR (see paper 1 for details). Please note the log scale of the 2nd axis.

Besides the large C component, the elemental composition of biochar consist of H and O, as well as different minerals (e.g. N, P, S) depending on the feedstock (Lehmann, et al., 2009). Mineral elements are predominantly found as heteroatoms incorporated into the aromatic rings, and are thought to contribute to the highly heterogeneous surface reactivity of biochar (Verheijen, et al., 2010). Depending on feedstock, the content of total nitrogen may range from almost none in wood-based biochar up to e.g. 64 g kg⁻¹ in biochar made from sewage sludge (Chan and Xu, 2009; Bridle and Pritchard, 2004). However, despite apparently high levels of nitrogen, the biochar total N content may not necessarily be accessible for crops, as N is fixed in inaccessible form (Verheijen, et al., 2010).

Biochar may contain numerous functional surface groups, such as hydroxyl-OH, keton-OR, ester-(C = O), aldehyde-(C = O)H, amino-NH₂, nitro-NO₂, and carboxyl-(C = O)OH groups (Amonette and Joseph, 2009). The highly heterogenic surface may thus exhibit hydrophilic and hydrophobic as well as acidic and basic properties, and contributes to biochar's capacity to react with a wide range of inorganic and organic compounds in the soil solution (Atkinson, et al., 2010). Freshly produced biochars, though, are usually hydrophobic in nature, due to predominantly non-polar surface characteristics (e.g. carbohydrate or aromatic characteristics) (Lehmann, et al., 2009). This was also the case for the FP-biochars studied in this thesis, where an added water droplet remained almost spherical to minimise surface contact (Figure 5, and 6b). In contrast, the SP-biochar seemed less hydrophobic. Despite the hydrophobic characteristics, water did not seem to be repelled by the particles, but rather engulfed the particles, when observed in a light microscope (Figure 6a). Water may, however, at the micro-scale level, be prevented from entering the biochar pores.

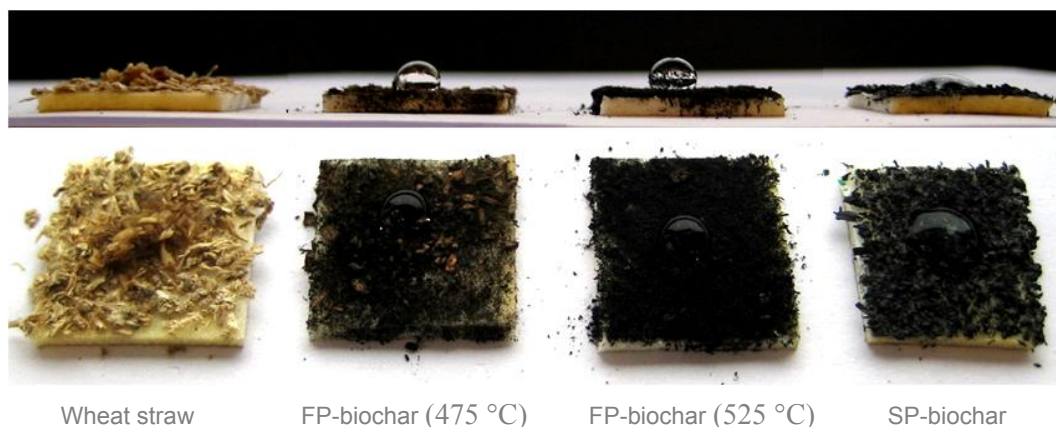


Figure 5. Drop of water added to a dense layer of wheat straw, FP-biochar (475 °C), FP-biochar (525 °C), and SP-biochar (left to right). The pictures were taken 15 minutes after the addition, illustrating the great hydrophobicity of fresh FP-biochar, where water remained in a spherical form.

Carboxylic acids and phenolic groups are especially important for the biochar's capacity to retain nutrients (Amonette and Joseph, 2009). Table 2 lists the concentration of these two functional groups for the different biochars used in the present PhD thesis. As is evident, the concentration increases slightly with increasing pyrolysis temperature. Qui et al. (2009) found similar concentrations of acidic surface groups (1.34 mmol g^{-1}) for fresh biochars made from straw by slow pyrolysis.

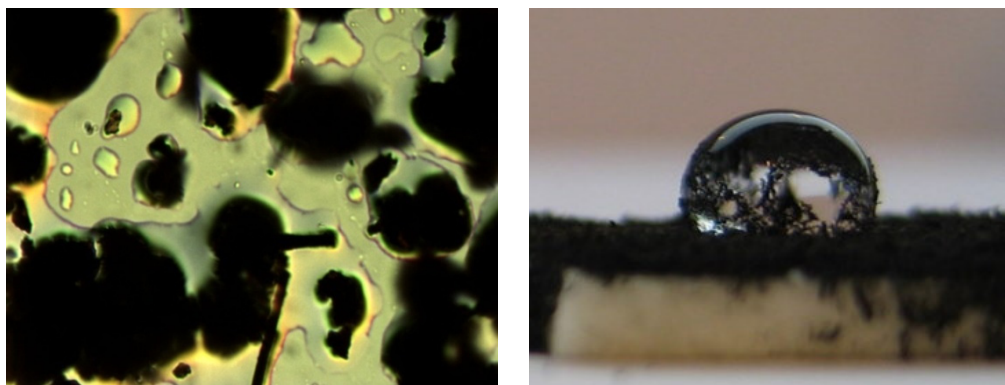


Figure 6. a) Biochar particles in water film at 500x magnification. The coloured part might contain labile carbohydrates (DOC). **b)** Close-up of FP-biochar (525 °C) from figure 5, showing small biochar particles on the surface of the droplet. Please note the acute outer angle between the horizontal surface and the sides of the drop, which illustrates the hydrophobic characteristics of the FP-biochar.

Besides biochar, the solid product of pyrolysis consists of minerals (ash). The size of this fraction is dependent on the ash content of the biomass feedstock. Feedstocks such as soft woods have low ash contents of less than 1 %, whereas herbaceous biomass (e.g. grasses and cereals) and manures have higher ash contents of up to 15 % (Yaman, 2004). During pyrolysis, the mineral content of the original feedstock is concentrated in the biochar

product, which ends up containing a considerably higher proportion of ash. The ash proportion, for example, increased from 5.9 % in wheat straw to 15.8 and 27.9 % in FP-biochars produced at 475 °C and 575 °C, respectively, in the present thesis (Table 2).

4.2 Porosity and Surface area

The pore size volume and pore size distribution of biochar affect its impact on important soil parameters, e.g. water retention, nutrient retention, and the total surface area. Pore size and volume is dependent on the biomass feedstock and pyrolysis settings (Downie, et al., 2009). During pyrolysis, loss of feedstock mass in the form of volatile organic compounds leaves voids, which creates an extensive pore network consisting of pores and cracks. By increasing the pyrolysis temperature and by using reactive agents the volatilization of the plant material increases and leaves a more porous biochar with a larger surface area. The pore sizes distribution of biochar is highly variable and encompasses micro-, meso-, and macropores with internal diameters below < 2 nm, 2-50 nm, and above 50 nm, respectively (Downie, et al., 2009). During pyrolysis the structure of the original plant materials is retained in the biochar, where vascular architecture may contribute to the macroporosity (Verheijen, et al., 2010). Biochars from woody biomass tend to exhibit larger surface areas (Downie, et al., 2009), and contain higher proportions of meso- and macropores compared to biochars produced on herbaceous feedstocks. By contrast, micropores are mainly formed during pyrolysis due to loss of water molecules during dehydroxylation of the biomass (Atkinson, et al., 2010; Bagreev, et al., 2001).

The surface area and microporosity of biochar are very important physical characteristics, which are positively related to the capacity of biochars to adsorb minerals and organic matter (Atkinson, et al., 2010). The predominant method for measuring the surface area of biochar is through gas adsorption, but comparisons between different studies can be somewhat challenging due to the range of adsorbents, temperatures, pressures, and algorithms to be chosen from. A method widely applied for determining the surface area is the measuring of N₂ adsorption using the Brunauer, Emmett, and Teller (BET) equation (Brunauer, et al., 1938), which also was the method employed in the present PhD.

In general, biochar surface areas can be correlated to biochar's micropore volume, as shown in an extensive literature review by Downie et al. (2009). The choice of feedstocks and processing conditions, and the presence of active reagents during pyrolysis, such as steam, CO₂ and O₂, greatly influence the surface area (Boateng, et al., 2010). In the review by Downie, surface areas of biochars produced in the interval from ~250 to 600 °C from different feedstocks and pyrolysis conditions, ranged from one m² g⁻¹ to at least 750 m² g⁻¹, the majority displaying surface areas above 300 m² g⁻¹. Some biochars with very large specific surface areas may even physically resemble commercially produced activated carbons (~ 1000 m² g⁻¹) (Mohan, et al., 2007).

Woody feedstocks with low ash content tend to generate biochars with higher surface areas than herbaceous, high-ash feedstocks (Karaosmanoglu, et al., 2000). It has been hypothesized that inorganic materials of high-ash feedstocks may partially fill or block access to micropores, thereby reducing the surface area. For example, Lee et al. (2010) found that the removal of inorganic materials by wet sieving of biochars led to higher

surface areas. Such mechanism would also help explaining the low surface areas of the high-ash wheat straw biochars studied in this thesis (Table 2).

The High Treatment Temperature (HTT) is the main factor governing the size of the surface area (Sohi, et al., 2010). In general, increasing HTT enlarges the surface area, until a temperature is reached at which deformation occurs, e.g. by fusion of micropores into larger pores, with subsequent decrease in the surface area again (Downie, et al., 2009). Another process parameter exerting decisive influence on the surface area is the heating rate applied in the pyrolysis process. High heating rates do not provide the time required for the development of micropores (Lua, et al., 2004), and have been shown to cause plastic transformation and melting of cell structures (Boateng, 2007; Cetin, et al., 2004). Lua et al. (2004) obtained the highest surface areas ($778 \text{ m}^2 \text{ g}^{-1}$) in pistachio nut shells at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$, while further increment of the heating rate up to $40 \text{ }^\circ\text{C min}^{-1}$ continuously decreased the surface area. These results are also consistent with the low surface areas reported for biochars produced by fast pyrolysis (heating rates typically $> 200 \text{ }^\circ\text{C s}^{-1}$) ranging from ~ 0 to $29 \text{ m}^2 \text{ g}^{-1}$ (Bech, 2008; Boateng, 2007; Lee, et al., 2010; Mohan, et al., 2007; Uzun, et al., 2010). Likewise, all FP-biochars studied in this work had very low surface areas, which increased only marginally with higher reactor temperatures (Table 2 and paper 2). However, it may be possible to process or ‘design’ FP-biochars that yield considerably higher surface areas by using active agents. In a study by Boateng (2010), the specific surface area of biochars generated by fast pyrolysis of soybean straw increased dramatically from just over zero to $837 \text{ m}^2 \text{ g}^{-1}$ when using steam activation.

4.3 Particle size distribution

The particle size distribution of biochar depends on the original biomass characteristics and pyrolysis conditions (Cetin, et al., 2004). During pyrolysis, the attrition and mass loss in the form of volatile matter causes the biomass to shrink, form cracks, and divide into smaller particles. Depending on the type of feedstock employed, the generated biochar material will be coarser or more brittle. Pyrolysis of woody biomass typically results in larger and coarser particles with more xylemic structures compared to pyrolysis of e.g. herbaceous biomass, which produces finer and more brittle particles (Verheijen, et al., 2010). The small feedstock particle sizes used in fast pyrolysis processes produce a very fine biochar powder, while slow pyrolysis processes can use much larger feedstock particles, which will result in larger biochars. The size distribution of biochars is important from a soil application point of view, in that different particle sizes are likely to cause different effects in soil (even if the biochar material is otherwise similar) (Angers and Recous, 1997; Zimmerman, 2010).

Table 2. Parameters of the biochars, wheat straw, and sandy loam soil used in the experiments.

Parameters		FP-biochar					SP-biochar	Wheat	Sandy
		475°C	500°C	525°C	550°C	575°C	525°C	straw	Loam
C (dry ash free)		537	602	643	670	692	859	462	
C		452	481	504	493	499	689	394	15.9
H		47	40	37	29	27	21	56	2.0
O ^a		332	266	230	202	185	79	481	
N		10.9	12.6	12.4	11.5	10.8	14	10.1	1.5
Ash fraction		158	201	216	264	279	198	59	
Cellulose ^b	g kg ⁻¹	300	160	74	42	27	0	403	
Hemicellulose ^b		55	30	14	15	07	0	228	
Total carbohydrates ^b		355	190	88	57	34	0	631	
Extractable organic C (DOC)			11.4	9.1	2.2		0.4		
Extractable NH ₄ ⁺ -N ^c			0.040	0.040	0.027		0.028		
Extractable NO ₃ ⁻ -N ^c			0.101	0.068	0.013		0.009		
Phenolic groups ^d	mmol g ⁻¹	0.48	0.73	0.72	0.99	1.89	0.61	0.40	~0
Carboxylic groups ^d	mmol g ⁻¹	0.77	0.81	0.90	0.96	2.01	0.48	0.47	0.05
Total acidic functional	mmol g ⁻¹	1.24	1.54	1.61	1.95	3.90	1.08	0.87	0.06
C/N ratio		41	38	41	43	46	49	39	11
pH (1:10 H ₂ O)				6.8	7.1		10.1		
Surface area (BET) ^c	m ² g ⁻¹	1.6	1.6	2.3	2.2	2.1	0.6	0.2	
Average particle size ^b	µm	71	50	23	12	12	113	< 1.4	
Bulk density	kg dm ⁻³	0.18	0.20	0.20	0.21	0.21	0.26	0.33	1.4

a: Oxygen determined by difference (100% - C, H, N, and ash)

b: Materials and methods, Paper 1

c: Materials and methods, Paper 2

d: Materials and methods, Paper 4

5 Impact of biochar on soil

The potential functions of biochar in soil are manifold. Provision of organic matter, sequestration of carbon, modification of soil water retention and soil physical characteristics, enhancement of cation exchange capacity (CEC), supply of plant available nutrients, modification of soil pH, microbial activity, and influence on GHG's emissions are all potential key functions of biochar. These areas will be discussed in the following sections in relation to own results.

5.1 Influence of biochar on soil structure

The incorporation of biochar into soil modifies soil physical properties, such as structure, texture, porosity, bulk density, and particle size distribution. This may in turn have consequences for important soil functions e.g. soil aeration, water holding capacity, and plant growth (Atkinson, et al., 2010). The density of biochars is much lower than mineral

soil (Table 2). Incorporation of biochar may therefore increase the soil volume and reduce the bulk density of the soil. In this thesis for example, an addition of 20 wt% FP-biochar (525 °C) to a sandy loam soil increased the soil-biochar volume with 100 %.

Incorporation of larger biochar particles (e.g. > 0.5 mm) could result in increased aeration of the soil and reduce anoxic microsites, which again influences various soil processes such as decomposition rates of organic matter, nitrification-denitrification dynamics, and GHG's emissions. Compaction of the soil after biochar application is another possibility. If fine biochar are incorporated in soil, particles may fill existing soil pores and thus potentially compact the soil and increase soil density. The FP-biochars used in the experiments of this thesis resulted in both a considerably decrease in total bulk density, but probably also in a more compact soil with a lower porosity, due to the very fine biochar component occupying soil pore space.

5.2 Addition of minerals and organic matter in the form of biochar

Aromatic 'black carbon', which resembles biochar chemically and biologically, is a natural residue after incomplete combustion processes e.g. occurring after wildfires. Black carbon has been found to be extremely recalcitrant in the environment and typically constitute the oldest soil organic matter (SOM) fraction in soil (Glaser, et al., 2002). Although biochar essentially is organic matter, the very slow decomposition in soil makes it different from other soil organic carbon pools, but physicochemically it may provide many of same soil services as SOM, such as soil stabilisation by aggregation, and retention of nutrients and water. Depending on the initial feedstock characteristics, the mineral ash content (and the mineralisation of biochar) may supply important macro- and micronutrients beneficial for the plant and soil microbial community. Due to alkaline properties of the mineral content in biochar, biochar usually has a neutral to alkaline pH value. Soil application of biochar may therefore have a liming effect.

Furthermore, labile organic biochar parts may be beneficial for the microbial community, as e.g. shown by Steiner et al. (2008a), and by Rillig et al (2010), who observed an increase in arbuscular mycorrhizal fungi after biochar additions (Rillig, et al., 2010; Warnock, et al., 2007). However, biochar could potentially also contain inhibitory substances, as suggested by De Luca et al. (2006). In order to test the FP-biochars for negative effects on the microbial biomass, a short-term incubation experiment was conducted using high concentrations of FP-biochar – see box 1.

Box 1 – short research question

Do high concentrations of fast pyrolysis biochar inhibit microbial growth?

Answer: Apparently not. The microbial growth was positively related to the amount of biochar applied. The microbial biomass increased from day 0 to 5 and from day 5 to 10 in all biochar treatments, except in the treatment with 20 wt% biochar, which peaked at an earlier stage (Figure 7a). Concurrently, the greatest decreases in soil mineral N were observed in the treatments with the high concentrations of biochar (Figure 7b). Even at very high concentrations of biochar (20 wt% and 50 vol% of the soil), the SMB-C seemed to benefit from the biochar addition, suggesting that the high concentration did not harm the overall population of microorganisms - at least in a short-term perspective. Moreover, the addition of the equally sized and inorganic perlite did not increase the microbial population as compared to the control soil (Figure 7a). This indicates that the increase in microbial biomass with the biochar additions should not simply be explained by a structural change of the soil such as improved soil aeration.

Materials and methods: 20 g of the sandy loam soil was amended with 0, 1, 2, and 4 g of FP-biochar (525 °C) and 4 g perlite, respectively. Perlite was used as a reference to biochar to test if physical/structural changes in the soil influenced the CO₂ emissions (not shown) and/or the dynamics of soil N and microbial biomass. Perlite is an inert amorphous volcanic glass with approx. the same average particle size as the FP-biochar. The experiment proceeded for 50 days and the soil was kept at approx. 30% water holding capacity throughout the period. Soil analyses were performed according to paper 2. All treatments were done in triplicates (n=3).

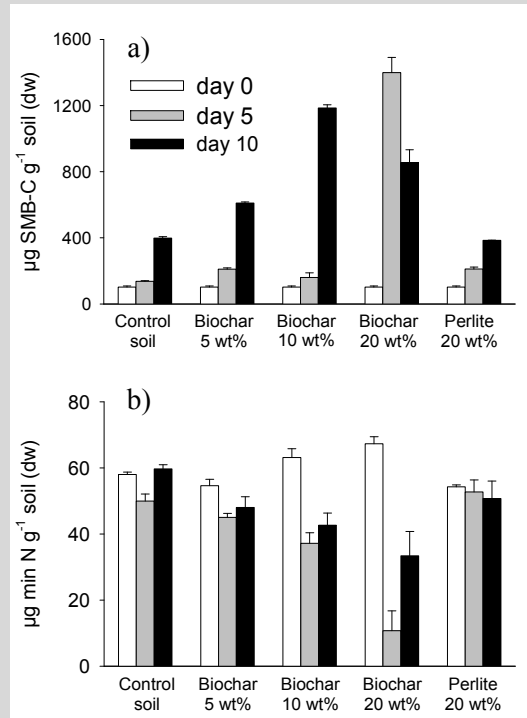


Figure 7. a) Soil microbial biomass carbon (SMB-C) and **b)** soil mineral nitrogen content in soil (20 g) with incorporation of 0, 1, 2, and 4 g biochar, and 4 g perlite, respectively. Samples were taken day 0, 5, and 10. Standard error bars are shown (n=3).

5.3 Influence of biochar on water retention in soil

Agronomic benefits of biochar are often ascribed to enhanced nutrient and water retention in soil. Biochar has been shown to improve the water retention in sandy soils and sand mixtures when applied at relatively high rates (25-45 vol%) (Brockhoff, et al., 2010), but also to decrease moisture content in clayish soils (Verheijen, et al., 2010). In a study by Trion (1948) wood-based charcoal (biochar) increased the moisture content of a sandy soil with 18 % after addition of 45 vol% biochar, while the moisture content decreased

after the addition to a clayish soil. One possible mechanism for decreased water retention in clayish soil could be simply that biochar replaced clay with a higher water retention capacity (Verheijen, et al., 2010). It has also been speculated that hydrophobic biochars may cause preferential flow, and/or decrease infiltration of water (as e.g. observed after natural fires), and thereby decrease the water holding capacity (WHC) of clay soils (Major, et al., 2010a).

Despite their hydrophobic nature, the FP-biochars (500 °C and 525 °C) at 10 wt% soil incorporation increased the WHC of the sandy loam soil with up to 32 %, while the SP-biochar only increased it moderately (Box 2). Biochars positive influence on soil water holding capacity has been linked to a great micropore volume, which may hold water (Verheijen, et al., 2010). However, this thesis demonstrate a markedly improved WHC by biochars with a very low surface area (and thus likely also micropore volume (Downie, et al., 2009)), which indicates that improved WHC rather should be attributed to the macropore volume. The scanning electron microscopy (SEM) images in Figure 3 visualise the noticeable macroporosity of the FP-biochars. Improvement of water retention in soil by biochar could moreover be due to biochar induced changes in distribution and connectivity of pores in the soil medium. Fine grained FP-biochar particles and ash could e.g. affect soil hydrology by decreasing the macroporosity of soil by partial or full blockage of soil pores. Incorporation of finer charcoal particles has previously been shown to increase the moisture content relatively more than larger particles (Tryon, 1948).

From a practical agronomical perspective, application of considerable amounts of biochar seems necessary in order to improve the water retention of soil. For example, a 15 % increase in WHC of the loamy soil (Box 2) requires an incorporation of 5 wt% FP-biochar, which corresponds to a total of 70 tons ha⁻¹ biochar (10 cm depth, soil density 1.4 kg dm⁻³). In practise, such large amounts of fine FP-biochar material would be very difficult to incorporate homogeneously (see e.g. Figure 10), and would, furthermore, require four times the amount of straw to be produced. However, the biochar effect on the soil water retention is likely additive, and therefore smaller amounts of biochar applied repeatedly over a number of years may do the job. Considering the reduced need for irrigation (as well as liming), along with increased crop yields and a potential income from sale of bio-oil, the combined pyrolysis concept may be feasible for the farmer (Fowles 2007; Gaunt and Lehmann, 2008).

5.4 Influence of biochar on nutrient retention in soil

Leaching of nutrients from agricultural soil depletes soil fertility, increases the need for artificial or organic fertilizer input, and furthermore leads to eutrophication of ground- and surface waters (Laird, et al., 2010). Evidence from several laboratory and field studies show that biochar application can reduce nutrient leaching from soil (e.g. Ding, et al., 2010; Glaser, et al., 2002; Laird, et al., 2010; Lehmann, et al., 2003; Novak, et al., 2009; Steiner, et al., 2008b). The capability of biochar to retain nutrients is mainly ascribed to biochars (often) great surface area providing adsorption sites for inorganic nutrients (bound by ion and covalent bindings). Moreover biochars apparent ability to increase the water holding capacity of soils may improve nutrient retention time in the topsoil. The attachment to biochar of organic matter or minerals with sorbed nutrients

(aggregation) may further increase the nutrient retention. However, biochar particles may also be transported downwards in the soil with the water movement or horizontally by surface water runoff, and thereby potentially facilitate the transport of nutrients out of the agricultural system (Leifeld, et al., 2007; Major, et al., 2010a).

Box 2 – short research question

Does fast pyrolysis biochar improve water retention in soil?

Answer: Incorporation of FP-biochar in a sandy loam soil (5 wt% and 10 wt%) considerably increased the soil's capacity to retain water (Figure 8a). The high concentration of FP-biochar improved the WHC (measured after 24 hours of drainage) by 30-32 %, while the SP-biochar reference (10 wt%) increased the WHC with 9 %. The positive effect of the FP-biochars on the water retention was sustained throughout the experiment (Figure 8b). After 13 days, soils with FP-biochar (10 wt%) contained 21-26 % more water than the control soil, whereas soil with SP-biochar (10 wt%) was similar to the control soil. Soils with incorporation of wheat straw improved the WHC by 18 %, (after 24 hours) while the straw-soil mixture was similar to the FP-biochar treatments at the last day.

Materials and methods: A 100 g mixture consisting of sandy loam soil (dry weight) with 0, 5, or 10 wt% biochar or straw incorporated was tested for water holding capacities (n=3). Small PVC-tubes (10 cm high, 4.5 internal cm in diameter), bottoms sealed with finely woven cloth, were filled approx. halfway with soil mixed with biochar or wheat straw. The feedstock wheat straw and three types of biochars were tested: SP-biochar (525 °C), FP-biochar (500 °C), and FP-biochar (525 °C). The soil mixtures were compressed slightly, and water (containing 0.01 M CaCl₂ to prevent alterations of soil structure) was slowly poured onto the soil until a water surface was observed just above the soil surface. The tubes were then placed vertically on paper towels and allowed free drainage and evaporation at room temperature (19-21 °C). The soils were weighed after 4, 24, 47, 62, 86, 148, 210, and 305 hours, and the water content determined by subtraction of tube and soil-mixture dry weight. One-way ANOVA and Tukey's test were used to compare means (according to paper 2).

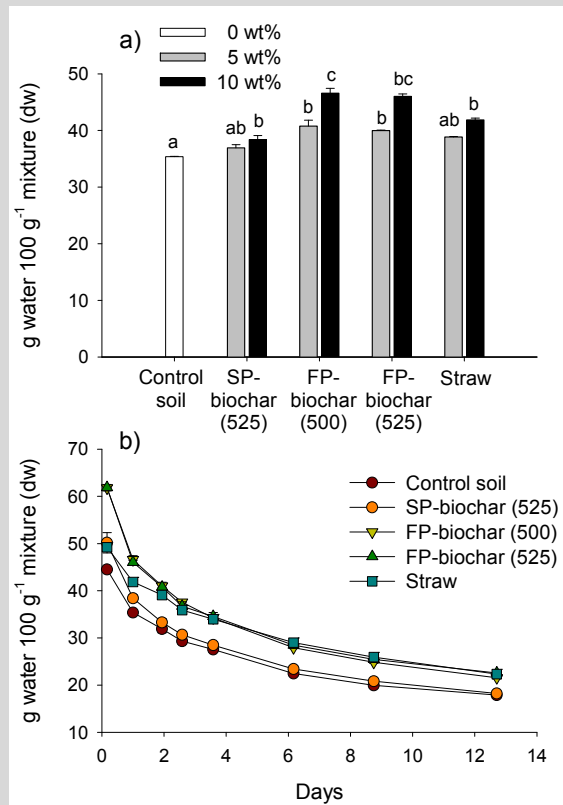


Figure 8. a) Water holding capacity of soils with 0, 5, or 10 wt% biochar or straw incorporated. **b)** Water content in soil mixtures over a 13 day period. Standard error bars are shown (n=3). Letters show significant differences according to the Turkey test (p < 0.05).

The Cation Exchange Capacity (CEC) of soil is a measure for how good cations e.g. ammonium, potassium, calcium etc. are bound in the soil. The cation retention of soils has been shown to increase after application of biochar, due to biochars (often) high surface charge density which enable the retention of ions (Liang, et al., 2006; Van Zwieten, et al., 2010). Cations are bound by ion- and covalent bindings to negatively charged sites on the reactive surface of biochar (and clay and organic matter). On the contrary anions (e.g. N-oxides and phosphates) are bound very weakly in soils under neutral to alkaline pH conditions, mainly due to the negative surface charge of clay. Whether biochar can play a role in the anion exchange capacity is an open question, which warrants further research.

Freshly produced biochar is hydrophobic and contains few polar, functional groups at the surface, but after exposure to water and oxygen in the soil the biochar surfaces oxidizes and forms more carboxylic and phenolic groups (Cheng, et al., 2008b). The biochar thus becomes more hydrophilic with time and increase its capacity to hold (cat-) ions, although it is not clear over what timescales these changes occur. In a setup where biochar (without soil and microorganisms) was exposed to high temperatures (70 °C) cation retention occurred within a few months (Cheng et al. 2006). An additional mechanism for increased CEC (besides biochars direct effect on adsorption sites) could be a potential liming effect of biochar. As acidic soils often have low CEC (due to H⁺ occupying available sites) a biochar induced pH increase could be beneficial. The liming effect of biochar has been discussed in the literature as one of the likely reasons for observed increases in crop yields after biochar application (Atkinson, et al., 2010).

Immobilisation of N in the microbial biomass, due to the addition of a labile carbon source with the added biochar, is another possible mechanism contributing to improved N retention in the topsoil (Sohi, et al., 2010). In general biochars have much higher carbon-to-nitrogen ratios considerably above 30 (Atkinson, et al., 2010; Table 1) than the requirements of bacteria and fungus with C/N ratios typically around 5 and 10, respectively. Thus, if part of the C in biochar is labile, the microbes, which tend to be more competitive than the plant, will completely exhaust the nitrogen resources in the soil. Contrary to the SP-biochar, soil application of FP-biochar (525 °C) resulted in immobilisation of N, when incubated in soil in 65 days (discussed in Paper 2 and 3).

5.5 Influence of biochar on soil fertility and crop production

Beneficial effects on crop yields have been documented in a number of pot and field trials (Asai, et al., 2009; Chan, et al., 2007; Chan, et al., 2008; Major, et al., 2010b; Van Zwieten, et al., 2010), although other studies have revealed only small or even negative crop yield responses upon biochar applications (Gaskin, et al., 2010; Van Zwieten, et al., 2010). Improved crop yields after biochar application have been ascribed to a number of mechanisms.

A liming effect of biochar has been suggested in literature as one of the likely reasons for improved crop yields on acidic soils (Verheijen, et al., 2010). Improved crop yields have also been attributed to a 'fertiliser effect' of added biochar and ash, supplying important plant nutrients such as K, N, Ca, and P. In a four year field study by Major et al. (2010), yields of maize grain increased by 28, 30, and 140 % in year two, three and four,

respectively, on a Colombian savanna Oxisol. The authors attributed this to a 77-320 % greater availability of Ca and Mg in the biochar amended soils. Increased nutrient retention by biochar may be the most important factor for increased crop yields on infertile sandy soils (Asai, et al., 2009; Chan, et al., 2007; Steiner, et al., 2008b). For example, Chan et al. (2007) found that additions of biochar plus fertiliser (NH_4^+) increased radish yields more than the addition of fertiliser alone, indicating reduced N leaching and increased N use efficiency (Chan, et al., 2007). Biochar effects on the water retention and nutrient retention are expected to continue year after year, while a nutrient supply and a liming effect are short-term.

Currently, no peer-reviewed field studies have been conducted using FP-biochars. However, commercial FP-biochar has been employed in a field study performed in Québec, Canada. The biochar was applied at approx. 3.9 t ha^{-1} to a $1,000 \text{ m}^2$ plot, and an adjacent, unamended plot was used as a control (Major 2010). The biochar was produced by fast pyrolysis of wood waste and consisted predominantly of fine particles below 0.5 mm. Soybean was grown the first year, mixed forage species the second. The application of biochar resulted in Soybean yield increases of 19 % over the control, while the forage biomass was doubled. However, the yield differences could not be clearly attributed to chemical soil fertility differences across the treatments (Major 2010). In this field experiment it was found that soil infiltration of water was greater in the biochar amended plot, but did not find increased soil moisture there. Furthermore, Major observed increased root colonisation by ectomycorrhizae in the forage crop, while the “total soil carbon, soil respiration and potential organic matter mineralisation were not measurably different in the biochar-amended plot” (Major 2010). Due to the lack of randomisation and replication of the experimental plots, statistical analysis could not be performed, and the author concluded that the results should be considered preliminary (Major 2010, BlueLeaf report).

In order to test the FP-biochar’s influence on crop yields, a pot trial with barley was established as part of the PhD and is presented in Box 3.

Box 3 – short research question

Does FP-biochar increase crop yields in a highly sandy soil?

Answer: Incorporation of FP-biochar into soil did not improve yields of barley (*Hordeum Vulgare* L cv. Anakin), but tended at high FP-biochar concentrations in fact to suppress growth when compared with respective controls (Figure 9a). Not surprisingly, soils with initial fertiliser additions resulted in the greatest crop yields. During the first few weeks, these soils showed rapid growth rates, while soils with only biochar lagged behind (Figure 9b). Around day 20-25, the barley in pots amended with biochar began to show signs of withering and nitrogen deficiency, yellow spots appearing on the leaves. We speculated that the biochar, due to its labile fraction with a high C/N ratio, had caused microbial immobilisation of soil N. In order to test this hypothesis, it was decided to add fertilizer N to all treatments at day 38. The subsequent increasing growth rates of the plants clearly indicated that N immobilisation was a main factor for the poor growth and lower final biomass yields observed in the pure biochar treatments.

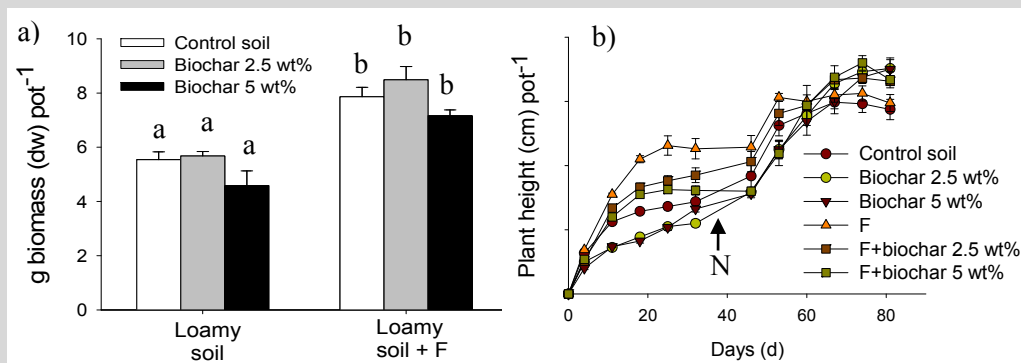


Figure 9. **a)** Biomass yields (common Barley) in soil with 0, 2.5 or 5 wt% biochar incorporated after 80 days. **b)** Plant heights during the 80 days. The arrow signifies time of N addition. Standard error bars are shown (n=3). Letters denote significant differences according to the Turkey test ($p < 0.05$).

Materials and methods: To test potential biochar effects on crop yields and growth, a pot experiment was conducted using a sandy loam soil (described in paper 1-4), barley seeds (four plants pot⁻¹), \pm FP-biochar (525 °C), and \pm fertilizer N. Different biochar concentrations (0, 2.5, or 5 wt%) were incorporated in the soil (660 g), which was blended with quartz sand (660 g) to resemble a highly sandy soil. The washed quartz sand had an average particle size of 0.7-1.2 mm. Fertilizer N (100 mg kg⁻¹ soil) was added to all treatments in one series, while another series received none. On day 38, additional fertilizer N (100 mg kg⁻¹ soil) was added to all pots, as the plants showed indications of N shortage (yellow withered spots). All treatments received plenty of water. Light was administered 16 hours a day⁻¹, and the temperature was kept constant at 16 °C. All treatments were done in triplicates. The experiment lasted 80 days. Statistics were performed according to paper 2.



5.6 Application strategies

A very fine dust fraction is most likely part of any biochar material, but particularly in biochars produced by fast pyrolysis. This fraction may, during handling and application to the field, give rise to considerable problems with dust and wind transport of fine particles, as illustrated by images from the field trial by Major (2010) (Figure 10). In the field trial, it was estimated that 25 % of the biochar was lost during application and transportation. Based on the experience from own trials and the study by Major (2010), it is highly likely that field application of the FP-biochar from the PCR plant would lead to similar problems. Moistening the FP-biochar could probably reduce the problems with dust during field application (Major 2010). However, as suggested by Blackwell et al. (2009), injection of fine biochar blended in a liquid fertiliser, such as slurry (as in paper 3), could facilitate biochar application to soil. Moreover, handling of the biochar material could have consequences for health related issues. Application strategies should therefore be carefully considered.



Figure 10. Clockwise from top left: Biochar losses during handling, transportation to the field, and application and incorporation in the field. Report by Major (2010). Copyright BlueLeaf Inc.

5.7 Impact of biochar on greenhouse gas emission

The stability of biochar and its influence on soil CO₂ and N₂O emissions is discussed extensively in paper 1-3, and will therefore be touched upon only briefly in the following. Usually, increases in the CO₂ flux occur directly after biochar additions to soil (Brodowski, et al., 2006; Bruun, et al., 2008; Hamer, et al., 2004; Steiner, et al., 2008a), but the effect is typically short-term in nature, lasting no more than a few weeks or

months, after which the biochar amended soil will deploy CO₂ rates similar to those of the control soil. The effect of biochar on the soil CO₂ emissions obviously depends on the soil environment and the microbial community present, as well as the physicochemical characteristics of the biochar. Microbial growth and activity may be stimulated by labile biochar fractions, while a more indirect biochar effect causing CO₂ emission for example could be improved soil water retention promoting decomposition of native SOM (Wardle, et al. 2008).

Nitrous oxide (N₂O) and methane (CH₄) are both potent greenhouse gasses, estimated, respectively, to be 298 and 21 times stronger a GHG than CO₂ (Forster et. al., 2007). On a quantitative basis, though, CO₂ is still by far the most significant GHG (Verheijen, et al., 2010). Emissions of nitrous oxide have been shown to decrease in a number of laboratory studies, which, have been suggested among others to be due to biochars influence on soil hydrology and nitrification-denitrification processes (Singh, et al., 2010; Spokas, et al., 2009; Yanai, et al., 2007). Results from the limited number of biochar-N₂O studies performed show furthermore that relatively high biochar rates (≥ 8.2 to 60 wt% biochar-to-soil) are required before N₂O production is restricted (Spokas, et al., 2009; Yanai, et al., 2007). Decreases in emissions of methane (CH₄) have also been observed following amendment of biochar (Rondon, et al., 2007; Spokas, et al., 2009). However, the mechanisms behind these observations remain unclear, and are not further discussed in the present thesis.

6 Synthesis

Pyrolysis of biomass offers a possibility to improve soil quality and sequester carbon by biochar soil application, while concurrently producing bioenergy (Laird, 2008; Lehmann, et al., 2006). However, the choice of pyrolysis technology and feedstock may significantly alter the extent of the different potential benefits. The results obtained during this PhD project have provided new insights into the impact of applying *fast pyrolysis* (PCR) biochar to soil. Despite the fact that fast pyrolysis processes optimised for bio-oil production have received increased attention commercially (Bridgwater and Peacocke, 2000), and that large-scale pyrolysis plants are being built or planned in several places (Laird, et al., 2009), there is only limited knowledge about the effect of applying FP-biochar to soil. Hence, in this context, it is relevant to study the effects and underlying mechanisms of applying FP-biochar to soil, and determine the main properties of FP-biochar produced by PCR technology (Brewer, et al., 2009).

The overall work of this thesis comprised four main topics: the influence of PCR temperature settings on the FP-biochar degradability in soil, and on the overall carbon abatement (paper 1); the effects of FP-biochar on soil C and N dynamics (paper 2); the impact of FP-biochar on N₂O emissions (paper 3); and the potential leaching of FP-biochar components in soil (paper 4). To allow for better comparisons of the results across the different soil experiments, all soil experiments presented were conducted on a sandy loam soil taken from the same batch (stored at two degrees Celsius), and all biochars were produced on the same feedstock batch. In the following synthesis,

conclusions drawn on the basis of the combined experiments are presented in relation to the overall research objectives stated in chapter 1.

6.1 Impacts of fast pyrolysis on biochar characteristics

Labile fraction. The most important characteristic of the FP-biochars in relation to short-term biological and chemical biochar-soil processes was found to be the presence of aliphatic labile fractions remaining after fast pyrolysis. These labile biochar fractions were shown to strongly influence: the emissions of CO₂ (paper 1, 2, and 3) and N₂O (paper 3), the soil dynamics of N and C (paper 2, and 3), the leaching of C (paper 4), and crop yields in the barley pot experiment (Box 3). Chemical analysis of the FP-biochars showed that the labile fractions consisted of unconverted cellulosic and hemicellulosic parts. In the temperature interval investigated, the carbohydrate content amounted to more than 35 % in FP-biochars made at low temperatures (475 °C), while the fraction decreased by a 1st order reaction down to 3 % in biochars produced at high temperatures (575 °C) (Table 1 and Figure 4). The reactor temperature of the specific fast PCR equipment thus strongly influenced the amount of carbohydrates remaining in the FP-biochar. Commercial fast pyrolysis plants may predominantly use reactor temperatures in the intermediate range for maximised bio-oil yields (Table 1), which means that the ‘FP-biochar co-product’ may contain relatively large labile fractions. Due to the much longer retention times of the slow pyrolysis process (chapter 3), labile fractions in SP-biochars are less likely to occur.

Characteristics of FP-biochar relative to SP-biochar. The experiments of the thesis showed that fast pyrolysis and slow pyrolysis of wheat straw generate two considerably different biochar products (paper 2; Brewer, et al., 2009). Contrary to the fast pyrolysis process, no carbohydrate fractions were left in the biochar after slow pyrolysis. In addition to the carbohydrate contents, the two methods resulted in different physical structures and porosity, particle sizes (113 and 23 µm), pH values (10.1 and 6.8), BET surface areas (0.6 and 1.6 m² g⁻¹), and elemental compositions of the SP- and FP-biochars (525 °C) (Table 1). These different physicochemical properties of the two biochar types will obviously have different effects on soil processes. Furthermore, the comparison between FP- and SP-biochar underscores the important fact that results obtained from soil studies using SP-biochars not necessarily are applicable for FP-biochars.

6.2 Impacts of fast pyrolysis biochar in soil

Mineralisation of FP-biochar in soil. Biochar is generally considered extremely resistant to microbial and chemical oxidation. However, observations show that biochar may degrade at very different rates in the environment by both biological and abiotic oxidation processes (Zimmerman, 2010 and references therein). In the present thesis, the short-term degradation rates of the FP-biochars in soil were in the high end of the scale compared to other studies (paper 1), and were found to be strongly controlled by the relative amount of carbohydrates left in the biochar. After four months of soil incubation, 3-12 % of the added biochar-C had been emitted as CO₂, and, on average, 90 % of the C loss occurred within the first weeks of the experiment. This wide range showed the influence which even small adjustments (± 25 °C) of the pyrolysis reactor temperature can have on the biochar quality and degradability (paper 1: figure 4). Yet, compared to the straw

feedstock, that lost more than half of its initial carbon content within two months in soil, the C sequestration potential of the FP-biochars were clearly evident (paper 2: figure 2).

When the SP-biochar reference was incubated in soil for two months, it emitted 2.9 % more C than the control soil (without biochar), despite no labile content (paper 2). This reveals that mechanisms other than decomposition of labile biochar fractions were involved in the CO₂ release observed. Abiotic processes (oxidation or release of chemisorbed CO₂) have been demonstrated by Zimmerman (2010) and Cheng et al. (2006) to contribute considerably to the emissions, but as yet only limited research has been conducted on potential abiotic decomposition processes of biochar, and the subject clearly warrants further research. Another possibility for increased CO₂ emissions in biochar amended soils could be biochar priming the mineralisation of native organic matter, as suggested by Wardle et al. (2008).

Influence of FP-biochar on soil microbial biomass. The addition of FP-biochar to soil was shown to stimulate microbial growth (SMB-C) compared to the SP-biochar reference and the control soil (paper 2: figure 3a) even at very high concentrations in soil (Box 1). Again, this probably should be attributed to the labile carbon source added with the FP-biochar. The microbial growth coincided with higher CO₂ emissions in all experiments. Greater microbial pools have e.g. also been observed after additions of fresh biochar and have mostly been explained by the availability of easily decomposable fractions of the added biochars (e.g. Kolb, et al., 2009; Kuzyakov, et al., 2009; Novak, et al., 2010; Steiner, et al., 2008a).

Influence of FP-biochar on nitrogen immobilisation. Soil application of biochar may lead to immobilisation of soil N, due to the developing microorganisms needing more N than the biochar provides. This has been observed in a few studies, in which extractable soil N was typically determined at the beginning and end of the experiment (Kolb, et al., 2009; Lehmann, et al., 2003; Novak, et al., 2010). The results presented in paper 2 show rather detailed short-term soil N dynamics after biochar application (paper 2: figure 4a). It was clearly demonstrated that soil amendment of FP-biochar caused immobilisation of considerable amounts of N (43 %) during the two month experiment, whereas soil incorporation of SP-biochar resulted in a net mineralisation of N (7 %). Nitrogen immobilisation after FP-biochar addition was also the likely cause for reduced growth and biomass yields of barley in the pot trial testing the effect of FP-biochar on plant biomass yields (Box 3). Moreover, N immobilisation was observed in the ‘doses-response’ experiment testing the effect of high concentrations of FP-biochar on the microbial population (Box 1). It is therefore evident that one should expect short-term soil mineral N reduction after FP-biochar application. In soils with low N levels, and in periods with high crop demand for N, application of FP-biochar may have direct detrimental effects on crop growth. One way to avoid this could be to apply the FP-biochar in periods with none or low crop demand for N e.g. in the autumn period. Application of FP-biochar in combination with an organic N-rich residue slurry (paper 3) is another possibility to counter soil mineral N depletion after biochar application.

FP-biochar effect on N₂O emissions. Biochar has been shown to decrease emissions of N₂O after soil application (Singh, et al., 2010; Spokas, et al., 2009; Yanai, et al., 2007; Zwieten, et al., 2009). The flush of N₂O usually observed after slurry application

(Senbayram, et al., 2009) could thus potentially be reduced by applying biochar in addition to the slurry. To test this hypothesis, FP-biochar was blended in two concentrations with anaerobic slurry and incorporated in soil (paper 3). A key finding from the study was that when a high concentration (3 wt%) of biochar was blended with slurry the N₂O emissions decreased by 47 %, relative to a slurry treatment receiving a lower amount of biochar (1 wt%). The reduced N₂O emissions concurred with enhanced soil microbial activity and immobilisation of nitrogen. It is therefore likely that the labile fraction of the FP-biochar played a key role by stimulating microbial growth.

Impact of FP-biochar on water holding capacity. Application of FP-biochar (10 wt%) to the sandy loam soil improved the WHC of the soil by 32 % (Box 2) as compared to ‘only’ 9 % when the SP-biochar reference was applied. The positive effect of the FP-biochar on the water retention was sustained throughout the 13 days experiment, and represents a clear agronomical advantage. From literature it is evident that biochar, most likely due to a great porosity, may increase the moisture content available for plants, but also that the effect will be largest on coarse sandy soils and moreover depends on the feedstock and pyrolysis conditions. Moreover, it seems necessary to apply relatively large amounts of biochar to soil before this effect will be manifested.

Mobility of FP-biochar carbon components in soil. The hypothesis that fine clay-sized biochar particles may disperse in the soil solution and potentially facilitate the leaching of adsorbed nutrients out of the topsoil by colloidal transport was tested in paper 4. Only few leachate studies with biochar have been performed, and they have focused primarily on the leaching of nitrogen, and have in general showed increased retention of N with biochar addition (Ding, et al., 2010; Laird, et al., 2010; Lehmann, et al., 2003; Major, et al., 2010a). The leaching experiment presented in this thesis clearly demonstrates highly mobile carbon components of FP-biochar (paper 4). The pyrolysis methods and temperature settings strongly influenced the leaching of C, which was found to be positively correlated with the labile fraction of the biochar. The mobility of organic C from FP-biochar highlights the risk of leaching of contaminants originating from or adsorbed to the biochar. By contrast, C components from slow pyrolysis biochar were retained in the topsoil.

In summary, the research of this thesis shows that, compared to its more inert ‘traditional biochar counter-part’ made by slow pyrolysis, FP-biochar, in a number of ways, acts more like the original organic matter feedstock when added to soil. As mentioned above, the FP-biochar, on a short-term basis, caused greater CO₂ emissions, C mineralisation (DOC), microbial biomass, and N immobilisation. However, on the longer term these effects are most likely a transient phenomenon as the labile part is used up after a few months leaving a much more recalcitrant biochar. It is still too early to recommend - or discourage - FP-biochar for agronomic use, since field trials are needed in order to verify potential benefits or drawbacks on soil fertility and crop yields. However, this thesis has improved the mechanistic understanding of the effects of applying FP-biochar to soil, and shows that wheat-straw FP-biochar has properties beneficial for agricultural soil, e.g. it improves soil WHC, adds minerals, enhances microbial activity/biomass, and increases the N and C turnover dynamics.

6.3 Impact of fast pyrolysis temperature on the overall carbon abatement

The PCR temperature settings strongly influenced the outputs of biochar, bio-oil, and syngas (paper 1: figure 2), as well as the stability of the biochar produced (paper 1: figure 4). Based on the different product distributions, it is possible to determine the optimum PCR temperature conditions, which provides the overall largest carbon abatement. This calculation was done in paper 1, and showed that when the biochar C sequestration was combined with the bio-oil substitution of fossil fuel (heavy fuel oil), the range of PCR reactor temperatures investigated (475-575 °C) resulted in the same overall level of carbon abatement (77-83 % of initial feedstock C input). The present fast pyrolysis concept can thus be regarded as rather dynamic, in giving the possibility of adjusting the PCR temperature for maximised output of either bio-oil (525-575 °C) or biochar (475-500 °C) without reducing the overall mitigation potential of C emissions.

7 Critical reflections

Significant contributions in the scientific literature about biochar were rather limited when initiating this PhD Marts 2008 (Lehmann, 2007) and biochar was regarded as a new research area. With my educational background as a biologist with emphasis towards soil nutrient dynamics, I had the basic scientific foundation for studying biochar and soil processes. However, the biochar subject had to be learned all from scratch, based on the very limited body of literature existing, which at the time predominantly concerned the charcoal amended 'Terra Preta' soils of the Amazon region. These ancient anthrosols may, as mentioned in chapter 2, not necessarily be direct applicable to modern biochar and effects in soil. Yet, the IBI conference about biochar, which I attended in Newcastle September 2008, gave me the impression of a highly dedicated research community and a research area rapidly expanding beyond the Terra Preta. I felt being a part of a pioneer field of research and was confident to fulfil my PhD objectives when arriving back home at Risø DTU.

It was originally planned, that the project should include field experiments in order to study the effect of FP-biochars on crop yields. However, since the planned up-scaling of the pilot-scale PCR plant got delayed, only limited biochar material was available (kilos instead of tons) during the experimental phase of the three year PhD. Accordingly, it was decided to focus primarily on laboratory experiments testing biochar stability and other related issues in soil and to downscale the experiment on crop yields to a pot trial. It was a disappointment to realise that it was not realistic to work with FP-biochar under field conditions and I hope future work opportunities will give me the possibility to test my lab scale assessments under more natural conditions.

During the experimental work, it became clear that the biochar material neither was fully inert nor necessarily acted in soil as traditional agricultural organic residues. An important lesson learned during the PhD project, was that, prior to larger experiments, pilot studies should be conducted - even though the design and setup had been tried many times before, just without biochar. In the pot trial (Box 3), for example, the biochar application resulted in both large soil water retention (soils almost waterlogged) and

considerably nitrogen immobilisation, which had severe effects on biomass yields. Moreover, I performed a large and also laborious incubation experiment with ^{13}C labelled biochar and sterilized biochar/soil to improve the more mechanistic understanding of decomposition of SOM and biochar carbon, respectively. Unfortunately, the experimental data eventually could not be used, due to a few adjustments in the setup (smaller incubation flasks) and a small change in the sampling procedure (too little time for accumulation of isotope labelled CO_2 in headspace prior to gas sampling). Such lessons to learn are tough, but I guess part of the learning process of many PhD projects. I have promised myself that it is the last time I haven't invested 1-2 weeks in some pilot experimentation, when modifying standard laboratory routine settings.

For the characterisation of the biochar and its effects on soil parameters, it was decided to employ well-tested standard methods (with the exception of the isotope study) developed for measurements of nitrogen and carbon in soil samples, e.g. the extraction procedure for ammonium and nitrate (Joergensen, et al., 1996) and the fumigation-extraction method (Vance, et al., 1987). Future research might require some optimisation of such methodologies specifically for biochar, but it was beyond the scope of this PhD to do so, taking into account both the objectives and time constraints.

8 Outlook

The large C sequestration potential of biochar is not enough to apply the biochar concept to a wider agronomical use (unless C credits for C-sequestration in soil is included in the C trading markets).

In order for biochar to become an agronomical success, consistent improvement of crop yields after biochar application must be documented for a long range of soil types and climates. In principle, it is possible to 'design' a beneficial biochar for a given soil through manipulation of pyrolysis settings and choice of feedstock. However, soils are very challenging and intricate systems, due to their inherent physical, chemical and biological complexity, and the development of 'designer' biochars on a basis of desk research alone will not suffice; numerous lab and field trials must be performed following the approach illustrated in Figure 11.

The long-term goal for biochar research should be to provide the data necessary for the compilation of a standard 'biochar catalogue', which, based on overall agrosystem parameters, such as soil type (sandy, loamy, or clayish), crop type, soil pH (acidic, neutral, alkaline), water conditions (water suffering or the opposite), and nutrient level (nutrient poor or nutrient rich), would match a given soil agrosystem with the appropriate type of biochar. Biochar has already proved its worth on sandy tropical soils. The question is whether, it will have the same effect on more fertile soil types.

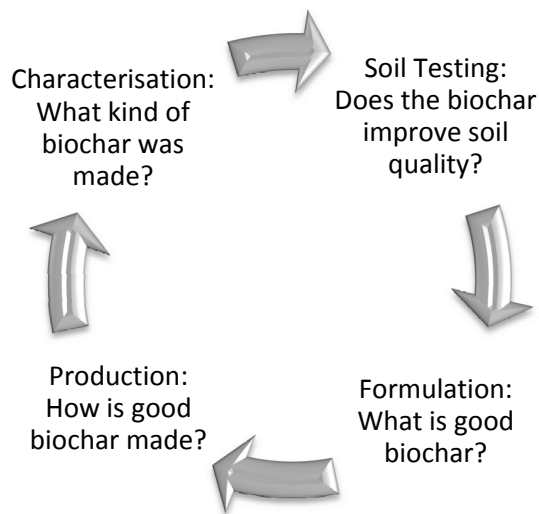


Figure 11. The ‘trial and error’ approach necessary for linking pyrolysis technology and resulting biochars with soil quality improvement. Adapted from www.cset.iastate.edu/research-projects/bio-char.html

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Appendix
Paper 1-4

Influence of fast pyrolysis temperature on biochar labile fraction and short-term carbon loss in a loamy soil

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Abstract

Production of bio-oil, gas and biochar from pyrolysis of biomass is considered a promising technology for combined production of bioenergy and recalcitrant carbon (C) suitable for sequestration in soil. Using a fast pyrolysis centrifuge reactor (PCR) the present study investigated the relation between fast pyrolysis of wheat straw at different reactor temperatures and the short-term degradability of biochar in soil. After 115 days incubation 3-12 % of the added biochar-C had been emitted as CO₂. On average, 90 % of the total biochar-C loss occurred within the first 20 days of the experiment, emphasizing the importance of knowing the biochar labile fraction when evaluating a specific biochar's C sequestration potential. The pyrolysis temperature influenced the outputs of biochar, bio-oil and syngas significantly, as well as the stability of the biochar produced. Contrary to slow pyrolysis a fast pyrolysis process may result in incomplete conversion of biomass due to limitations to heat transfer and kinetics. In our case chemical analysis of the biochars revealed unconverted cellulosic and hemicellulosic fractions, which in turn were found to be proportional with the short-term biochar degradation in soil. As these labile carbohydrates are rapidly mineralized, their presence lowers the biochar C sequestration potential. By raising the pyrolysis temperature, biochar with none or low contents of these fractions can be produced, but this will be on the expense of the biochar quantity. The yield of CO₂ neutral bio-oil is the other factor to optimize when adjusting the pyrolysis temperature settings to give the overall greatest climate change mitigation effect.

Keywords: bio-char, charcoal, carbon sequestration, biochar stability, Pyrolysis Centrifuge Reactor, *Triticum aestivum*.

Introduction

Replacing fossil fuel energy production can be obtained by renewable sources such as wind, solar energy or biomass. Another climate change mitigation option is to sequester carbon in soil by application of biochar (charcoal) produced by pyrolysis of plant biomass (Lehmann, et al., 2006). Because of biochars recalcitrant nature, only a very slow release of the biochar-C occurs, resulting in a long-term removal of C from the atmosphere. In addition, pyrolysis of biomass generates a bio-oil and a syngas, which can be used to replace fossil fuels e.g. by using the bio-oil as fuel in power plants and the gas to provide heat for the pyrolysis process. Combining these three pyrolysis outputs renders the whole process not only carbon neutral, which is very often the vision for bioenergy solutions, but actually carbon-negative (Lehmann, et al., 2006).

The stability of biochar in soil is of fundamental importance for the C balance, as it determines for how long the biochar-C applied will remain sequestered (residence time). In the literature, residence time estimations range from centennial up to millennial timescales (Lehmann, 2007; Preston and Schmidt, 2006). In principle, long-term studies are required to fully address biochar sequestration potentials and limitations, however, long-term studies are expensive and laborious, and therefore also rare. Consequently, residence time estimations are typically based on short-term studies (months to a few years) and concurrent use of dynamic models (Lehmann, et al., 2009). Although short-term studies do not give direct information about the longer-term stability of biochar, increased knowledge about short-term dynamics is required to improve the model interpretations of longer-term stability.

In the evaluation of a given biochar's stability, the labile fraction remaining in the biochar after pyrolysis is important to be quantified, as this fraction strongly influences the short-term biochar degradability (Lehmann, et al., 2009; Zimmerman, 2010). At low heating rate processes (slow pyrolysis) nearly all carbohydrates are converted to volatiles at a temperature of 475 °C (Yang, et al., 2008). However, in a fast pyrolysis process like the present there are limitations to both heat transfer and kinetics that restrict the biochar formation process within the few seconds residence time in the reactor. As a result, the biochar may contain an unconverted biomass fraction, which will mineralize rapidly in soil.

Both biotic and abiotic processes have been shown to contribute to biochar degradation. Cheng et al. (2006) examined changes in functional groups after four month incubations and considered abiotic processes more important for the initial degradation of fresh biochar. Contrastingly, Zimmerman (2010) found microbial degradation to account for approximately half of the CO₂ emitted in a one-year study including sterile biochar-soil incubations. Presently, the relative importance of biotic and abiotic processes for the mineralization of biochar is unclear and likely depends strongly on soil environment (moisture, temperature) and biochar characteristics.

In addition to carbon sequestration in soil, biochar provides other important beneficial ecosystem functions and services. A number of studies, mainly done in the tropics, have examined biochar effects on soil fertility and have documented beneficial effects on crop yields (Glaser, et al., 2002; Lehmann, et al., 2006; Oguntunde, et al., 2004). These effects have mainly been ascribed to biochars documented ability to absorb plant nutrients (Chan, et al., 2007; Glaser, et al., 2002; Steiner, et al., 2008b) and increase the soil water holding capacity (Pietikainen, et al., 2000). Moreover, laboratory studies have shown that biochar

amendment to soil is able to reduce emissions of the potent greenhouse gases methane (CH₄) and nitrous oxide (N₂O) (Spokas, et al., 2009; Spokas, et al., 2010), although a study by Clough et al. (2010) showed contradictory results.

The number of biochar studies and publications has increased rapidly in the last few years, resulting in a growing knowledge pool about biochar and the pyrolysis process in general. However, so far only a limited number of biochar stability studies have been performed, exclusively using biochars produced by slow pyrolysis (e.g. Bruun, et al., 2008; Cheng, et al., 2006; Hamer, et al., 2004; Zimmerman, 2010). The main objective of the present study was to investigate the influence of the fast pyrolysis process temperature on biochar-C degradability. Incubation studies with biochar applications to soil were conducted to improve the understanding of short-term degradation of fast pyrolysis biochar in a sandy loam soil typical for temperate regions. Wheat straw was used as pyrolysis feedstock representing a valuable lignocellulosic agricultural crop residue.

Materials and methods

Pyrolysis

The biochar produced for this study was made on a fast Pyrolysis Centrifuge Reactor (PCR; Figure 1). The set-up consists of a screw type feeder, an electrically heated ablative centrifuge reactor, a cyclone used for biochar collection, a condenser and a coalescer used for bio-oil collection. A pump is used for recirculation of the formed gas. The straw feedstock was introduced by the screw feeder into the horizontally oriented tubular reactor (Ø 82 x 200 mm).

A three-bladed rotor rotates in the reactor with 50 Hz creating a centrifugal force that presses the biomass particles against the hot reactor wall. Undergoing reaction, the particles are moved down the reactor pipe before leaving through the tangential outlet suspended in the gas. Larger biochar particles were removed by a change-in-flow separator, whereas finer particles were collected by the cyclone. Vapors were condensed in a direct water-cooled condenser filled with previously produced bio-oil. The temperature in the condenser was controlled to be 55 to 75 °C by means of a water-cooled pipe coil. Aerosols that were not retained by the condenser were collected in the coalescer filled with rockwool fibers. The gas was pumped to the pre-heater and heated to 400 °C before it was recirculated to the reactor in order to maintain a desired gas residence time and avoid condensation of liquid products within the reactor. Detailed descriptions of the reactor can be found elsewhere (Bech, et al., 2009).

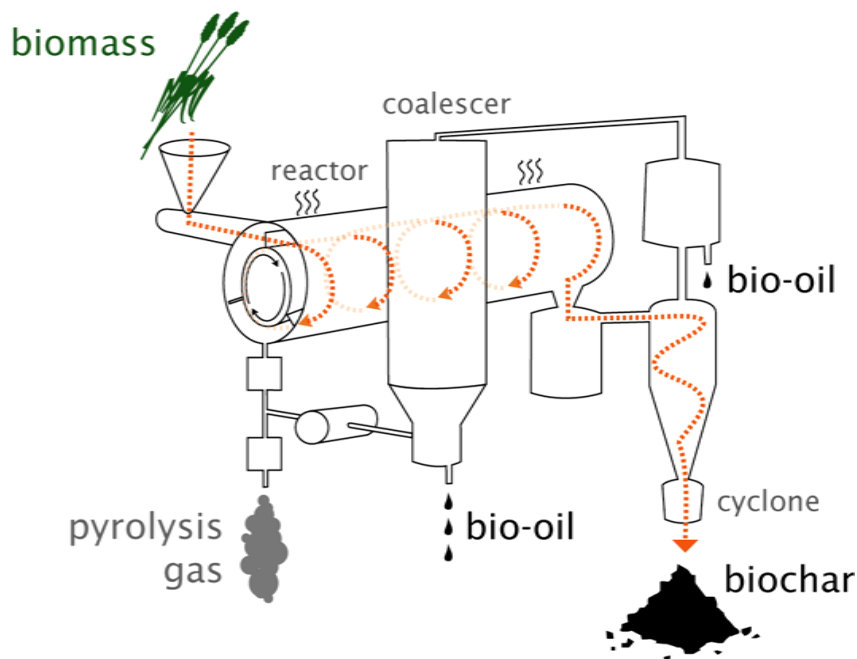


Figure 1. Pyrolysis Centrifuge Reactor (PCR) laboratory flash pyrolysis unit used in the present study (modified from Bech 2008 by T. Thomsen).

The feedstock was wheat straw, of unknown provenance or date of harvest, this precludes repetition of the pyrolysis, and while the sample used has provided useful data, it is recommended that future studies be done on samples for which a full description is provided following the principles of Barton, et al. (1989) for woody biomass materials. The straw was ground and sieved to obtain particles below 1.4 mm before it was pyrolyzed at reactor temperatures of 475, 500, 525, 550 and 575 °C. The straw feeding rate to the reactor was approximately 23 g min⁻¹ with an approximate gas reactor residence time of 0.2 sec., a particle residence time of a few seconds, and an initial heating rate ranging from 250-1000 °C s⁻¹. A mass balance of the PCR system could be determined gravimetrically by comparing the feedstock input with the yield of the products in the form of oil, gas and biochar. The gas yield was calculated by application of the ideal gas law to the measured gas volume produced.

Biochar characteristics

The biochemical composition of the biochar was determined by classical wet chemical methods (Kaar, et al., 1991; Thomsen, et al., 2008). To conduct this analysis, the biochar was subjected to a strong acid hydrolysis, where a sample was treated with 720 g kg⁻¹ H₂SO₄ at 30°C for one hour, then diluted to 40 g kg⁻¹ H₂SO₄ and eventually autoclaved at 121°C for one hour. The hydrolysates were filtered and the lignin plus biochar content determined as the weight of ash-free filter cake (Kaar, et al. 1991). The composition of the released carbohydrates found in the filtrate was determined by HPLC-analysis using a Shimadzu HPLC system equipped with a refractive index detector. Separation of the sugars was achieved by an Aminex HPX-87H ion exchange column with H₂SO₄ at 4 mmol dm⁻³ in water as eluent (flow: 0.6 ml min⁻¹ at 63 °C).

In addition, the carbohydrates were converted into acetates and analyzed by GCMS in order to further support their identification. GCMS analysis was performed using a Varian 3400 gas chromatograph interfaced to a Saturn II ion trap mass spectrometer. A Factor Four capillary column VF-23ms 30m x 0.32 mm id DF 0.25 μm gave an appropriate separation with a temperature gradient of 50 – 250 °C. The temperature of the transfer line (GC to MS) and the manifold of the mass spectrometer were 200 °C, respectively.

Total C, H, and N was measured on biochar samples on an elemental analyzer (EAflash1112 ThermoQuest) using 2 mg subsamples.

Biochar application to soil

Biochar soil experiments were performed using soil collected from the plough layer (0-25 cm) in a conventional agricultural field at Risø DTU (55°41'N, 12° 05'E). The climate is temperate with a 25 year mean annual rainfall of 550 mm, mean annual air temperature of 8 °C with maximum and minimum monthly air temperature of 16 °C (July) and -1 °C (February). The soil is characterized as a sandy loam (Typic Hapludalf) with 11 % clay, 14 % silt, 49 % fine sand, and 25% coarse sand (Hauggaard-Nielsen and Jensen, 2001). The soil was sieved (2 mm) and portions of 40 g fresh weight (38 g dry weight) were mixed thoroughly with 2 g biochar or in 100 ml containers (ID=48 mm) and slightly compressed to obtain a density of approx. 1.4 g cm⁻³. Before incubation, 20 g air-dried soil was finely ground by mortar and total C and N was measured on 30 mg soil sub-samples on an elemental analyzer (EA 1110 CHN CE instruments).

The soil incubation experiment included six treatments, i.e. soil amended with five different biochar types produced at different reactor temperatures (475, 500, 525, 550 and 575 °C) and a control soil. The incubation period was 115 days. During the incubation period the soil was kept at constant water content (30 % of maximum water holding capacity) by weighing and replacing water to constant weight. The incubation was conducted at room temperature (20-23 °C). All treatments were included in quadruplicates. The carbon dioxide (CO₂) emission from each container was measured using infra-red gas analysis (LICOR 8100). The overall degradation of biochar was calculated using simple difference, i.e. CO₂ emission from the treatment soil minus emission from the control soil (no biochar added).

Statistics

Treatment effects on the CO₂-rate were analyzed by repeated analysis of variance (repeated measures ANOVA) and homogeneity of variance was investigated with residual plots using SAS 9.1, the proc mixed procedure. The model included treatment, day and the interaction between the two. CO₂-rate data was log transformed to obtain appropriate variance homogeneity. The optimal covariance structure was selected using Akaike's Information Criteria (AIC). Cumulated CO₂-data after 115 days was tested by ANOVA one way and homogeneity of variance was investigated with residual plots using SAS 9.1, the proc mixed procedure. Tukey adjusted differences of least square means were used to compare treatments.

Results and discussion

Pyrolysis products

Figure 2 shows the PCR product distributions as a function of increasing reactor temperature. The product distribution followed the typical pattern, where the yield of syngas increased, the biochar yield decreased and a maximum bio-oil yield was obtained at intermediate temperatures (525 °C in our case) (Bridgwater, et al., 1999). The bio-oil produced was a polar low-molecular-weight organic fraction with a high water content. As the temperature was raised, more volatiles were released into the bio-oil and gas fractions, thereby reducing the biochar output. At higher temperatures, cracking of bio-oil to secondary gasses most likely occurred and at some point this process exceeded the bio-oil generation and the overall quantitative output of bio-oil decreased.

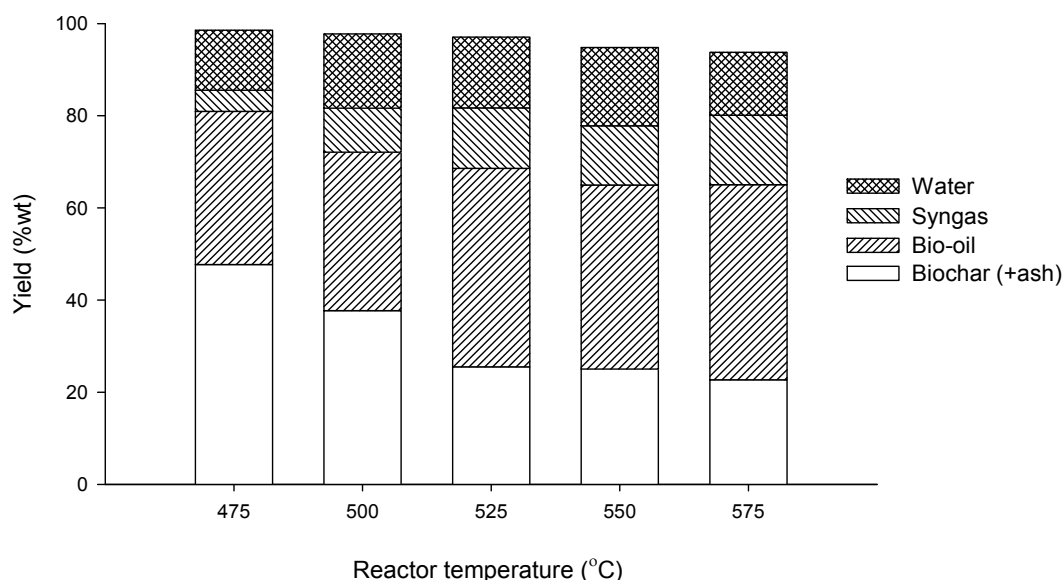


Figure 2. Mass balance of pyrolysis products as a function of increasing reactor temperature.

In the PCR reactor the generated biochar was pulverized to small particle sizes that decreased with increasing pyrolysis temperature (Table 1). Scanning Electron Microscope (SEM) images of biochars made at 475, 525 and 575 °C visualize the increasing decomposition and porosity (Figure 3).

Table 1. Average particle sizes of the added biochars determined by light microscopy.

	Biochar 475°C	Biochar 500°C	Biochar 525°C	Biochar 550°C	Biochar 575°C
Average size ($\mu\text{m} \pm \text{SE}$)	71 \pm 6	50 \pm 5	23 \pm 1	12 \pm 1	12 \pm 1
Min-max size	19-490	11-223	3-101	2-56	2-60

In table 2 results of chemical analysis of the PCR biochars are shown. Initial analysis of the five different biochars revealed declining cellulosic and hemicellulosic contents from 30 % in the 475 °C biochar down to 5.5 % in the 575 °C biochar. In line with other studies, the biochar elemental composition was influenced by increasing pyrolysis temperatures (Antal and Gronli, 2003; Zimmerman, 2010). As the temperature increased, the O and H content decreased, leaving behind a more condensed biochar with a larger C fraction, while the N content stayed rather constant. Pyrolysis of woody and herbaceous biomass usually provides a more C-rich biochar compared to other feedstocks such as sewage sludge and animal manures, which tend to leave a biochar with a higher content of nitrogen (N) and phosphorous (P) (Chan and Xu, 2009). As a result, the availability of important nutrients for plants and microbes may vary considerably after application of biochar. A convenient measure of a soil's N availability to crops is the C/N ratio. In general, a C/N ratio above 20 for organic substrates is considered the critical limit above which immobilization of N by microorganisms occurs, resulting in less soil N available for crops (Chan and Xu, 2009).

Table 2. Characterisation of biochar, feedstock and soil used in the trial.

		Biochar					Straw	Soil
		475°	500°C	525°C	550°C	575°C		
C (daf ^a)	g kg ⁻¹	537	602	643	670	692		
C	g kg ⁻¹	452	481	504	493	499	394	13
H	g kg ⁻¹	47	39.7	37	29.3	26.6	55.7	
O ^b	g kg ⁻¹	332	266	230	202	185	437	
N	g kg ⁻¹	10.9	12.6	12.4	11.5	10.8	10.1	1.5
Cellulose	g kg ⁻¹	300	160	74	42	27	403	
Hemicell. (xylan)	g kg ⁻¹	55	30	14	15	7	228	
Cellulose+hemicell.	g kg ⁻¹	355	190	88	57	34	631	
Cellulose+hemicell. C ^c /tot. C ^d	%	34.4	17.3	7.6	5.0	3.0	68.6	
Ash content	g kg ⁻¹	158	201	216	264	279	59	
C/N ratio		39.5	38.9	39.4	43.7	46.2	39.0	8.7

a: Dry ash free

b: Oxygen determined by difference (100% - C, H, N and ash %)

c: Cellulose-C calculated as: cellulose (%) * 6 (C in glucose) * 12.01 (C molar mass) / 162.15;

Hemicellulose-C calculated as: hemicellulose (%) * 5 (C in pentose) * 12.01 (C molar mass) / 150.13 (Xylan monomeric unit)

d: Total biochar-C

The biochars in this study had C/N ratios between 38.9 and 46.2 (Table 2), which are considerably above this limit. However, N immobilization after application of fresh biochar is most likely a transient phenomenon, because of the relative small fraction of easy degradable carbohydrates in the biochar. After the initial mineralization of this labile C-pool, the N immobilization can be expected to be negligible, due to the recalcitrance of the remaining biochar-C.

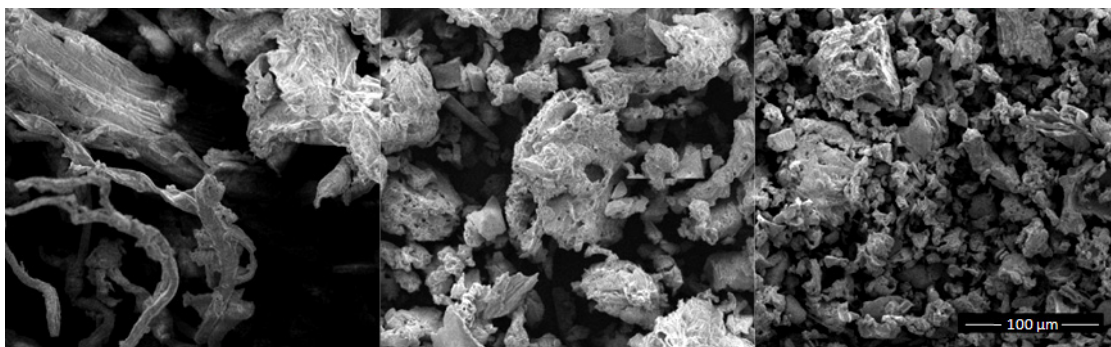


Figure 3. Scanning Electron Microscope (SEM) images of biochar particles taken at the same magnification. Left to right: biochar made at 475 °C, 525 °C and 575°C respectively. Pictures from LightSmyth Technologies Inc.

Pyrolysis reactor temperature and biochar stability

It is incontrovertible that pyrolysis of biomass and subsequent biochar application to soil sequesters carbon compared to normal agricultural practise of direct incorporation of biomass, which results in immediate and rapid mineralization and CO₂ release. For example Scheller (Scheller and Joergensen, 2008)) and Angers (Angers and Recous, 1997) reported wheat straw-C losses of 37 % to 48 % after 63 and 102 days incubation, respectively. Figure 4 shows the CO₂ emissions and cumulative C loss from the different biochar treatments. Compared to the control soil (without biochar) all five biochar types had considerably larger CO₂ emissions during the first week of the experimental period ($p < 0.001$), after which the CO₂ evolution stabilised to the same level as the control (Figure 4a). This initial flush of CO₂ was most likely due to microbial decomposition of an easy degradable fraction of the added biochar (Hamer, et al., 2004; Steiner, et al., 2008a). In addition, CO₂ might have been released by abiotic oxidation of biochar surfaces, a process described to be more important for biochar just produced and applied to soil, than for biochar aged in soil for longer periods (Cheng, et al., 2006).

The highest biochar-induced CO₂ emissions were generally observed from the samples containing the low temperature biochar with decreasing emissions with increasing pyrolysis temperatures (Figure 4b). Significant differences were found between all biochar treatments ($p < 0.001$), except for the treatments separated with only ± 25 °C in process temperature. After 115 days of incubation, the cumulative emissions ranged progressively from 11.9 % C loss for the 475 °C treatment, down to 3.1 % C loss for the 575 °C treatment (Figure 4c). Thus, in accordance with other studies, mineralization of biochar decreased with increasing degree of thermal conversion of the feedstock (e.g. (Baldock and Smernik, 2002; Bruun, et al., 2008)). Interestingly, biochar carbon losses of up to 12 % are considerably higher than observed in other degradation studies with short-term losses of a few percent or lower (e.g. (Baldock and Smernik, 2002; Hamer, et al., 2004; Zimmerman, 2010; Kuzyakov, et al., 2009). For instance Hamer et al. (2004), Zimmerman (2010), and Baldock and Smernik (2002) reported biochar-C losses ranging from 0.3 to 3 %. These incubation studies were conducted in sand medium, which has the obvious advantage of excluding decomposition of native soil organic matter (evolved CO₂ = biochar-C), but also the disadvantage of excluding aggregation and biochar-clay interactions. Encapsulation of biochar particles into micro-aggregates (Brodowski, et al., 2006) or adsorption of non-biochar organic matter (Liang, et

al., 2006; Nguyen and Lehmann, 2009) could for example reduce the degradation of biochar. Using ^{14}C labelled biochar made by slow pyrolysis of Rye grass Kuzyakov et al. (2009) reported an average cumulative biochar-C loss of app. 4 % after 3.2 years incubation in a loamy soil. As addition of glucose strongly stimulated biochar decomposition the authors concluded that the decomposition mainly involved CO-metabolism (Kuzyakov, et al., 2009). Our study demonstrated nevertheless relatively large biochar-C losses without addition of a labile co-metabolite, which is in agreement with the results of Zimmerman (2010). The considerably higher biochar degradation in the present study we ascribe to the specific PCR technology used (resulting in incompletely pyrolyzed biochar at the lower temperatures) and the fact that most other studies so far have used slow pyrolysis biochar, which contains less easy degradable substrate.

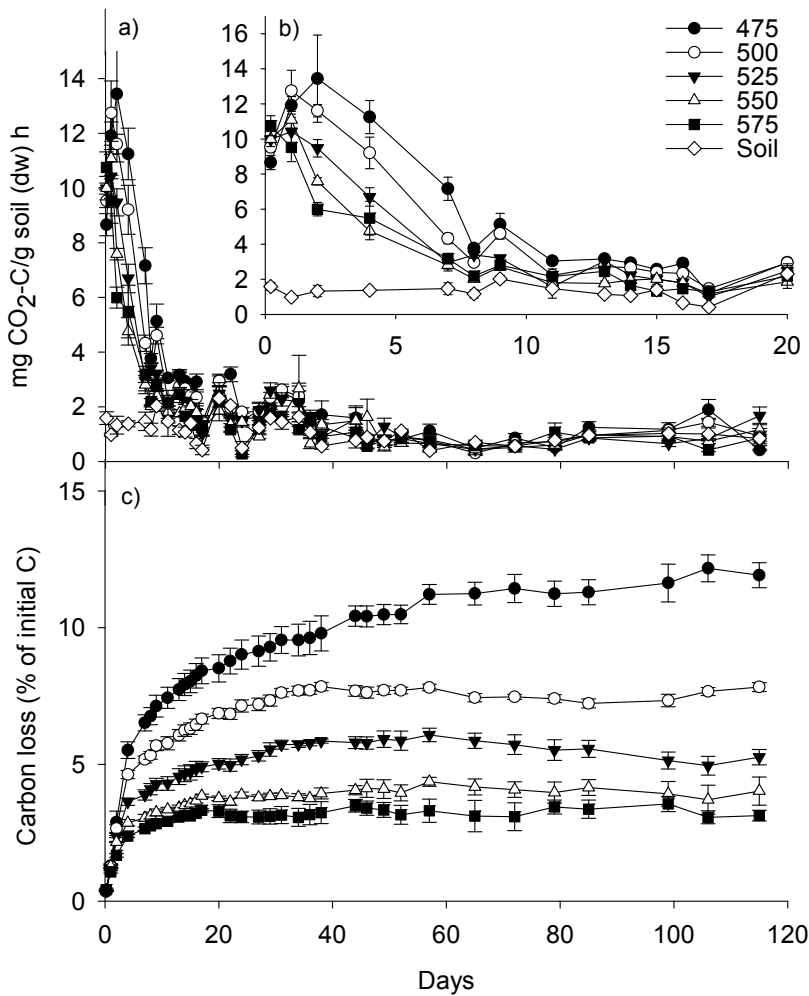


Figure 4. a) Measured soil surface CO₂-fluxes after incorporation of 40g soil with 2g biochar produced at different reactor temperatures of 475, 500, 525, 550 and 575 °C, respectively, and no amendment (soil). b) Insert shows initial 20 days CO₂-fluxes to differentiate between biochar types. c) Cumulative biochar decomposition measured as net biochar-C emitted in proportion to biochar-C added. SE are shown (n=4).

Biochar stability according to chemical characterization

As discussed above and explored by Yang et al. (2008), an increasing pyrolysis temperature increases the proportion of feedstock cellulose and hemicellulose decomposition (Table 2). An examination of the relationship between cellulosic + hemicellulosic contents and cumulated CO₂ losses after 115 days showed a strong positive correlation ($R^2 = 0.99$; Figure 5), emphasising the importance of measuring the labile fraction when evaluating a given biochar's longevity in soil. Contrary to the high temperature biochars (≥ 525 °C), the lower temperature biochars (≤ 500 °C) had C losses considerably below their cellulosic plus hemicellulosic C content. This might be explained by the low temperature biochars markedly larger particle sizes (Table 1) and hence lower surface-volume ratios than biochars ≥ 525 °C. It is likely that a part of the cellulose and hemicellulose was enclosed by recalcitrant aromatic and unconverted ligneous structures making it inaccessible for microorganisms (and reducing abiotic oxidation) in the short-term (Brodowski, et al. 2006; Cheng, et al. 2006; Lehmann, et al. 2009). From a longer-time perspective, the biochar particles undergo abiotic surface transformations and oxidation, which creates carboxy- and phenolate groups making the surface more negatively charged and hence hydrophilic (Cheng, et al., 2006; Kramer, et al., 2004). It has been hypothesized that this oxidation helps facilitate the microbial metabolism of the otherwise highly recalcitrant aromatic ring structures and hydrophobic surfaces (Cheng, et al., 2006; Lehmann, et al., 2009).

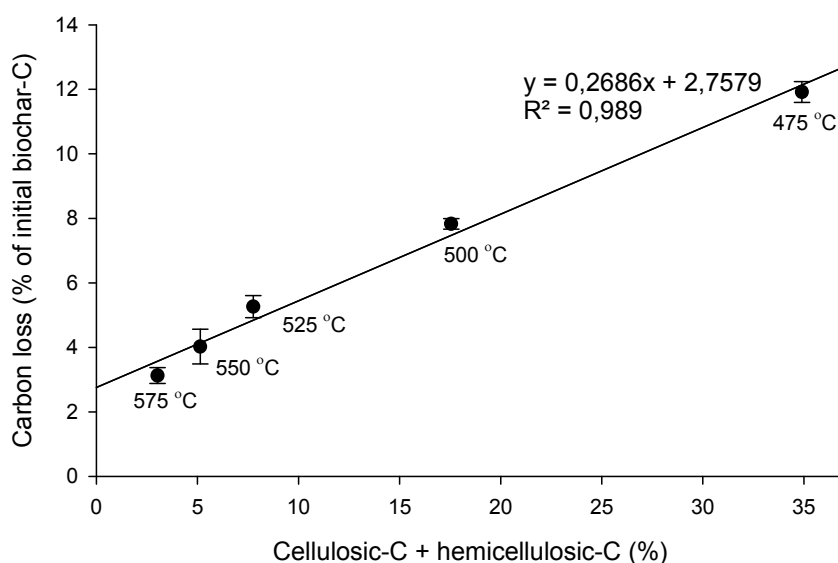


Figure 5. Cumulative biochar-C loss (%) as a function of the cellulose plus hemicellulose C content (%) of the five biochars after 115 days of incubation. Values are means ($n=4$) \pm SE.

The regression in figure 5 predicts (y-axis interception) that a part of the non-cellulosic+hemicellulosic biochar-C is susceptible to degradation to CO₂ on a short-term scale. This ~3 % loss may be due to abiotic oxidation of biochar surfaces (Bruun, et al., 2008; Cheng, et al., 2006) as well as degradation of labile biochar C-sources other than cellulose and hemicellulose e.g. fats, fatty acids, phenolics and phytosterols (Lehmann, et al.,

2009). In addition, ‘priming’ of the microbial biomass by physical/chemical biochar properties could stimulate increased microbial degradation of native SOM, as suggested by Wardle (Wardle, et al., 2008) and thereby mask the loss of biochar-derived C. Investigation of this aspect requires isotope labeled biochar or soil C in order to differentiate between decomposition pathways, which is beyond the scope of the present study.

Mitigation of overall carbon emissions

Mitigation of carbon emissions is obtained not only from biochar soil application, but also from substitution of fossil fuel by the produced bio-oil. The quantity of fossil fuel replaced depends on a range of parameters such as the efficiency of the technology used to convert bio-oil into the desired energy form, the kind of fossil fuel it substitutes, and the handling and transportation of biomass and bio-oil (Caputo, et al., 2005; Fowles, 2007). To assess the capability of the bio-oil to offset fossil carbon emissions, it was assumed that the bio-oil is used to displace heavy fuel oil consumption in a power plant (Figure 6).

To make the bio-oil substitution of fuel oil comparable with the biochar-C sequestration, the overall C mitigation potentials are related to the initial feedstock C content. The highest carbon offset from substitution of fossil oil by the produced bio-oil is around 50 % and occurs when pyrolysis temperature is raised to ≥ 525 °C (Table 3).

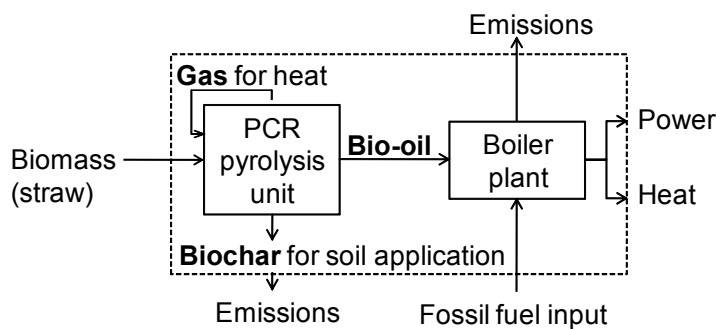


Figure 6. Principal flow diagram of the PCR pyrolysis process (Figure 2) when connected to a power plant.

In the assessment of the different biochars’ sequestration potentials, the stability and quantity of produced biochar are the two main parameters to assess. As discussed, the stability can be increased by raising the pyrolysis temperature (Figure 4c), but this will be at the expense of the quantity produced (Figure 2). This inverse relation makes it possible to determine the pyrolysis temperature that gives the highest C sequestration. Based on the assumption that all biochar carbohydrates will be mineralized to CO₂ within a relatively short timeframe, the original feedstock sequestration potentials is calculated and shown in Table 3. Interestingly, the highest biochar carbon sequestration is achieved at 500 °C, despite the fact that biochar made at higher temperatures is relatively more recalcitrant than low temperature biochars.

Table 3. Overall mitigation of carbon emissions in relation to initial straw-C, when combining biochar-C sequestration and bio-oil fossil fuel C substitution. The following assumptions are included: i) bio-oil has a higher heating value of 16.4 MJ kg⁻¹, ii) straw has a C content of 39.4 wt% (as received basis), the heavy fuel oil has a C content of 85 wt% and a higher heating value of 40 MJ kg⁻¹.

PCR Temp. °C	Biochar		Bio-oil			Overall C mitigation		
	Yield ^a g C kg ⁻¹ C	Stability ^b % of wt	Yield ^c g kg ⁻¹	Substitute g kg ⁻¹	Substitute g C kg ⁻¹	Biochar ^d ----- g C kg ⁻¹ C -----	Bio-oil	Total
475	550	66	463	190	161	360	410	770
500	464	83	505	207	176	380	450	830
525	329	92	584	239	204	300	520	820
550	316	95	570	234	199	300	500	800
575	291	97	560	230	195	280	500	780

a: Feedstock-C that ends up in biochar

b: Total biochar cellulosic-C+hemicellulosic-C percentage subtracted from 100%

c: Yield of bio-oil per kg feedstock. Based on actual measurement (see Figure 2) including water generated during pyrolysis and feedstock water

d: Biochar-C sequestration per kg feedstock-C pyrolyzed. Calculated as biochar ‘Yield’ multiplied by ‘Stability’.

When combining the bio-oil substitution with the biochar C sequestration, the five PCR reactor temperatures result in the same overall level of carbon mitigation (77-83 %) with slightly higher mitigations obtained at the intermediate reactor temperatures (see ‘Total’, Table 3). Thus, the present pyrolysis concept can be regarded as rather dynamic, giving the possibility to adjust the PCR temperature for either maximized output of bio-oil (525-575 °C) or biochar (475-500 °C) without reducing the overall mitigation potential of C emissions. A farmer approach could favor biochar over bio-oil due to the value of applying biochar to the field to improve soil fertility and thereby crop productivity. An alternative strategy for a company investing in pyrolysis facilities would be optimization of bio-oil production due to its market value.

Conclusion

This study investigated the influence of fast pyrolysis reactor temperature (475-575 °C) on biochar chemical quality and short-term stability in soil. It was shown that the stability of fast pyrolysis biochar was correlated to the degree of thermal alteration of the feedstock. Relative small adjustments in reactor temperature (± 25 °C) strongly influenced the amount of easy degradable cellulose and hemicellulose remaining in the biochar with a large impact on the short-term C loss after soil amendment. When optimising specific pyrolysis technologies, it is recommended to include bio-oil fossil fuel substitution together with biochar carbon sequestration to obtain the best possible solution according to local needs and market possibilities for gaining the greatest climate change mitigation effect.

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Effects of slow and fast pyrolysis biochar on soil C and N turnover dynamics

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Abstract

This study compared the effect of two principal pyrolysis methods on the chemical characteristics of biochar and the impact on C and N dynamics after soil incorporation. Biochar was produced from wheat straw, that was thermally decomposed at 525 °C by slow pyrolysis (SP) in a nitrogen flushed oven and by fast pyrolysis (FP) using a Pyrolysis Centrifuge Reactor (PCR). After 65 days of soil incubation 2.9 % and 5.5 % of the SP- and FP-biochar C, respectively, was lost as CO₂, significantly less than the 53 % C-loss observed when un-pyrolyzed feedstock straw was incubated. Whereas the SP-biochar appeared completely pyrolyzed, an un-pyrolyzed carbohydrate fraction (8.8 %) remained in the FP-biochar. This labile fraction possibly supported the higher CO₂ emission and larger microbial biomass (SMB-C) in the FP-biochar soil. Application of fresh FP-biochar to soil immobilized mineral N (43 %) during the 65 days of incubation, while application of SP-biochar led to net N mineralization (7 %). In addition to the carbohydrate contents, the two pyrolysis methods also influenced the pH (10.1 and 6.8), particle sizes (113 and 23 μm), and BET surface areas (0.6 and 1.6 m² g⁻¹) of the SP- and FP-biochars, respectively. The study showed that independently of pyrolysis method, soil application of the biochar materials had the potential to sequester C, while the pyrolysis method did have a large influence on the mineralization-immobilization of soil N.

Keywords: bio-char, charcoal, soil microbial biomass, carbon sequestration, nitrogen immobilization, Pyrolysis Centrifuge Reactor, *Triticum aestivum*.

Introduction

Thermal decomposition of biomass in an oxygen-free environment (pyrolysis) is a way to produce bio-oil, gas and char. All three products can be used for generating renewable energy (heat, electricity), but an emerging new use of recalcitrant char (biochar) is to apply it to soil in order to enhance soil fertility and at the same time mitigate climate change by long-term carbon (C) sequestration in soil (Lehmann, et al., 2006).

Inherent physicochemical characteristics of biochars (Liang, et al., 2006; Liang, et al., 2006) make these materials a promising and attractive soil additive for crop producing farmers.

Biochars have been reported to be highly porous (Bird, et al., 2008; Purevsuren and Davaajav, 2001), to exhibit high surface areas (Glaser, et al., 2002), to increase soil cation exchange capacities (CEC) (Bird, et al., 2008; Liang, et al., 2006; Purevsuren, et al., 2003) and to improve soil moisture (Pietikainen, et al., 2000) and permeability. Depending on the parent organic material, biochars also contain a variable pool of plant nutrients (Chan and Xu, 2009; Gaskin, et al., 2008) and often have a liming effect when added to soil (Van Zwieten, et al., 2010). Modification of biochar occurring in the soil over time, can increase the value of biochar even further through enlarging the surface area and increasing soil CEC due to creation of negative functional groups on the biochar surface (Liang, et al., 2006).

The classical example of soil fertility building was demonstrated for the Amazon Basin 'Terra Pretta' soils (Lehmann, et al., 2003; Steiner, et al., 2008b), but increased crop yields in response to biochar applications have also been demonstrated in a number of pot and field-scale trials using rather nutrient-poor soils (Asai, et al., 2009; Chan, et al., 2007; Chan, et al., 2008; Major, et al., 2010; Van Zwieten, et al., 2010; Oguntunde, et al., 2004). The growth promoting mechanisms of biochar have often been attributed to the liming effect and nutrient addition/retention capabilities. However, effects on crop yields remain rather inconclusive as other studies have revealed only small or even negative crop yield responses upon biochar applications (Gaskin, et al., 2010; Van Zwieten, et al., 2010). Currently, the underlying mechanisms controlling the transformation of biochar and its effect on soil properties are poorly understood (Sohi, et al., 2010) and moreover difficult to compare, as soil, biochar, feedstock, climate, methodology etc. vary considerably from study to study.

The organic feedstock material used for pyrolysis has a strong influence on the initial biochar characteristics (Gaskin, et al., 2008), but in terms of biochar stability in soil, the pyrolysis conditions seem to be most important (Zimmerman, 2010). In particular, the pyrolysis peak temperature, particle residence time and heating rate are important for the quality of the biochar produced (Sohi, et al., 2010). Pyrolysis can be divided into basically three sub categories: slow pyrolysis (SP), fast pyrolysis (FP) and full gasification systems. Contrary to the SP and FP systems gasification produce only limited amounts of biochar (Laird, et al., 2009) and was not dealt with in the present study.

Slow pyrolysis can be categorized as a rather low-tech and robust technology optimized for biochar production. In SP the organic material is slowly (minutes to hours) heated to ~ 400 °C in the absence of oxygen. Modern SP units often work in a continuous mode stripping off bio-oil and gas products (Brown, 2009). The FP technology is typically more advanced with a continuous process optimized for bio-oil production (Laird, et al., 2009). Small-grained organic material is blown into a hot reactor (~ 400-550 °C) and exposed to heat transfer for just a few milliseconds to seconds (Laird, et al., 2009). Fast pyrolysis systems require dried organic material in order to grind it down to small particles to allow for rapid heat transfer and conversion in the reactor. A number of FP technologies exist, such as fluidized bed systems, systems using ablative reactors, and systems using Pyrolysis Centrifuge Reactors (PCR) (Bech, et al., 2009; Bridgwater, et al., 1999).

Differences in construction - and running cost, as well as products generated, are essential when comparing the economic feasibility of SP and FP technologies. Although the many specific (and rotating) parts of the FP technology increases the construction and maintenance costs as compared to the SP technology, the greater amount of bio-oil generated together

with increasing demands for bio-energy products (Demirbas, 2011) may push the evolution towards the FP technology. However, potentially the biochar-product could be turned into an economical advantage as well (favouring SP, due the greater biochar yield), if biochar is incorporated into the carbon trading markets and if it can be documented that soil applications of biochar result in consistent and economically feasible yield increases in crop production.

So far, soil-biochar studies have almost exclusively been performed using biochars made by SP, despite that FP appears to be an equally important technology among the small, but growing, number of companies capable of producing biochars in larger quantities (see e.g. www.eprida.com; www.dynamotive.com; www.ensyn.com). A better understanding of the nutrients dynamics, decomposition and potential advantages and drawbacks associated with soil application of FP-biochar is therefore critical.

Slow and fast pyrolysis results in biochars with different physicochemical qualities thus providing differentiated effects on the soil environment upon application (Brewer, et al., 2009). A FP at low temperatures or with large feedstock particles may result in incompletely pyrolyzed biomass providing bio-available C for the microbial population and thus a lowered potential for biochar-C sequestration in soil (Bruun, et al., 2011). As a consequence, application of incompletely pyrolyzed biomass may cause immobilization of soil N as more N is needed by the developing microorganisms than is provided by the substrate (Laird, et al., 2009; Brewer, et al., 2009). On the contrary, for SP processes the longer particle retention time results in a more completely pyrolyzed biochar-product with less volatile C-substrate and hence less risks of N immobilization.

The objective of the present study was to i) describe physiochemical characteristics of biochar from slow- and fast pyrolysis, and ii) compare the short-term carbon sequestration and adjacent C and N turnover in soil amended with biochar from slow and fast pyrolysis.

Materials and methods

Production of slow and fast pyrolysis biochar

Conventional wheat straw was used as feedstock for the production of SP-biochar and FP-biochar. The straw had a moisture content of 6.20 wt% and an ash content of 5.9 wt%, and was ground (below 1.4 mm) before pyrolysis (for details see Bech, 2008). To produce SP-biochar wheat straw was pyrolyzed in an electrically heated oven with a heating rate of 6 °C min⁻¹, a total solids residence time of 2 hours, constant nitrogen gas sweep, and a max temperature of 525 °C (Egsgaard, et al., 2005). The FP-biochar was made on a pilot-scale fast PCR at a reactor temperature of 525 °C (Bech, et al., 2009). The PCR unit consist of a screw type feeder, an electrically heated ablative centrifuge reactor, a cyclone used for biochar collection, a condenser and a coalescer used for bio-oil collection. The straw feedstock was introduced by the screw feeder into the nitrogen purged reactor, where a reactor rotor creates a centrifugal force to press the biomass particles against the hot reactor wall. During pyrolysis, the approximate particle residence time was a few seconds, and the initial heating rate ranged from 250-1000 °C s⁻¹.

The two pyrolysis methods gave similar biochar yields being 34 % for SP and 36 % for FP according to original parent wheat straw input. Subsequently, the SP- and FP-biochars was kept dark at room-temperature in air-tight PVC containers.

Soil

Soil samples were collected from the plough layer (0-25 cm) in an agricultural field at Risø DTU (55°41'N, 12° 05'E) and afterwards air-dried and sieved to obtain < 2 mm fraction. The soil was a sandy loam, Typic Hapludalf, with 11 % clay, 14 % silt, 49 % fine sand, and 25 % coarse sand (Hauggaard-Nielsen and Jensen, 2001).

Experimental design and treatments

An incubation experiment was conducted with four treatments, (1) SP biochar, (2) FP biochar, (3) wheat straw, and (4) a control soil with no added organic material. In 100 ml containers (ID=48 mm) 40 g soil (38 g dry weight) was mixed thoroughly with 2 g dry biochar or 2 g straw (1.89 g dry weight), respectively, and compressed to obtain a soil density of 1.4 g cm⁻³. The soil water content was kept constant at 35 % water holding capacity (WHC) by regular weighing of the containers and watering according to evaporation loss. The incubation was conducted at an average temperature of 23 °C (SE ± 0.02 °C) measured by a temperature logger (Tinytag Explorer 4.6) every 30 minutes throughout the 65 days of incubation.

Gas sampling and Analysis

The soil CO₂ flux of each sample was determined by infra-red gas analysis (LICOR 8100) with decreasing frequency throughout the experiment, ranging from daily to twice a week. The degradation (C loss) of the three added organic materials was calculated as the difference in CO₂ emissions between the control soil and the soils containing either biochar or straw.

Soil mineral N (NO₃⁻ and NH₄⁺), dissolved organic carbon (DOC), and soil microbial biomass (SMB) C and N were determined by extraction at day 0, 14, 28, 42, 56, and 65. Samples of 5 g wet soil were suspended in 25 ml 0.01 M CaCl₂ and shaken on a low speed reciprocal shaker for 1 hour. The supernatant was filtered through a No. 41 Whatman filter and a micro-filter (0.45 μm) to keep fine particulate (<1 μm) biochar from contaminating the extract. The extracts were analyzed on an AutoAnalyzer 3 (AA3 Bran and Luebbe) for soil mineral N and on a TOC-VCPH (Shimadzu) for DOC. Soil microbial biomass C and N content was determined using the chloroform fumigation-extraction procedure (Vance et al., 1987). The soil microbial biomass C was measured from the relationship $C_{\text{biomass}} = 2.22 \times \text{EC}$, EC being $C_{\text{fumigated}} - C_{\text{unfumigated}}$ (WU, et al., 1990) and the soil microbial biomass N was measured from the relationship $N_{\text{biomass}} = 1.85 \times \text{EN}$, EN being $N_{\text{fumigated}} - N_{\text{unfumigated}}$ (Joergensen, et al., 1996). Total C, H and N content was measured in air dried and finely ground soil, biochar, and straw samples on an EAMS elemental analyzer (EAflash1112; ThermoScientific) using 2 mg packed in combustion tin capsules. Surface areas, using the Brunauer, Emmett and Teller (BET) method, were determined from adsorption isotherms of nitrogen using a Micromeritics (Gemini 2375, V4.01) surface area analyzer. Prior to BET analysis the samples were degassed for two hours at 105 °C. Scanning electron microscopy

(SEM) pictures was performed using a FEI Quanta 400 Scanning Electron microscope (Light Smyth Company).

The carbohydrate composition of the biochar and wheat straw was determined by strong acid hydrolysis and HPLC analysis. A SP- and FP-biochar sample was treated with 72 w/w% H₂SO₄ at 30 °C for one hour, then diluted to 4 w/w% H₂SO₄ and eventually autoclaved at 121 °C for one hour. The composition of the released carbohydrates found in the filtrate was determined by HPLC analysis, using a Shimadzu HPLC system equipped with a refractive index detector. The sugars were separated by an Aminex HPX-87H ion exchange column with 4 mM H₂SO₄ in water as eluent (flow: 0.6 ml min⁻¹ at 63 °C). For further characterization, the carbohydrates were converted into acetates and analyzed by GC-MS using a Varian 3400 gas chromatograph interfaced to a Saturn II ion trap mass spectrometer.

Statistics

Statistical analysis of the CO₂ data was conducted using repeated analysis of variance (repeated measures ANOVA) and homogeneity of variance was investigated with residual plots using SAS 9.1, the proc mixed procedure (SAS institute Inc. 2003). Soil mineral N, DOC, SMB-C and SMB-N data were analyzed by ANOVA two-way to compare treatments across time and furthermore with ANOVA one-way (SAS institute Inc. 2003) to compare treatment effects at any given time. The model included treatment, day and the interaction between the two. Homogeneity of variance was achieved by log transformations where needed and Tukey adjusted differences of least square means were used to compare treatments.

Results

Biochar properties

Scanning Electron Microscope (SEM) images of parent wheat straw and the produced SP- and FP-biochars illustrate the large impact of the two pyrolysis technologies on the particle size and other structural characteristics (Fig. 1). Overall plant structure was clearly visible in the SP-biochar, while FP-biochar particles were much finer with large macropores and less visible resemblance to the parent straw material.

The rapid volatilization taking place during slow and fast pyrolysis respectively, decreased the feedstock particle size 6 and 27 times (based on mean diameter), leaving a very fine fragmented char powder (Table 1). The surface area increased only slightly as a result of the pyrolysis processing from 0.4 m² g⁻¹ for the wheat straw to 0.6 and 1.6 m² g⁻¹ for SP- and FP-biochar, respectively.

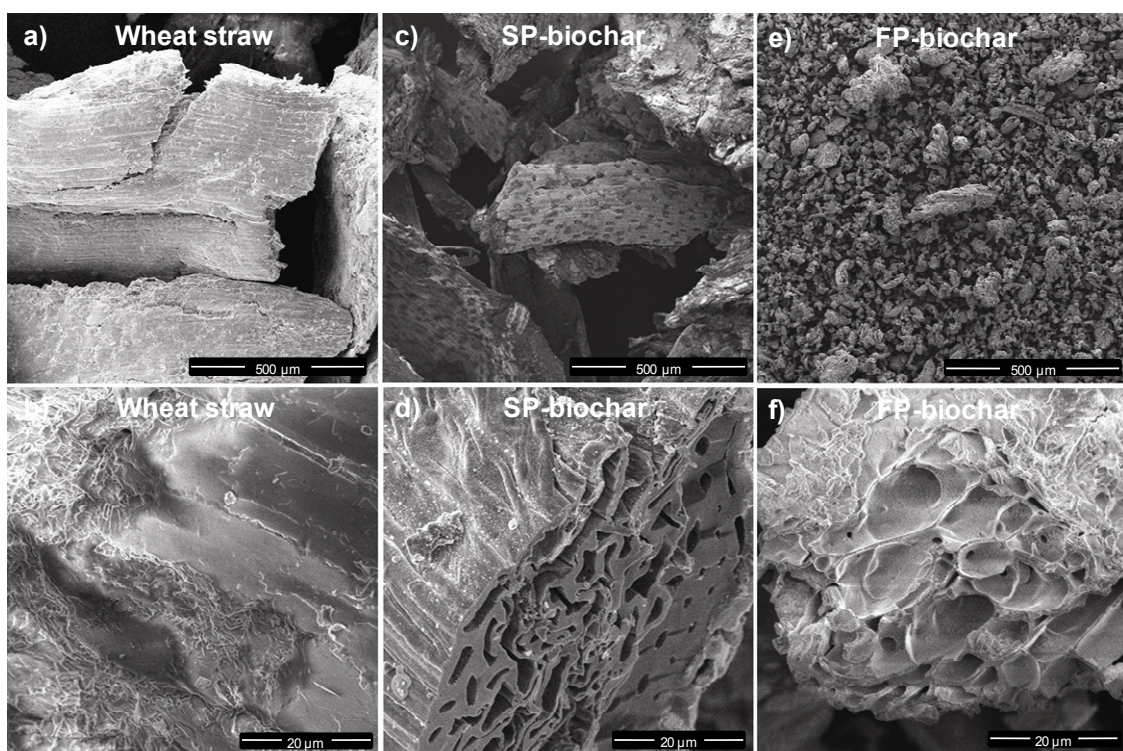


Figure 1. Scanning Electron Microscope (SEM) images of (a-b) feedstock wheat straw (c-d) SP-biochar and (e-f) FP-biochar particles. Upper row SEM images taken at 200x magnification and lower row at 3500x magnification.

The carbon proportion in the organic material increased during pyrolysis and the degree was influenced by the technology used (Table 1). The SP-biochar had a considerably higher C content (68.9 %) than the FP-biochar (50.4 %). This difference was also reflected in the O/C and H/C ratios where the FP-biochar was 2 to 4 times greater. Moreover the SP-biochar contained no cellulose and hemicellulose, while a fraction of 8.8 % remained in the FP-biochar.

Table 1. Physicochemical properties of slow pyrolysis (SP) and fast pyrolysis (FP) biochar as compared to the parent wheat straw and soil. All analyses were conducted in duplicates (n=2).

	Unit	Soil	SP-biochar	FP-biochar	Straw
Total C	%	1.6	68.9	50.4	39.4
N	%	0.2	1.4	1.3	1.0
O	%		7.9	23.0	48.1
H	%	0.20	2.1	3.7	5.6
H/C		0.13	0.03	0.07	0.14
O/C			0.11	0.46	1.22
C/N		10	49	39	39
Ash	%		19.8	21.6	5.9
Cellulose	%	-	0	7.4	40.3
Hemicellulose	%	-	0	1.4	22.8
pH		-	10.1	6.8	-
Mean diameter	$\mu\text{m} \pm \text{SE}$	-	113±15	23±2	~ 630
Min-max size	μm	-	8-630	4-99	-
Surface area (BET)	$\text{m}^2 \text{g}^{-1}$	4.2	0.6	1.6	0.4

a: Oxygen determined by difference (100% - C, H, N and ash %)

Carbon mineralization

Soil CO₂ emissions were significantly different between the four treatments ($P < 0.01$). Within the first week, peak CO₂ emissions were observed for all four treatments with the straw treatment showing the greatest emissions (Fig. 2a). During the incubation period, the straw treated soil lost the equivalent to 53 % of the added C as CO₂, while the cumulated C losses for SP- and FP-biochar amounted to 2.9 % and 5.5 %, respectively (Fig. 2b). Half of the cumulated C loss for straw and SP-biochar occurred within the first eight days, while the FP-biochar lost 63 % in this period. The dotted lines in Figure 2b indicate the total cumulated C loss when including C volatilized during pyrolysis in relation to the initial straw C. The cumulated C losses for SP- and FP-biochar amounted to 43 % and 57 %, respectively.

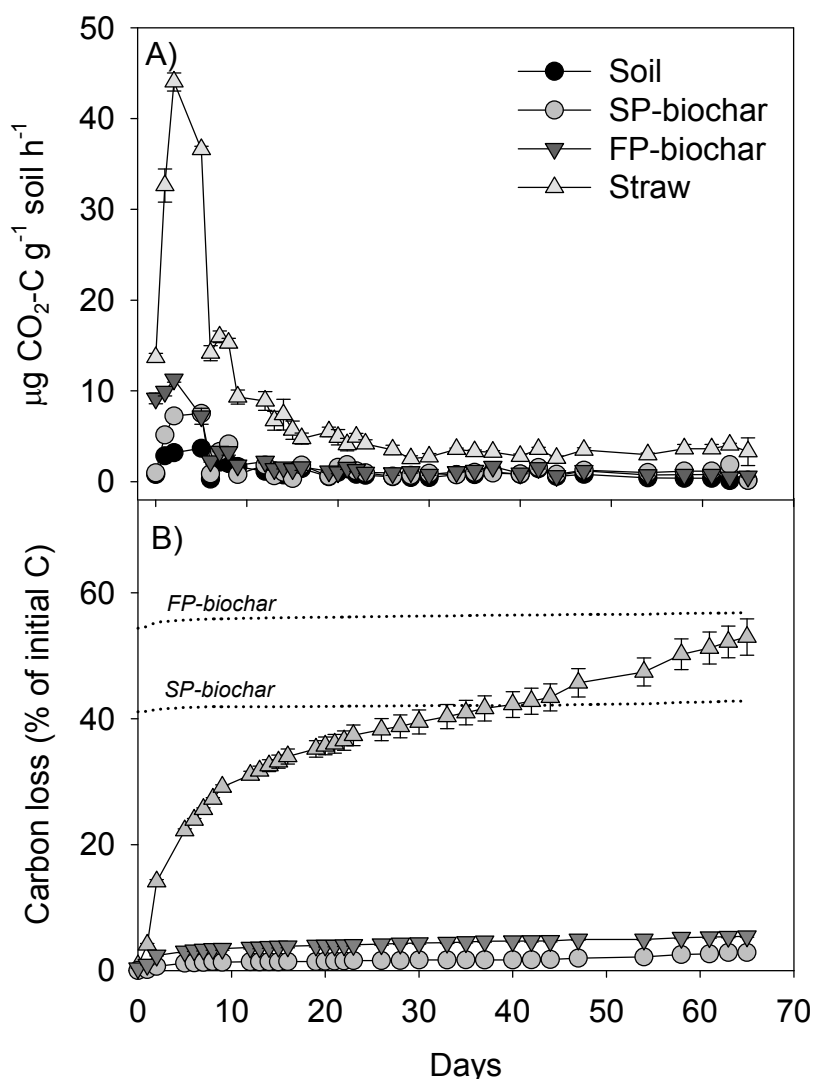


Figure 2. A) Soil surface CO₂-fluxes after soil application of slow pyrolysis (SP) biochar, fast pyrolysis (FP) biochar and parent wheat as compared to no amendment (soil). B) Net cumulative decomposition of straw, SP-biochar and FP-biochar in proportion to C added. Dotted lines show the total cumulated C loss in proportion to the parent wheat straw C including the C loss during pyrolysis. Values are the mean (n=4) ± S.E. (bars)

Microbial biomass and extractable C and N

The treatment with straw incorporation supported an increased microbial biomass throughout the experimental period ($P < 0.001$) (Fig. 3a). The SP-biochar soil had a SMB-C evolution almost identical to the control soil, whereas the FP-biochar treatment showed a SMB-C content significantly higher than both the SP-biochar soil ($P = 0.04$) and control soil ($P < 0.01$) when tested across dates. When comparing the treatments at specific sample days, the FP-biochar soil could only be separated from SP-biochar and control soils ($P < 0.01$) at day 56. The notable drop in biomass-C at day 40 for all treatments could indicate changes in incubation conditions like soil water content or temperature or potentially incomplete fumigation, but no such was observed. The dissolved organic carbon concentrations, shown in Fig. 3b, were considerably higher at day 0 in the FP-biochar and straw soils compared to

the control soil and SP-biochar. The drop in DOC levels from day 0 to day 28 corresponded to concurrent increases in SMB-C levels for FP-biochar and straw. The DOC concentrations in control and SP-biochar soils did not differ and remained constant during the study course.

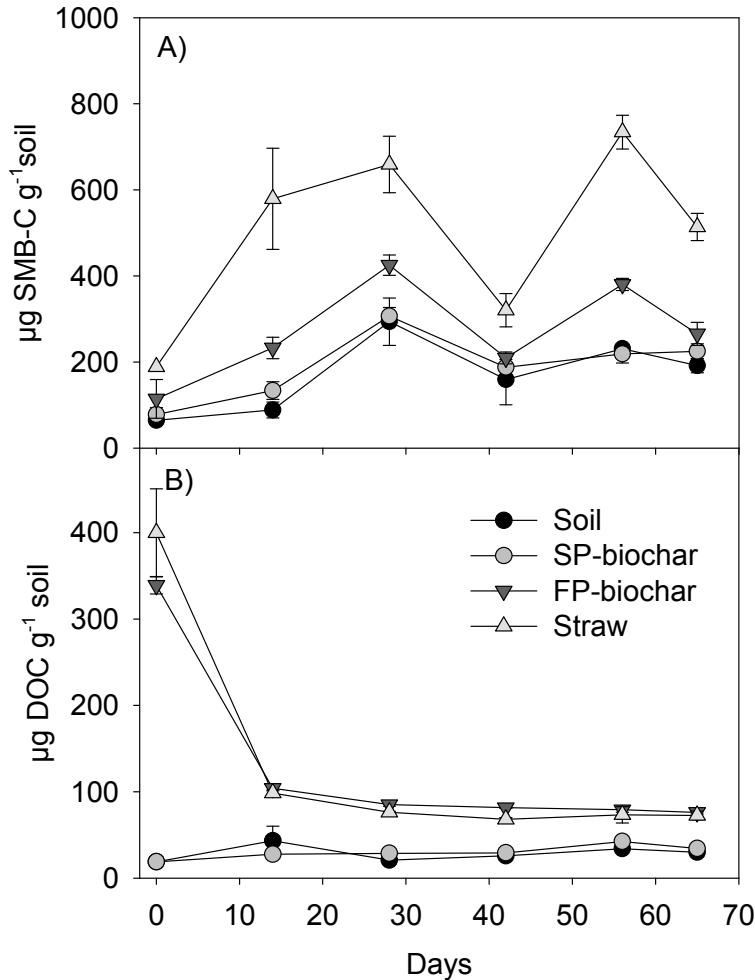


Figure 3. A) Soil microbial biomass carbon, and B) dissolved organic carbon (DOC) during the 65 days incubation period. Values are the mean ($n=4$) \pm S.E. (bars)

The SMB-N evolution (Fig. 4a) corresponded to the overall trends of the SMB-C comparing straw and biochar, but only the straw treatment reached levels significantly different from the other treatments when tested across dates ($p < 0.001$). SMB-N in the FP-biochar treatment was significantly higher than that in the SP-biochar treatment at day 14 ($P < 0.04$).

The soil mineral N content in the control soil and the SP-biochar treatments increased by 7 % over the incubation period, while a N immobilization of 43 % and 98 %, respectively, occurred in the FP-biochar and wheat straw treatments ($P < 0.001$) (Fig. 4b). The net N depletion with FP-biochar and straw mounted to 20 and 38 mg N kg^{-1} , respectively, of which 25 % and 91 % took place during the initial 14 days. Nitrate consistently formed the dominant part of the mineral N-pool (93-100 %) in the biochar soil and control soil

independent of time, while nitrate did vary more in the straw soil (10-98 %) due to very low values of both nitrate and ammonium (data not shown).

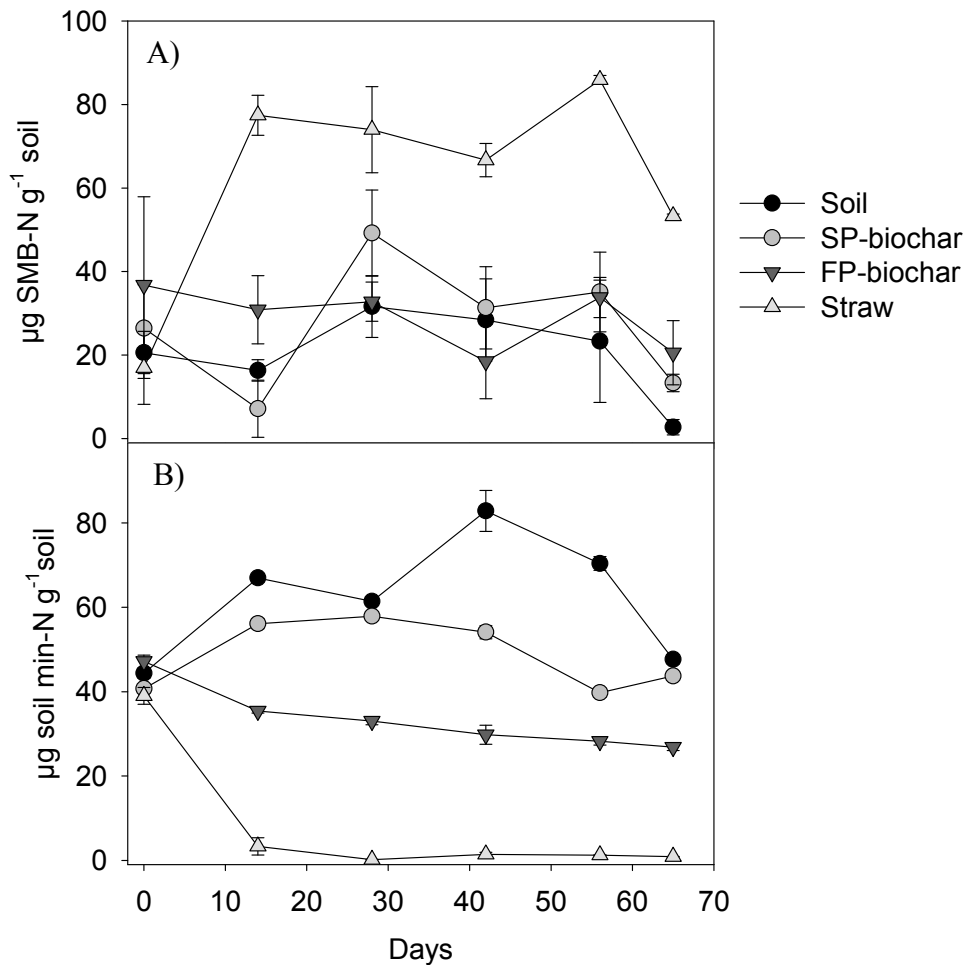


Figure 4. A) Soil microbial biomass nitrogen in all treatments measured six times during 65 days of incubation. B) Soil mineral N at different sampling days during the 65 days incubation period. Values are the mean ($n=4$) \pm S.E. (bars).

Discussion

Biochar Carbon mineralization

The parent wheat straw feedstock material was mineralized ten to eighteen times faster than the two biochars applied, supporting the C-sequestration potential of biochar in general (Fig. 2b). However, the different chemical qualities (Table 1) and physical structures (Fig. 1) of the two biochars influenced the short-term biochar-C losses (Fig. 2a). A significant difference between cumulative C loss comparing the SP-biochar ($2.9\% \pm 0.11$) and the FP-biochar ($5.5\% \pm 0.16$) was found, despite the fact that the same feedstock batch and pyrolysis peak temperature was used in both pyrolysis processes. These biochar derived soil CO₂-losses are within the range of findings from other works demonstrating cumulated

losses after a few months/years of a few percent or lower (e.g. Baldock and Smernik, 2002; Hamer, et al., 2004; Hilscher, et al., 2009) up to 12 % - 31 % year⁻¹ (Bruun, et al. 2011; Nguyen and Lehmann, 2009; Zimmerman, 2010). From this wide range, it follows that the short-term (< 1 yr) mineralization of biochar is to be considered a key-parameter in the assessment of biochar C-sequestration potentials.

The higher apparent C-mineralization of the FP-biochar in the present study compared to the SP-biochar is most likely due to incompletely pyrolyzed fractions of feedstock material in the FP-biochar. As a consequence, the labile organic C fraction of the two biochar types differed considerably. The FP-biochar contained a pool of DOC almost comparable to straw (Fig. 3b) and a fraction of 8.8 wt% unconverted cellulose/hemicellulose compared to none in the SP-biochar. Although DOC only represents a relatively small proportion of the organic carbon content in a typical biochar, it represents a mobile water soluble component and provides a highly labile source of energy and nutrients for soil microorganisms. The DOC pools were depleted rapidly (probably within days) in the FP-biochar and straw treatments, but the amount of DOC consumed could not account for the total cumulated CO₂ loss during the incubation (corresponding to 18 % and 3 %, respectively). We therefore propose that decomposition of more complex polymers including cellulose and hemicellulose constituted the major source for FP-biochar short-term C loss. A correlation between the cellulose and hemicellulose content of FP-biochar and the degree of short-term biochar-C mineralization was shown by Bruun, et al., 2011.

The different pools of labile carbon in the four treatments were also reflected in the microbial response. Soil microbial biomass C increased during the initial 28 days in all treatments, but most notable for straw and FP-biochar. The significantly higher SMB-C in the FP-biochar treatment compared to the control soil, demonstrated beneficial effects on the soil microbial population, although the SMB-N increase was less clear being significantly higher only at day 14. Increased microbial biomass responses have been reported after application of fresh biochar to agricultural soils, which likewise have been explained mainly by the availability of an easily decomposable non-aromatic fraction of the biochar (Kolb, et al., 2009; Kuzyakov, et al., 2009; Novak, et al., 2010; Steiner, et al., 2008a). In contrast, the 'low quality' SP-biochar treatment closely matched the evolution of the control soil during the incubation in terms of low SMC-C and low DOC, indicating the recalcitrance of this type of biochar (Fig. 3). The microbial population in the SP-biochar was probably C-limited, while the microbial population in the FP-biochar appeared to be N-limited (Fig. 4b).

In addition to biological mediated degradation, abiotic production of CO₂, due to oxidation of biochar surfaces (Cheng, et al., 2008; Zimmerman, 2010) or desorption of chemisorbed CO₂ on biochar (Spokas, et al., 2009; Spokas, et al., 2010), has been shown to contribute considerably to the biochar-C loss. As the SP-biochar contained almost no easy degradable labile material and did not increase SMB-C, but still lost 2.9 % of its C, this point to abiotic decomposition as the dominating CO₂ releasing process. Carbon dioxide were likely chemisorbed initially to SP-biochar particles, due to the high pH of the pure SP-biochar (10.1), but was desorbed after biochar amendment in soil (lowering the pH).

One further mechanism that could explain increased CO₂ releases after biochar application could be biochar priming the microbial degradation of native soil C, as proposed by Wardle (2008) (Wardle, et al., 2008a; Wardle, et al., 2008b). Yet, no significant biochar effects on

native soil C decomposition were found in an incubation study by Kuzyakov using ^{14}C -labelled biochar (Kuzyakov, et al., 2009). Investigation of this aspect requires more studies using stable isotopes in different soils and environments.

In order to assess the overall potential for climate change mitigation of the two pyrolysis processes, it is essential to evaluate the complete C budget, including the feedstock C 'loss' during pyrolysis, which should be added to the C loss during decomposition in the soil. With a total feedstock C loss of 43 % for the SP-biochar and 57 % for the FP-biochar, SP provided the greatest potential for C-sequestration (Fig. 2b). However, assuming that all C 'lost' during pyrolysis is collected as bio-oil and gaseous products, the FP process probably offers the best overall mitigation result, as the produced bio-oil and gas substitutes fossil fuels. It is not clear though, if the use of the FP pyrolysis technology for maximized bio-oil production (usually on the expense of the biochar quantity) will be the best solution in terms of environmental impact. In e.g. developing countries in need of high food production at low costs, maximizing biochar yields to support crop yields (Asai, et al., 2009; Major, et al., 2010) and potentially reducing fertilizer needs (Lehmann, et al., 2003; Dünisch, et al., 2007), might turn out to be the most important contribution of the pyrolysis process (see e.g. 'The Cameroon trial', www.biocharfund.org).

Influence of Biochar Particle size and Surface area

The very fine particle sizes of the FP-biochar (Fig. 1) potentially make the FP-biochars more susceptible to microbial attack than the SP-biochars, due to a better soil-biochar contact (larger surface-volume ratio) (Table 1). Zimmerman (2010) showed for a number of parent organic materials, that when biochar was separated in two size fractions by sieving (<0.25 mm and 0.25-2 mm) and incubated with soil, the fine fractions always released more CO_2 than the coarse fraction. On the other hand, fine biochar particles are also more likely to be physically protected against degradation by interactions with mineral surfaces or encapsulation into micro-aggregates (Brodowski, et al., 2006). Yet, protection by aggregation is probably limited in a short-term incubation experiment like the current, which excludes natural soil dynamics such as fluctuations in water content, temperature, oxic conditions and soil mixing by fauna (Nguyen and Lehmann, 2009).

The large porosity and relative surface area often observed for biochar improves the capability of biochar amended soils to maintain moisture (Pietikainen, et al., 2000) and retain cations (Liang, et al., 2006). Moreover, a large surface area has been hypothesized to benefit the microbial population by providing attachment sites to colonize, close proximity to soil organic matter, and protection against predation (Warnock, et al., 2007).

In this study, the feedstock BET surface area was only marginally increased by the two pyrolysis processes resulting in similar and very low biochar surface areas (Table 1). Compared to that frequently reported for wood-based and low-ash biochars having BET values $>100 \text{ m}^2\text{g}^{-1}$ (Downie, et al., 2009), high-ash biochars tends to have lower values (Joseph, et al., 2009; Karaosmanoglu, et al., 2000). Thus, rather than the pyrolysis type used, intrinsic wheat straw characteristics such as a high ash content, might be the main cause for the low surface areas. Taking into account the importance of a large surface area as discussed above, wheat straw might thus not be as suitable a feedstock for biochar as woody biomass. On the other hand, the larger ash content of wheat straw compared to woody biomass,

benefits crops by providing more nutrients. In general though, the surface area is described to be influenced by the pyrolysis conditions (temperature, heating rate) and the presence of active reagents such as steam, CO₂ and O₂ (Boateng, et al., 2010). It is therefore plausible that activation of the wheat straw biochar would improve the surface area considerably. For instance in a study by Boateng (2010) the surface area increased dramatically from virtually zero to 837 m²g⁻¹ when soybean straw was pyrolyzed with steam activation. Over a longer time period, the ‘aging’ process in soil with biotic decomposition and abiotic oxidation of the biochar surfaces has been shown to increase the surface area (Cheng, et al., 2006; Liang, et al., 2006), but the speed and degree remain unclear and require more research.

Soil nitrogen mobilization and immobilization

Initial decomposition of residues with wide C:N ratios usually leads to immobilization of soil mineral N after application to soil (Ambus, et al., 2001; Bengtsson, et al., 2003; Craine, et al., 2007), which may result in negative effects on crop yields. Nitrogen immobilization was also confirmed in this study, where almost all mineral N in the straw treatment (C:N=39) was immobilized rapidly (Fig. 4b). Also the two biochar treatments immobilized N during the course of the experiment, compared to the control soil, which corroborates other studies documenting concurrent N immobilization with application of fresh biochar (Kolb, et al., 2009; Lehmann, et al., 2003; Novak, et al., 2010). Yet, at the end of the incubation the SP-biochar had similar soil mineral N levels as the control soil indicating that any effect of SP-biochar on the immobilization of N was only short-term in nature (despite similar C:N ratio as the straw). This was opposite to the FP-biochar soil, which during the period continued to immobilize mineral N and maintained a mineral N level at 50 % of the control soil at day 65. As N immobilization is coupled to the quantity of C readily available for microbial assimilation, we expect the larger labile fraction of the FP-biochar compared to SP-biochar (Table 1) to explain the different N evolutions. In general, the N immobilization after biochar amendment is most likely a transient phenomenon as the labile part is used up after a few months leaving a much more recalcitrant biochar for the longer term microbial interactions.

From an agricultural point of view - and independently of pyrolysis technology used, soil application of biochar materials containing a substantial labile C fraction should be carried out in the autumn to reduce the risks of N-immobilization during early crop season. Autumn application furthermore has the potential to decrease leaching and gaseous losses of N during fallow periods and thus preserve N in the agricultural system (Ambus, et al., 2001).

Conclusion

This study compared slow- (SP) and fast-pyrolysis (FP) of wheat straw feedstock with respect to biochar characteristics and effects on microbial C and N turnover upon soil incorporation. The pyrolysis methods had a significant impact on biochar pH, particle size, and surface area. The specific FP equipment used left a labile un-pyrolyzed biomass fraction (8.8 % carbohydrates) in the biochar, while the SP-biochar was completely pyrolyzed. The labile FP-biochar fraction possibly supported a somewhat higher biochar-C loss and a larger soil microbial biomass. Moreover, soil application of fresh FP-biochar resulted in a considerable immobilization of N (43 %) during the 65 days experiment, whereas SP-biochar led to a net N mineralization (7 %). The study showed that soil application of FP-

biochar materials has the potential to sequester C while simultaneously providing a substrate for N retention. We recommend treating biochar as a rather complex organic material very much influenced by pyrolysis technology and settings.

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Application of biochar to soil and N₂O emissions: potential effects of blending fast-pyrolysis biochar with anaerobically digested slurry

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Summery

Soil applications of recalcitrant biochar offers the possibility of mitigating climate change through long-term carbon sequestration and, potentially, also through reducing emissions of the potent greenhouse gas nitrous oxide (N₂O). This laboratory study examined the effect of combining a fast-pyrolysis biochar at low (1% by weight) and high (3%) concentrations with anaerobically digested slurry, on soil N₂O and carbon dioxide (CO₂) emissions over a period of 55 days. The results showed that fast-pyrolysis biochar applied on its own increased N₂O emissions from soil. However, when biochar was applied together with slurry, the larger biochar concentration decreased N₂O emissions by 47%, relative to that from the slurry treatment that received the smaller rate of biochar. Reduced N₂O emissions coincided with enhanced soil microbial activity and immobilization of nitrogen. A combined application of biochar and anaerobic digested slurry could therefore be beneficial for cropping systems in terms of soil nitrogen retention while concurrently mitigating N₂O fluxes and sequestering carbon in soil.

Introduction

Nitrous oxide (N₂O) is an important greenhouse gas (GHG), comprising 8% of global GHG emissions (CO₂e) in 2004 (Denman *et al.*, 2007). Since the pre-industrial age, anthropogenic activities have led to increases in the atmospheric concentration of N₂O from 270 to 319 ppb (in 2005), with the agricultural sector being the biggest single contributor (Denman *et al.*, 2007; Del Grosso *et al.*, 2005). Mitigation options to reduce N₂O emissions from agriculture, without losing productivity, are therefore regarded as being very important.

The production of N₂O in soil by the nitrification and denitrification processes is affected by several factors, of which the availability of oxygen is particularly important (Firestone & Davidson, 1989). The major controller of the oxygen availability is the soil moisture content, often expressed as a percentage of water-filled pore space (WFPS). Under soil aerobic conditions (low WFPS), the production of N₂O is usually small, and originating to a greater extent from the nitrification process (Bateman & Baggs, 2005; Senbayram *et al.*, 2009). At higher WFPS (> 70%), larger N₂O production rates occur, most commonly associated with

the denitrification process (Bollmann & Conrad, 1998; Firestone & Davidson, 1989; Dalal *et al.*, 2003). In addition to soil oxygen status, the emission of N₂O from soil is influenced by substrate availability (ammonium, nitrate and organic C), as well as soil pH, temperature and microbial community structure (Firestone & Davidson, 1989).

Soil carbon sequestration by application of recalcitrant carbon-rich biochar has been increasingly advocated as a means to mitigate climate change and to improve soil fertility (Chan *et al.*, 2007; Laird *et al.*, 2009; Lehmann *et al.*, 2006; Lehmann *et al.*, 2003). Yanai *et al.* (2007) showed that biochar-amended soils (8–10% biochar: note that all biochar amendments will be expressed on a dry weight of soil basis) reduced N₂O emissions by 89% and stated that the observed effect was caused by an increase in soil aeration. Likewise, Spokas *et al.* (2009) reported reduced N₂O emissions by up to 74% in soils with relatively large biochar concentrations (20, 40 and 60%), while no suppression was observed at smaller amendment rates (2, 5 and 10%). Singh *et al.* (2010) did not observe an immediate reduction of N₂O emissions when soils were amended with different types of biochar (0.8%) at 85% WFPS. However, during two subsequent rewetting cycles, N₂O emissions were reduced by up to 73%, possibly as a result of an increased sorption capacity of the biochar over time, thus decreasing the bioavailability of soluble organic substances. van Zwieten *et al.* (2010) showed reduced N₂O emissions in an incubation study involving different biochar types and ascribed this mainly to an increased adsorption of nitrate (NO₃⁻) to the biochar surfaces. In contrast, Clough *et al.* (2010) did not observe any reductions in N₂O emissions after addition of biochar (4%) to soil, either alone or in combination with large concentrations of bovine urine. However, in a follow-up experiment in the field, the application of 30 t biochar ha⁻¹ reduced N₂O emissions from ruminant urine patches by 70%, but no significant reduction was observed with half the rate applied (Taghizadeh-Toosi *et al.*, 2011). These authors observed a reduced NO₃-N pool in soil in the biochar-amended plots and attributed that mainly to a possibly enhanced adsorption and uptake of NH₃ by the biochar particles.

The stability of biochar results in small nutrient release rates by mineralization, and biochar itself is therefore not regarded as a balanced fertilizer (Steiner *et al.*, 2008). As a sustainable way to maintain soil fertility, the use of organic residues as soil amendments is gaining worldwide importance, especially with the rise of new bio-energy conversion technologies (Senbayram *et al.*, 2009). However, microbial transformation of organic fertilizer nitrogen (N) to N₂O constitutes a considerable source of N₂O (Denman *et al.*, 2007; Thomsen *et al.*, 2010), with emission factors that can even be larger than that of mineral fertilizers (Senbayram *et al.*, 2009). We hypothesized that blends of biochar and organic amendments, such as anaerobically digested (AD) slurry, might, on the one hand, increase nutrient availability in biochar-amended soils and, on the other, decrease N losses from soil by reducing N₂O emissions after the application of organic residues.

The purpose of this research was therefore to (i) examine how soil applications of different concentrations of biochar, alone or blended with AD slurry, affect the emissions of N₂O and (ii) improve the understanding of underlying mechanisms involved.

Materials and Methods

Soil, biochar and slurry used for incubations

A loamy soil from an agricultural field at Risø DTU (55°41'N, 12° 05'E) with 11% clay, 14% silt, 49% fine sand and 25% coarse sand (Typic Hapludalf) was selected for the incubation experiments (Table 1). The soil was collected from the 0–25-cm layer and afterwards it was air-dried and sieved to obtain the <2 mm-fraction. The biochar was produced by fast pyrolysis at 525°C on a pilot-scale pyrolysis centrifuge reactor (PCR) (Bech, 2008). Wheat (*Triticum aestivum* L.) straw was used as the feedstock for the production of biochar. The straw had a moisture content of 6.20% and an ash content of 5.9%, and was ground and sieved to a particle size of <1.4 mm before pyrolysis. The AD slurry used was the fermentation effluent from a pilot biogas plant at Risø DTU, Denmark, where cattle manure was fermented at 53°C for 15 days. Important soil characteristics determined prior to incubation, and biochar and slurry characteristics are presented in Table 1.

Table 1. Characteristics of the soil, biochar and slurry used in the experiment. Biochar BET area, biochar ash fraction and biochar carbohydrate content are based Bruun et al (2011).

Characteristics	Soil	Biochar	Slurry
Total C /%	1.6	50.4	0.66
Total N /%	0.16	1.3	0.3
C/N	10	39	2.2
pH (1:5 H ₂ O)	7.0	6.8	-
Surface area (BET) /m ² g ⁻¹	4.2	1.6	-
Ash fraction /%	-	21.6	-
Carbohydrates /%	-	8.8	-

Experimental Design and Treatments

The experiment was carried out with 200 g soil (dry weight) per replicate (4 replicates per treatment), incubated in a 330-ml PVC container, and comprised six different substrate treatments combined with two different soil moisture levels. The substrate treatments were (i) biochar 2 g + 200 g soil ('biochar-L', where L = low), (ii) biochar 6 g + 200 g soil ('biochar-H', where H = high), (iii) slurry + 200 g soil ('slurry'), (iv) slurry + 2 g biochar + 200 g soil ('blend-L'), (v) slurry + 6 g biochar + 200 g soil ('blend-H') and (vi) soil 200 g ('control soil') to give 12 treatments in total.

Before the start of the incubation, the soil was wetted and pre-incubated at room temperature for five days. Subsequently, the biochar was thoroughly mixed with the soil at a rate of 1% or 3%. The treated soils were gently pressed to obtain a bulk density of approximately 1.4 g cm⁻³. Soil moisture was adjusted to a WFPS of 40% (LW, low water content) or 80 % (HW, high water content), corresponding to 32 and 64 % of water holding capacity, respectively. Finally, 2.9 ml of anaerobically digested slurry equivalent to 150 kg total N ha⁻¹ was added

to the appropriate treatments. Each individual container was sealed with a pierced lid, and the gravimetric moisture content was kept constant during the experiment. The containers were incubated at $16 \pm 0.3^\circ\text{C}$ in a controlled temperature cabinet throughout the 55 days experiment, except when CO_2 and N_2O measurements were made at room temperature.

Analyses

Carbon dioxide and N_2O emissions were measured in all four replicates on days 1, 2, 3, 5, 7, 11, 20, 27, 34, 41, 48 and 55 after the start of the incubation. The container lids were opened and each container was placed in a 2-l gas-tight glass jar. Gas accumulation in the headspace was measured using a Photoacoustic Field Gas-Monitor (INNOVA 1412 Photoacoustic Field Gas Monitor, LumaSense Technologies, Ballerup, DK) equipped with three individual optical filters (for CO_2 , N_2O and water vapour), connected in a closed loop to the glass jar *via* two valves mounted in the lid and side of the jar, respectively. Headspace concentrations were measured approximately 0, 30, 60, and 90 minutes after closing the jars and flux rates were calculated using linear regression. Linearity of emissions was always tested and only measurements with an R^2 value ≥ 0.95 were taken into account. Measurements were carried out under controlled temperature conditions, which minimized potential drift in analyser sensitivity (Flechard *et al.* 2005). Calibration of the INNOVA gas monitor was verified with independent GC analyses (data not shown).

Additional PVC containers – identical to those used for measuring emissions – were set up and kept at 16°C . The water content was held constant by regular watering to weight. At day 1, 4, 10, 16 and 55 of the incubation period, 3 units per treatment were harvested destructively for analyses. Ten-g of soil sample were extracted with 50 ml 0.01 M CaCl_2 for 60 minutes and the extracts were filtered through pleated filters (Grade 74, Frisenette Aps, Denmark). Concentrations of ammonium (NH_4^+) and nitrate (NO_3^-) were determined by standard colorimetric procedures (Keeney & Nelson, 1982) on an AutoAnalyzer 3 instrument (Bran+Luebbe, Norderstedt, Germany). Dissolved organic carbon (DOC) was extracted by the same procedure and analysed on a TOC-VCPH (Shimadzu Corporation, Kyoto Japan).

Soil microbial biomass carbon (SMB-C) was measured with the chloroform-fumigation extraction technique (Vance *et al.*, 1987). In brief, duplicate 10-g soil samples were taken from each treatment replicate at each destructive sampling date; one for the immediate extraction with CaCl_2 as described above and one for vacuum-fumigation with chloroform (20–24 hours) and subsequent extraction. For each soil sample, the SMB-C was calculated from the difference in DOC between non-fumigated and fumigated samples and by applying a K_{EC} factor of 0.45 (Jenkinson *et al.*, 2004). However, the results from the destructive sampling at day four had to be taken out of the dataset, because of incomplete fumigation.

Soil pH was determined in a 1:5 (w:w) suspension of fresh soil in deionized water.

Statistics and calculations

Statistical analyses were performed using STATISTICA software (Statsoft Inc., 2010). All tests of significance were conducted at $P < 0.05$. When data were not normally distributed or

showed heterogeneity of variances, they were square-root or log-transformed before analysis. Trends of CO₂ and N₂O fluxes over time were analysed using repeated measures ANOVA. The cumulative emissions were calculated by linear interpolation between measured daily fluxes and then analysed with one-way ANOVA. To detect overall treatment effects during the course of the incubation, soil mineral N, DOC and SMB-C data were subjected to a two-way ANOVA with time and treatment as factors. For treatment effects on single sampling dates, data were analysed with a one-way ANOVA. When significant *F* tests were obtained, multiple mean comparisons were carried out using Tukey's Honest Significant Difference (HSD) test.

Results

Carbon Dioxide Emission

The contrasting soil moisture contents did not affect the CO₂ emission rates (Figure 1a, b). In all treatments, the greatest CO₂ emissions (up to 0.76 μg CO₂-C g⁻¹ soil hour⁻¹) occurred within the first three days after the start of the incubation. Within each soil moisture level (LW or HW) significant CO₂ peaks were observed when the larger doses of biochar had been applied (biochar-H and blend-H), compared with all other treatments (*P*<0.001) (Figure 1a, b).

Correspondingly, the mean cumulative CO₂ losses at the end of the incubation (day 55) were significantly larger in biochar-H and both biochar-slurry combinations (blend-L and blend-H) at both levels of WFPS than in their respective control soils (*P*<0.001) (Figure 1c, d). Cumulative CO₂ emissions from the slurry alone treatment did not differ from the control soil (*P*<0.001) (Figure 1c, d). In the LW soils, the treatments receiving the larger rates of biochar emitted, on average, 3.3 times more CO₂ than the treatments receiving the smaller rate (after adjusting for the emissions from the control). In the HW series, the cumulative loss from the larger application was 4.3 times greater than that from the smaller rate.

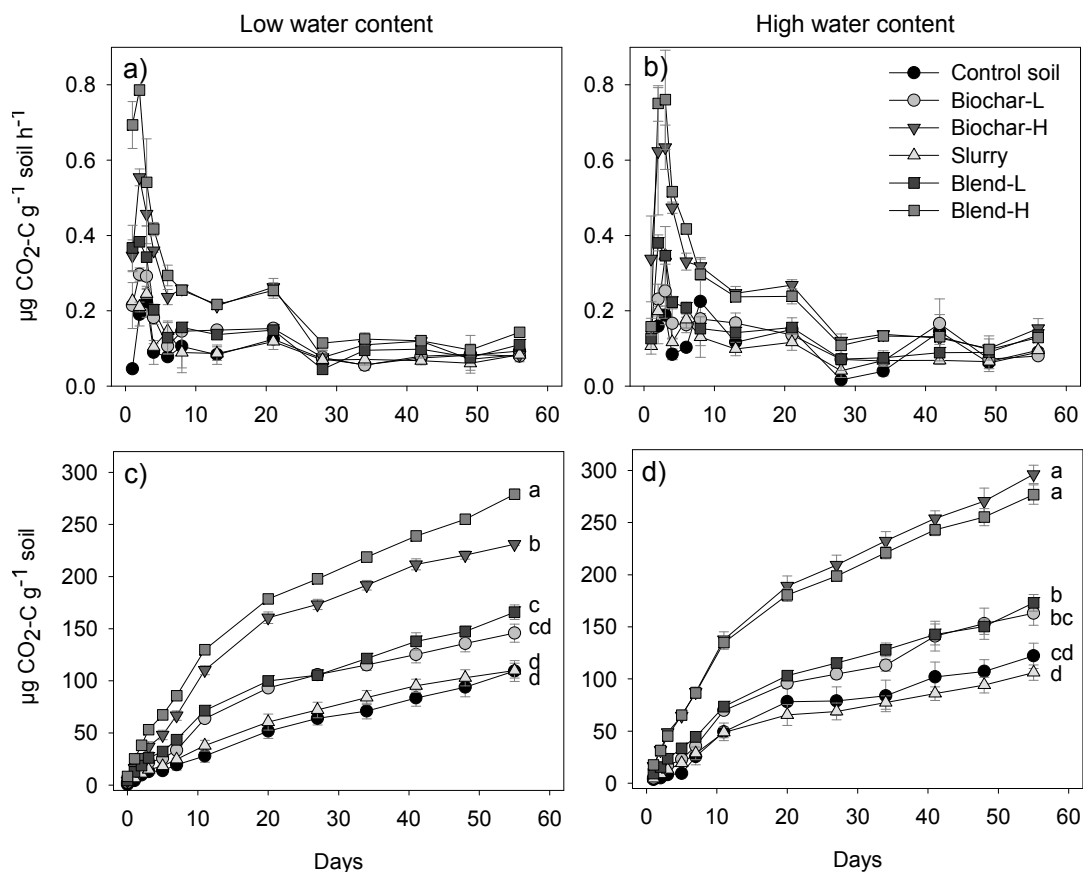


Figure 1 a and b) Soil surface CO₂-fluxes following application of 2 g biochar (biochar-L), 6 g biochar (biochar-H), slurry and two biochar-slurry blends (blend-L and blend-H) to 200 g soil (dw) compared with no amendment (control soil). c and d) Net cumulative CO₂-C loss per g (dry weight) soil during 55 days incubation. Left column shows treatments with drier (LW) soils and right column wetter (HW) treatments. Letters show significant differences (after 55 days) according to the Turkey test ($P < 0.05-0.01$). Values are the mean ($n = 4$) \pm S.E. (bars)

Nitrous Oxide Emission

Moisture content strongly affected N₂O emissions ($P < 0.001$) (Figure 2a, b). The cumulative N₂O emissions in the HW treatments were 8 to 23 times greater than those from the corresponding LW treatments, with the exception of the control soil, which only increased by 1.4 times. The smaller N₂O emissions from the LW treatments were not significantly different from each other when N₂O emissions were tested over time (Figure 2a). Thus, the LW series can therefore be considered of less importance to the objective of studying the effects of biochar and slurry interactions on N₂O emissions. For simplification, we therefore only present data for the HW series.

In the slurry treatment N₂O emissions were prolonged until day 10, while in the biochar amended soils virtually all N₂O emissions occurred within the first five days of incubation, whereafter N₂O fluxes stabilized abruptly at the level of the control soil. The treatments biochar-L, biochar-H, and blend-L had significantly higher N₂O emission rates over time compared to the control soil (Figure 2b). At the end of the experiment, all treatments showed

significantly larger cumulative N_2O losses compared with the control soil ($P < 0.01-0.001$) (Figure 2d). The greatest cumulative N_2O production (day 55) occurred in the blend-L treatment with a loss of $0.95 \mu\text{g } N_2O\text{-N g}^{-1}$ soil, seven times larger than the control soil. Cumulative emissions from the blend-H treatment were 47% smaller than in the blend-L treatment (Figure 2d).

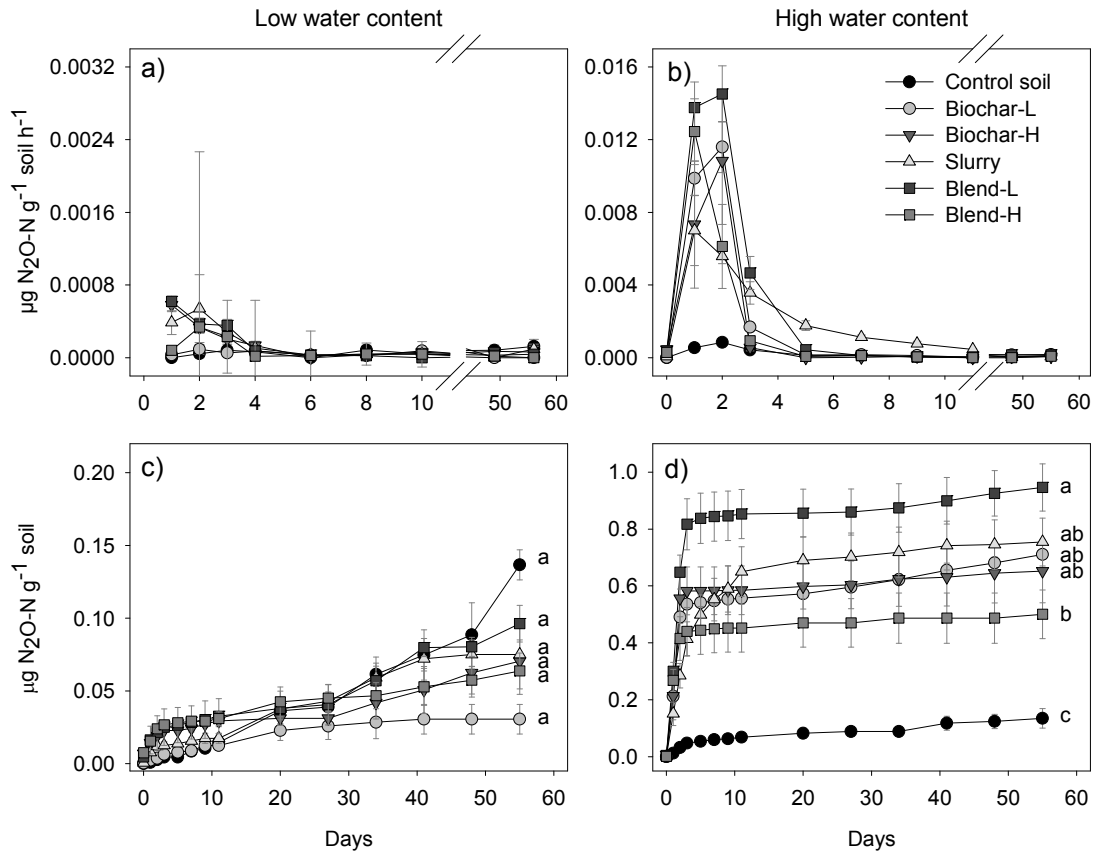


Figure 2 a and b) Soil surface N_2O -fluxes following application of 2 g biochar (biochar-L), 6 g biochar (biochar-H), slurry and the two biochar-slurry blends (blend-L and blend-H) to 200 g soil (dw) compared with no amendment (control soil). c and d) Net cumulative N_2O -N loss per g (dry weight) soil during 55 days incubation. Left column shows with drier (LW) soils and right column wetter (HW) soil treatments (please note the different scales of the Y-axis). Letters show significant differences (after 55 days) according to the Turkey test ($P < 0.05-0.01$). Values are the mean ($n = 4$) \pm S.E. (bars)

Dynamics of extractable C and N

The DOC concentrations measured on day 1 reflected the amounts of biochar applied (0, 2, and 6 g) (Figure 3a). From day 1 until the end of the study, the DOC concentrations in the treatments receiving the larger applications of biochar (biochar-H and blend-H) remained greater than those in the low or no-biochar treatments ($P < 0.001$). In the first three days, especially, there was a steep decline in DOC concentrations in all treatments, including the control, with the greatest decreases being observed in the biochar-H and blend-H treatments.

Soil microbial biomass C increased in all treatments during the incubation period with no significant effect of treatment (Figure 3b). The greatest increase was generally observed prior to day 10 in all treatments (except blend-L), when blend-H peaked with an average microbial biomass of 228.4 $\mu\text{g C g}^{-1}$ soil. After day 10, SMB-C decreased in all treatments towards the end of the incubation period.

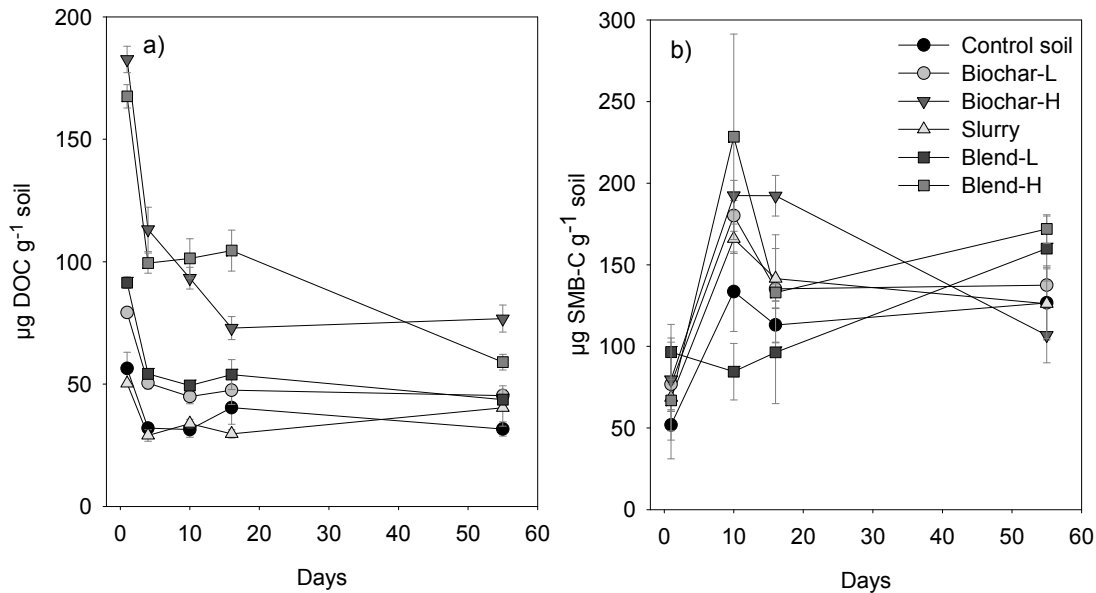


Figure 3 a) Dissolved organic carbon (DOC) and b) soil microbial biomass carbon (SMB-C) in the wetter soil treatments (HW series) during the 55-day incubation period. Values are the mean ($n = 3$) \pm S.E. (bars)

After being very similar at the first sampling date, the NO_3^- -N concentrations decreased in all treatments during the first four days of incubation, especially in the biochar-H and blend-H treatments with decreases of 58% and 51%, respectively. After day 4, a generally increasing trend of the NO_3^- -N content was observed in the slurry, control and in blend-L treatments, whereas in biochar-H and blend-H, the NO_3^- -N contents remained small. Relative to the control soil, the slurry treatment had a greater mean NO_3^- -N content, increasing by 89% during the experiment (from 47.0 to 88.6 $\mu\text{g NO}_3^-$ -N g^{-1} soil), whereas that in the blend-L treatment was similar to that in the control soil. Biochar-L had significantly smaller NO_3^- -N concentrations than blend-L, while biochar-H had the smallest NO_3^- -N contents throughout the experiment (Figure 4a) which were significantly different from those in biochar-L and blend-L treatments.

The mean NH_4^+ -N concentration for all treatments fluctuated between 4.2 and 10.4 $\mu\text{g NH}_4^+$ -N g^{-1} soil during the incubation period, with the maximum mean NH_4^+ -N concentrations at day 1 in the blend-L and blend-H treatments (Figure 4b). No overall treatment effects were observed, however, at day 1, slurry-treated soils had a significantly larger NH_4^+ content compared with soils without slurry.

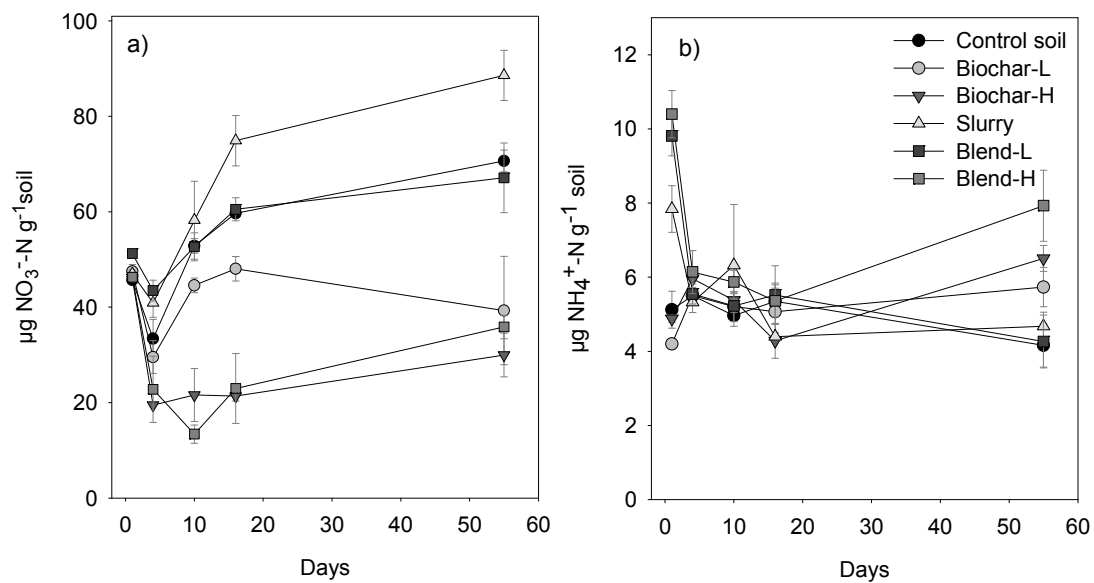


Figure 4 a) Nitrate (NO_3^- -N) and b) ammonium (NH_4^+ -N) in the wetter soil treatments (HW series) during the 55-day incubation period. Values are the mean ($n = 3$) \pm S.E. (bars)

Soil pH

The mean soil pH ranged from 7.2 to 8.2 and fluctuated over time with no significant treatment effects, except for that in the blend-H treatment being significantly greater than the control soil (Figure 5). The most alkaline pH (8.2) was measured on day 10 in the blend-H treatment. At day 55, the biochar-L and -H treatments had greater pH values than the other treatments.

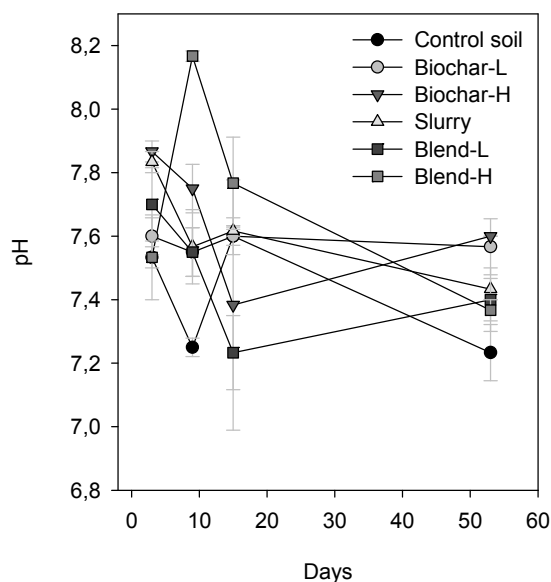


Figure 5 pH during the course of the incubation in the wetter soil treatment (HW series). Values are the mean ($n = 3$) \pm S.E. (bars)

Discussion

CO₂ emissions

Biochar consists predominantly of recalcitrant conjugated aromatic structures, but aliphatic carbohydrate fractions may remain depending on pyrolysis type and settings (Lehmann et al., 2009; Bruun, et al., 2011). Thus a fast-pyrolysis process using low temperatures is more likely to leave incompletely pyrolyzed fractions in the biochar compared with a slow pyrolysis process with much longer particle retention time. In our case, the fast-pyrolysis biochar contained 8.8% carbohydrates (Bruun et al., 2011). Decomposition of this fraction together with the labile DOC pool (Figure 3a) explains the large CO₂ emission during the first week of incubation with the greatest emissions from the treatments with larger biochar contents (biochar-H and blend-H) (Figure 1a, b) (Bruun et al., 2011). Spokas et al. (2009) also reported increasing CO₂ emissions with increasing amounts of moist biochar samples produced by fast pyrolysis at 500 °C. The rapid microbial population growth in biochar-H and blend-H treatments from day 1 to 10 (Figure 3b) and the larger mean SMB-C content at days 10 and 16, respectively, corresponded with the greater amounts of DOC and greater initial emissions of CO₂ in these treatments. The blend-L, in contrast, had the smallest SMB-C in the same period.

In addition to biochar-derived CO₂, priming of the microbial biomass by beneficial physicochemical biochar properties, such as provision of labile C, could stimulate CO₂ emissions from decomposition of native organic soil matter (Wardle et al. 2008). Examination of this aspect would require use of isotope labelled biochar material in order to differentiate between biochar C and native soil organic C.

The addition of N-rich biogas slurry did not increase CO₂ production in the control or in combination with biochar (Figure 1c and d), which suggests that the soil microbial community was C-limited rather than N-limited. This was also supported by the accumulation of NO₃⁻-N in the slurry soil, which probably originated from nitrification of ammonium contained in the slurry and mineralized from the organically-bound N pool in slurry (Figure 3a and 4a).

N₂O emissions in relation to underlying C and N dynamics

Nitrous oxide production was several times greater in HW soils than in LW soils, in agreement with the stimulation of the denitrification process under oxygen-limited conditions (Firestone & Davidson, 1989). Nearly all the N₂O emissions in the biochar-amended soils occurred within the first five days of incubation (Figure 2) corresponding with the maximum CO₂ emission rates (Figure 1). An initial peak after biochar amendments is in accordance with the findings of van Zwieten *et al.* (2010) and Yanai *et al.* (2007), and confirms that biochar induced N₂O emissions are usually short-lived. In the HW series, the addition of biochar-slurry combinations increased N₂O emissions relative to those from the control soil (Figure 2b and d), which contrasts with other studies reporting suppression of N₂O emissions after biochar amendment (Singh *et al.*, 2010; Spokas *et al.*, 2009; Yanai *et al.*, 2007; van Zwieten *et al.*, 2009), but corroborates the findings of Clough *et al.* (2010).

Different physicochemical characteristics of the various biochars applied are probably the predominant factor in explaining the different rates of N₂O emissions observed in these studies. Moreover, although comparisons between studies should be made with caution caused by differences in soil moisture contents, temperature and soil type, it seems that smaller biochar concentrations in soil ($\leq 5\%$) do not result in initial N₂O emission reduction (Clough *et al.*, 2010; Singh *et al.*, 2010; Spokas *et al.*, 2009). Biochar might increase the potential to reduce emissions from soil over a few months (Singh *et al.*, 2010). This is in accordance with a study of Taghizadeh-Toosi *et al.* (2011), who observed reductions in N₂O emissions seven months after incorporating approximately 2.3% biochar into the soil. In contrast, immediate reductions in N₂O emissions in the range of 57–89% were observed after the application of large amounts ($\geq 8\text{--}60\%$) of biochar (Spokas *et al.*, 2009; Yanai *et al.*, 2007). These results indicate the existence of a biochar concentration threshold above which immediate N₂O production is restricted. In our study, the three times larger amendment rate of biochar did not result in a significantly reduced N₂O emission rate, but tended to cause a smaller cumulative emission (0.65 ± 0.11 compared with 0.71 ± 0.01 $\mu\text{g N}_2\text{O-N g}^{-1}$ soil) (Figure 2d). In contrast, the low and high biochar-slurry blends showed a pronounced difference regarding the N₂O flux from soil (Figure 2d). Here the blend-H treatment had a 47% smaller N₂O emission than the blend-L treatment. Thus, although the biochar amendments (1 and 3) increased the N₂O emission relative to the control soil, this increase was considerably less pronounced at the larger biochar content (3%). When expressed as emission factors (cumulated N₂O-N emission of the respective treatment minus the emission from the control soil as a proportion of the added total N from slurry) the soil amended with slurry emitted 1.4% of the added slurry N, while blend-L emitted 1.8%, and blend-H only 0.8%.

Reduced N₂O emissions from the blend-H treatment could be caused by direct physiochemical biochar-induced inhibition of one of the nitrification-denitrification steps. At a certain threshold, compounds from biochar could potentially become microbial toxic (Clough *et al.*, 2010). However, inhibition of the nitrification process, as suggested by Clough *et al.* (2010), may explain the smaller N₂O emission in blend-H treatments compared with blend-L treatments, since no NH₄⁺ accumulation was observed in the 3% biochar treatments (Figure 4b).

Reduced N₂O emissions after biochar and slurry amendment could also be caused by biochar-soil interactions indirectly affecting the major denitrification controllers (oxygen, NO₃⁻ and soil organic C) caused by changes in soil water retention capacities, microbial biomass or nutrient levels for example. The addition of labile C and N with the biochar and slurry application caused a rapid increase in the SMB-C pool. At day 10, the blend-H soil had more than three times its microbial biomass relative to day 1 (Figure 3b). Such rapid biomass increase may have resulted in further depletion of the oxygen content in the already poorly oxygenated soils (80% WFPS). In contrast, the blend-L soil had a considerably smaller SMB-C pool at day 10 and thus probably had less anoxic conditions. As anoxic conditions favour reduction of N₂O to N₂ (Firestone & Davidson 1989; Nguyen and Lehmann 2009), a difference in O₂ levels could explain the smaller net N₂O emission from the blend-H treatment relative to that in the blend-L treatment.

The rapid initial increase in the microbial population in blend-H along with the concurrent decreases in the NO₃⁻ concentrations (Figure 4a and 3a) may be an indicator for N

immobilization, so that NO_3^- may have become a limiting factor for denitrification. In the blend-L soil, however, the smaller SMB-C pool (day 10) compared with that in the blend-H soil and a more than double NO_3^- concentration at day 10, suggested that substrate availability was sufficient.

Increases in soil pH values after addition of biochars have also been hypothesized to cause N_2O reductions by decreasing the $\text{N}_2\text{O}:\text{N}_2$ emission ratio (van Zwieten *et al.*, 2009). However, in the present experiment, the pH measured on day 1 and 3 in blend-H and biochar-H (the period where almost all N_2O emissions occurred), was not different from that in the other treatments (Figure 5). Changes in pH are therefore unlikely to explain the smaller N_2O emission rate of the blend-H.

Biochar and slurry incorporation in agricultural soils

Immobilization of N typically occurs rapidly after incorporation of organic residues with large C:N ratios (Ambus *et al.*, 2001; Bengtsson *et al.*, 2003; Craine *et al.*, 2007). The present study clearly demonstrated that biochar application can cause short-term immobilization of N (Kolb *et al.*, 2009; Lehmann *et al.*, 2003; Novak *et al.*, 2010). As a consequence, application of biochar may have short-term detrimental effects on crop growth if applied during the initial growth period to soils with a small mineral N content. A reduced N uptake in rice plants after the application of biochar without additional N fertilizer has been observed (Asai *et al.*, 2009). An immobilization of N can be avoided by applying a balanced slurry-biochar blend as demonstrated in the present study, where the biochar-L treatment immobilized N relative to the control soil, while the blend-L treatment did not.

In contrast, application of N-rich slurry alone may lead to leaching of slurry N if applied in excess to crop demands or in fallow periods. This is especially a problem during high rainfall periods and in C-limited soils, where microbes are incapable of assimilating the extra N (Saenger *et al.*, 2010). Nitrogen leaching could be reduced by blending slurry with a larger proportion of C-rich biochar. This could increase N immobilization (as observed in the blend-H treatment; Figure 4a) and potentially preserve more N in soil during times where crop demand is absent or minimal. The possibility of blending N-rich AD slurry with different proportions of biochar could be used by farmers as a management tool for improving the retention of N fertilizer in the topsoil. However, depending on the pyrolysis technology and conditions, biochar may not contain labile C, for example if produced at high temperatures by slow pyrolysis, and will therefore probably have less impact on the short-term N dynamics in soil than the fast pyrolysis biochar used in our study.

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Biochar mobility and effects on nitrogen leaching in repacked sandy soil

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Abstract

Biochar amendment to soil may cause translocation of dissolved carbon to subsoil layers depending of the physicochemical properties. Fine clay-sized biochar particles may disperse in the soil solution and potentially facilitate the leaching of adsorbed nutrients from the topsoil by colloidal biochar facilitated transport. The present leaching experiment investigated fine grained biochars effect on the retention of N (applied as ammonium, NH_4^+) using repacked sandy soil columns with and without biochar applied in the top layer (2 wt%). Three biochar types (with wheat straw as feedstock) were used in the experiment: one produced by slow pyrolysis and two produced by fast pyrolysis at 525 and 550 °C, respectively. Results showed, contrary to our expectations, that the cumulated NH_4^+ -N leached increased with biochar application (28-31 % of initial N in the top layer) relative to the unamended Control soil (21 % of initial N in the top layer). The overall N retention (NH_4^+ plus NO_3^-) was not improved by the application of biochar, and was even increased by the application of slow pyrolysis biochar. Our study moreover revealed a high mobility of labile C components originating from the fine grained fast pyrolysis biochar. The mobility of organic C from FP-biochar highlights the risk of leaching of contaminants originating from the biochar and other substances adsorbed to the biochar. By contrast, C components from slow pyrolysis biochar were retained in the topsoil.

Key words: Wheat straw charcoal, Nitrogen leaching, Biochar carbon leaching, Bromide tracer, Biochar particle transport

Introduction

Intensive use of fertilizers on agricultural lands and subsequent leaching of nitrogen (N) is a major contributor to the eutrophication of surface and groundwaters (Camargo and Alonso, 2006). In addition, nitrogen leaching implies economic impacts by limiting the fertilizer-use efficiency in crop producing systems, and it may consequently contribute to climate change by raising the demands for fossil fuel based fertilizers. In order to address these problems,

techniques and agricultural practices must be developed that preserve N in the top-soil. One promising option that in recent years has received increased attention is the application of recalcitrant biochar to agricultural soils. Biochar, produced through thermal decomposition (400 °C to 600 °C) of biomass in the absence of oxygen (pyrolysis), may when added to soil enhance soil quality and mitigate climate change through long-term carbon sequestration (Atkinson et al., 2010; Lehmann et al., 2006; Lehmann, 2007; Sohi et al., 2010).

The ability of biochar to retain nitrogen (and other nutrients) has been documented in a number of studies and is considered a key characteristic for the improvement of soil fertility. Retention of nitrogen in biochar amended soil has e.g. been shown in lysimeter experiments (Ding et al., 2010; Lehmann et al., 2003), in adsorption experiments where ammonium readily was adsorbed to biochar (Ding et al., 2010; Duenisch et al., 2007) and in field trials using weathered biochar (Steiner et al., 2008). Furthermore, the cation exchange capacity (CEC) of soils has been shown to increase after application of biochar (Liang et al., 2006; Van Zwieten et al., 2010). The nutrient retention capability of biochar is attributed to its (often) great surface area providing adsorption sites for inorganic nutrients, and to its great porosity composed of both micro- and macropores, which may absorb nutrient-carrying soil solution. The attachment to immobile biochar of organic matter or minerals with sorbed nutrients may further increase the nutrient retention. The surface area and porosity of biochar varies to a great extent depending on pyrolysis conditions, the feedstock used, and ageing processes in soil (Verheijen et al., 2010). Biochar's surface area is governed mainly by the pyrolysis process temperature, and is correlated to the relative content of micropores (nm-scale) (Downie et al. 2009; Sohi et al. 2010), while the porosity to a large degree is determined by the structure of the original plant materials retained in the biochar (Verheijen et al., 2010).

Biochar's nutrient retention potential is affected by the biochar particle sizes. Smaller particles have a greater surface volume ratio than larger particles and thus in general a larger capacity to hold nutrients. However, fine biochar particles may also be transported downwards in the soil with the water movement (Leifeld et al., 2007; Major et al., 2010). Very fine biochar particles will most likely be present in the biochar material after pyrolysis, especially if small sized feedstock particles are used as in e.g. fast pyrolysis processes (Laird et al., 2009). Biochar handling, soil application, and weathering processes in soil furthermore results in smaller biochar particle sizes over time. It is therefore likely that fine (clay-sized) biochar particles may be dispersed in the soil solution and is transported downwards in the soil by water. Such fine biochar particles may potentially also facilitate the colloidal transport of nutrients out of the topsoil.

Pore size distribution, pore continuity and water-filled porosity of the soil are critical for nutrient leaching and mobility of fine particles. Processes counteracting the transport of particles with a moving water phase comprise adsorption, sedimentation and sieving (e.g. Laegdsmand et al. 1999). Such processes are most pronounced in relatively small pores. Near saturated water transport in coarse textured (sandy) soil layers or structural heterogeneity, in particular the presence and activation of continuous macropores (e.g. Petersen et al., 2004), may therefore enhance the mobility of soil particles.

The objectives of the present study were (i) to investigate effects of adding fine biochar particles to a sandy soil on nitrogen leaching under wet soil conditions following the application of N-fertilizer, and (ii) to investigate the downward movement of biochar components (dissolved and particulate) in a sandy subsoil. The study was conducted under laboratory conditions.

Materials and methods

Biochar, soil and sand

The biochars used in the soil column experiment consisted of one slow pyrolysis (SP) biochar and two fast pyrolysis (FP) biochars. The pyrolysis feedstock was wheat straw with a moisture content of 6.2 wt%, an ash content of 5.9 wt%, and a feedstock particle size below 1.4 mm. The SP-biochar was produced in a nitrogen flushed electrically heated oven with a heating rate of 6 °C min⁻¹, constant nitrogen gas sweep, a total solids residence time of 2 hours, and a max temperature of 525 °C (Egsgaard, et al., 2005). The two FP-biochars were produced in a Pyrolysis Centrifuge Reactor (PCR) at reactor temperatures of 525 and 550 °C, respectively (for details: see Bruun et al., 2011). All three biochars were hydrophobic (created micelles on water surfaces), and in particular the two FP-biochars, was characterized by a relative large labile carbon fraction and small particle sizes (Table 1).

Table 1. Parameters of the biochars, soil (top layer), and sand (bottom layer) (SP525, FP525 and FP550) used in the experiment.

Parameters		Biochar			Top layer	Bottom layer
		SP525	FP525	FP550		
C	g kg ⁻¹	696	493	496	16	0
N	g kg ⁻¹	15	12	11	1.6	0
H	g kg ⁻¹	21	37	29	2	0
O ^a	g kg ⁻¹	9	23	22	-	0
Phenolic groups	mmol g ⁻¹	0.61	0.72	0.99	0.00	-
Carboxylic groups	mmol g ⁻¹	0.48	0.90	0.96	0.05	-
Total acidic functional groups	mmol g ⁻¹	1.08	1.61	1.95	0.06	-
Extractable organic C (DOC)	g kg ⁻¹	0.43	9.10	2.16	0.09	0.05
Extractable NH ₄ -N	g kg ⁻¹	27.8	40.2	27.2	0.01	0
Extractable NO ₃ -N	g kg ⁻¹	0.009	0.065	0.013	0.044	0
pH (1:10 H ₂ O)	-	10.1	6.8	7.1	7.0	-
Ash fraction ^b	%	19.8	21.6	26.4	-	-
Carbohydrates ^b	%	0	8.8	5.7	-	-
Surface area (BET) ^b	m ² g ⁻¹	0.6	1.6	2.4	4.2	-
Average particle size	µm	113	23	12	-	175

a: The oxygen concentration was determined by difference from contents of C, N, H and ash.

b: Biochar BET area (n=2), biochar ash fraction and biochar carbohydrate content are based on Bruun et al. (2011b).

The sandy loam soil used as top layer in the laboratory experiment was collected from the plow layer in an agricultural field at Risø-DTU (55°41'N, 12° 05'E). The soil was classified as a Typic Hapludalf with 11 % clay, 14 % silt (2-20 µm), 49 % fine sand (20-200 µm), and 25 % coarse sand (200-2000 µm). The soil was air-dried, passed through a 2-mm sieve, mixed to get a homogeneous bulk sample, and subsequently stored at 2 °C. Prior to experimental start-up the soil was rewetted and acclimated to room temperature for one week. The hydrophilic sand used as the bottom layer in the experiment contained no nitrogen and very low amounts of carbon. It had a relatively narrow particle size distribution with diameters below 0.3 mm, and a repacked bulk density of 1.40 g cm⁻³. Chemical and physical characteristics of the soil layers and biochars are listed in Table 1 and Figure 1 shows the particle size distributions.

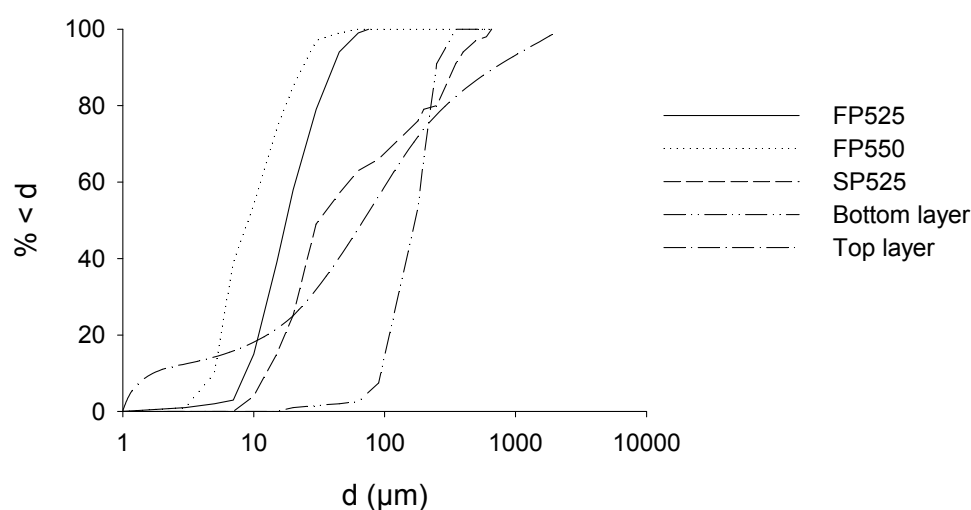


Figure 1. Particle size distribution of the three biochar types, bottom layer (sand), and top layer (sandy loam) used in the experiment.

Experimental design and irrigation system

The experiment was conducted using fifteen aluminium columns with repacked sand, soil, and biochar (2 wt%) and included the following five treatments done in triplicates:

- 300 g topsoil ('Control soil'),
- 300 g topsoil + 6.00 g slow pyrolysis biochar ('SP525'),
- 300 g topsoil + 6.00 g fast pyrolysis biochar produced at 525 °C ('FP525'),
- 300 g topsoil + 6.00 g fast pyrolysis biochar produced at 550 °C ('FP550'),
- 2.00 g fast pyrolysis biochar produced at 550 °C exclusive soil ('FP550xs').

Each soil column was packed with a 48 cm thick bottom layer of the sand representing a sandy 'subsoil', a relatively thin (3 cm) top layer of the sandy loam soil with and without

biochar amendment, and a water distribution layer on top (see schematic diagram, Fig. 2). The bottom layer of the columns was packed and tamped in one centimetre increments. Before application of the top layer, the bottom layer in each column was irrigated to reach steady state conditions (influent = effluent), after which irrigation was stopped and the sand was allowed to drain. Then the top layer (\pm biochar) was carefully added and irrigation water (21.4 mL) was dispersed uniformly on the soil surface to reach a water content of app. 30 % corresponding to its water holding capacity, WHC at 50 cm drainage ($pF=1.7$). The applied irrigation water (21.4 mL) contained ammonium chloride as N fertilizer ($106 \text{ mg column}^{-1}$ equivalent to 300 kg N ha^{-1}) and potassium bromide for water movement tracing ($21.4 \text{ mg column}^{-1}$). Immediately following the initial irrigation, fully moist sand ‘distribution layers’ (5.0 cm) were added to each column to promote homogeneous dispersion of irrigation water to the top layer soil (Fig. 2). Hereafter the column irrigation (and experiment) was initiated.

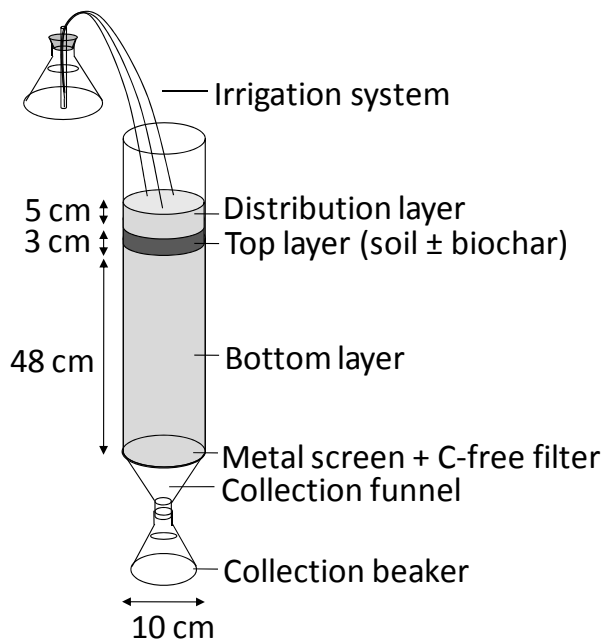


Figure 2. Schematic diagram of the experimental design.

The irrigation system was constructed as a Mariotte device delivering a relatively constant flow rate ($36 \text{ mm d}^{-1} \pm 3.1 \text{ mm d}^{-1}$) on three separate locations on the surface of each column via three identical plastic tubes with adjusted hydraulic resistance (Fig. 1). All applied irrigation water contained CaCl_2 (10 mM) in order to protect soil structure in the sandy loam. The water-filled pore volume (WFPV) for each column was calculated by adding the volume of water retained in the sand to the water volume retained in the top soil (if any). Influent to and effluent from the columns were determined on a daily basis yielding both amounts and rates. Extra effluent samples were taken on Day 3, 4, and 5 in order to measure more detailed on the second pore volume breakthrough. The effluent samples were stored in a freezer ($-15 \text{ }^\circ\text{C}$) for later analyses. The experiment took place at room temperature ($18\text{-}22 \text{ }^\circ\text{C}$).

A metal screen with a carbon-free filter (Whatman, quartz microfiber filters, QMA) was placed at the bottom of the column. The ‘Particle Retention in Liquid (μm)’ cut-off of the

filters was 2.2 μm (<http://www.whatman.com/AirSamplingandQuartzFilters.aspx>). After the experiment, different depth increments of the bottom layer were analysed for total C, and the filters were carefully inspected for visual traces of biochar particles in order to investigate, if transport of biochar particles had occurred.

Chemical and physical analysis

Prior to experimental start, the soil was analysed for nitrate, ammonium, and dissolved organic carbon (DOC). Five g of soil was extracted with 10 mM CaCl_2 (1:5), filtered through a Whatman no. 42 and shaken on a reciprocal shaker for one hour. The filtrated effluent water samples from the columns (containing 10 mM CaCl_2) were likewise analysed for nitrate, ammonium, and DOC. The Nitrogen content was measured on an AutoAnalyzer 3 (AA3 Bran and Luebbe), while carbon was measured on a TOC-VCPH (Shimadzu). Total C and N content of bottom layers was measured on air dried sand samples after the experiment. The columns were carefully disassembled and the bottom layer sand were separated in the layers 0.5-1 cm, 1-3 cm, 3-5 cm, 5-10 cm, 10-28 cm, and 28-48 cm, and stored in a freezer for later C analyses. Each layer was homogeneously mixed in order to get representative samples, and approx. 5 g of soil materials was finely grounded on a mill. Next, three 40 mg subsamples from each pool was packed in combustion tin capsules and analysed on an EAMS elemental analyzer (EAMS EA 1110 CHN CE instruments).

A bromide electrode and a Methrom 713 pH meter were used to measure bromide concentration in the effluent. The particle size distribution of sand (data provided by the company) and of biochars (determined by optical microscopy) is shown in Fig. 2 and Table 1. Considerably smaller biochar particles likely existed but were invisible in the optical microscope. Surface areas were determined by the Brunauer, Emmett and Teller (BET) method using a Micromeritics (Gemini 2375, V4.01) surface area analyzer (see Bruun et al., 2011b).

Carboxylic and phenolic groups on the biochar surface were determined by titration according to (Strobel et al., 2001). Each sample (0.100 g) was accurately weighed and equilibrated for 48 hrs with 20 ml of 0.1 M KNO_3 in 50-ml conical flasks. Afterwards 10 ml 0.01 M NaOH was added and the mixture was titrated with 0.01 M HCl until pH 3 was reached.

Statistics

Trends of N and C concentrations in the leachate over time were analysed by repeated measures ANOVA using STATISTICA software (Statsoft Inc., 2010). In order to compare leachate N and C concentrations between treatments, the time of sampling (hours) was used in the ANOVA assuming similar water flow in all columns. For treatment comparisons on single days ANOVA one-way test were performed and multiple mean comparisons were carried out using Tukey's Honest Significant Difference (HSD) test. Any differences between the mean values were considered significant if $P < 0.05$.

Results

Biochars surface characteristics

The elemental analysis showed that FP-biochars contained more O and H than the SP-biochar, implying that the FP-biochars possessed more oxygen containing functional groups (Table 1). In accordance with this, acid titration showed more carboxylic and phenolic groups in the FP-biochars with the greatest content in the high temperature biochar FP550 (Table 1). The FP-biochars thus had slightly higher surface acidities than the SP-biochar. The specific surface areas (m^2g^{-1}) of the three biochar types were all very small. The increase in pyrolysis reactor temperature from 525 to 550 °C only increased the specific surface area slightly, i.e. from 1.6 to 2.4 m^2g^{-1} (Table 1).

Bromide transport

The drainage rate averaged for all determinations across all columns was $1.6 \pm 0.13 \text{ mm h}^{-1}$, and the total drainage per column was $431 \pm 43 \text{ mm}$ during the 14 days experiment. The bromide tracer in the effluent showed similar outflow rates in all columns with breakthroughs at an amount of drainage corresponding to 0.56-0.68 WFPV (effluent sampling hour 68) (Fig. 3a). In all columns peak concentrations of bromide were found at WFPV's in the range 0.80-0.88 (hour 90-99). The FP550xs without top layer had a steeper increase of the bromide concentration, a faster decreasing tail, and a bromide peak value 25 % higher than the other treatments. The cumulated bromide in the effluent corresponded to 87-95 % of the added bromide, which indicates that the top layer was almost completely infiltrated (Fig. 3d). The 5-13 % which could not be accounted for, could have been assimilated by microorganisms or held in dead organic matter.

Nitrogen concentration in leachate

The temporal changes of the $\text{NH}_4^+\text{-N}$ concentration in the leachate of the soil columns is shown in Fig. 3b. Only treatment FP550xs had a significantly different breakthrough curve compared to the other treatments. The FP550xs peaked rapidly at about one WFPV (1.04 WFPV; Day 4.5) with a peak concentration value of 34.1 mg L^{-1} , while the other biochar treatments peaked considerably later (1.40-1.43 WFPVs; Day 6.8) and with lower peak values ranging from 17.6 to 20.5 $\text{mg L}^{-1} \text{ NH}_4^+\text{-N}$. The Control treatment had the lowest average peak concentration value (14.2 mg L^{-1}) with the latest appearance (1.63 WFPVs; Day 7.9). The Control treatment tended to be different from the FP525, FP550 and SP525 at 1.43 WFPV (Day 6.8) with *P* values of 0.10, 0.058 and 0.11 respectively. At 1.28 WFPV (Day 6.1) the Control treatment tended to be different from FP525 with a *P* value of 0.054.

Nitrate breakthroughs and peak concentrations in the leachate appeared earlier than the observed ammonium peaks (Fig. 3b and c). Under the Control treatment the observed peak of $\text{NO}_3^-\text{-N}$ appeared at 0.95 WFPV (Day 4.5) with a maximum level of 35.1 mg L^{-1} . All biochar-soil treatments (FP525, FP550, and SP525) had breakthroughs concurrently with the bromide and peaked at 0.77-0.85 WFPVs at a concentration of app. $21 \text{ mg L}^{-1} \text{ NO}_3^-\text{-N}$. Thereafter the concentration decreased gradually for all treatments to below 1.7 mg L^{-1} at the

end of the experiment. The notable NO_3^- -N leachate peak of the Control soil was significantly higher than the other treatments, except for the SP525 ($P=0.079$).

Figure 4c and 4d show the cumulated effluent NH_4^+ -N and NO_3^- -N content in percent of the top-layers added fertilizer-N plus amount of initially extractable mineral N, during the 14 days infiltration experiment. The increase of NH_4^+ -N took place at a very fast rate under the pure biochar treatment (FP525xs) with a cumulative leaching of 73 % NH_4^+ -N over time. Significantly less NH_4^+ -N were leached from the biochar amended top layers (SP525, FP525, FP550) corresponding to 28-31 % of total mineral N. The lowest leached amount of NH_4^+ -N (21 %) was observed in the Control soil. The relative cumulative leaching losses of NO_3^- -N were inversely related to the ammonium leaching. The Control soil and SP525 showed the highest leached percentage (50 and 52 %, respectively) of the total soil mineral N, while FP525xs only lost a small amount (5 %). The fast pyrolysis biochars FP525 and FP550 leached 38 % and 43 % NO_3^- -N respectively.

The cumulated leaching of mineral N (NO_3^- -N + NH_4^+ -N) relative to the initial total mineral N amount in the top-layer is shown in Figure 5. The SP525 amended soil had a significantly greater leaching (79 %) than both the Control soil (71 %) and the FP525 amended soil (68 %). Also the FP550xs (78 %) had a higher leaching percentage of applied N than the FP525. None of the biochar treated soils showed less cumulative leaching than the Control soil.

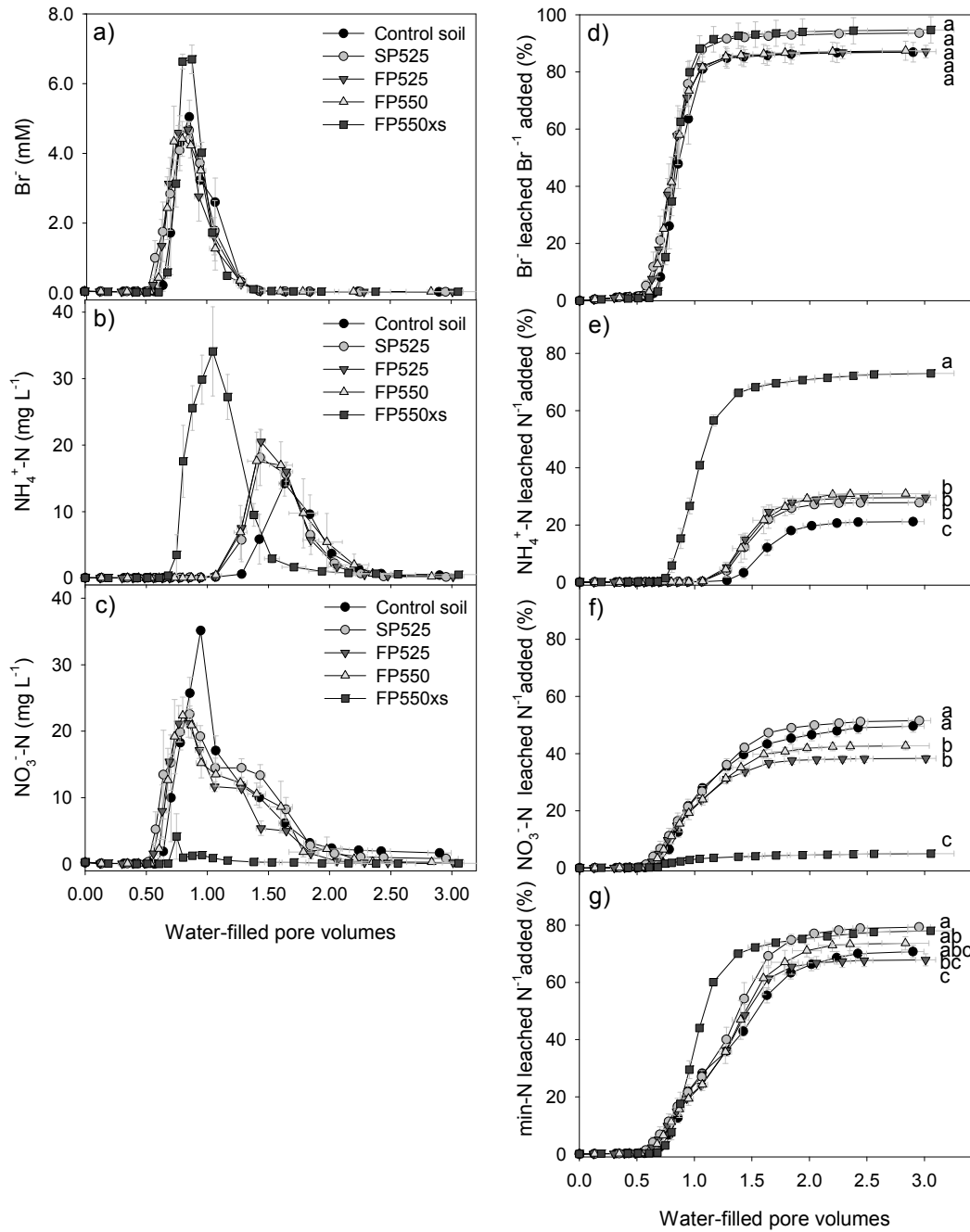


Figure 3. a) Average effluent water-filled pore volumes for each treatment as a function of the average bromide tracer effluent measurement (mM). b) Average effluent $\text{NH}_4\text{-N}$, and c) $\text{NO}_3\text{-N}$ for the five treatments measured during the 14 days infiltration experiment. d-g) shows cumulated effluent of Br^- , $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and total mineral N ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$) content, respectively, in percent of added bromide (d), and fertilizer-N plus topsoil's extractable mineral-N (e-f) (treatment FP550xs is in percent of added fertilizer-N only, due to lack of soil). Letters denotes significant differences day fifteen according to Tukey's test. All values are shown as mean \pm standard error (n=3).

Carbon content in effluent and bottom layer

The columns with fast pyrolysis biochar had notable carbon concentration peaks in the leachate. The concentrations increased steeply from WFPV= 0.6-0.7 (Fig. 4a). Hence, the break-through times were close to those found for bromide. The highest average peak value on 35 mg L^{-1} was observed in the treatment with FP525, while the FP550 had a peak value of 21 mg L^{-1} . From the breakthroughs till the end of the study, the DOC concentrations in the FP525 and FP550 stayed higher than in the other treatments. The treatment with biochar only (FP550xs) had two lower peak values, which were due to one replicate having an early very high peak value (18 mg L^{-1} , 0.75 WFPV), while the two other replicates peaked somewhat later (0.86 and 0.96 WFPV, respectively). In the treatments with FP-biochars the appearance of the leachate changed from clear to a light yellow-brownish colour concurrently with the DOC breakthroughs. The DOC concentration in the leachate of the SP525 matched the concentration of the Control soil closely, and both had low peaks concurrently with the other treatments (Fig. 4b). Moreover, the initially higher but rapidly decreasing C concentration in the leachate revealed that the bottom layer of the columns were not fully carbon free at the start of the experiments.

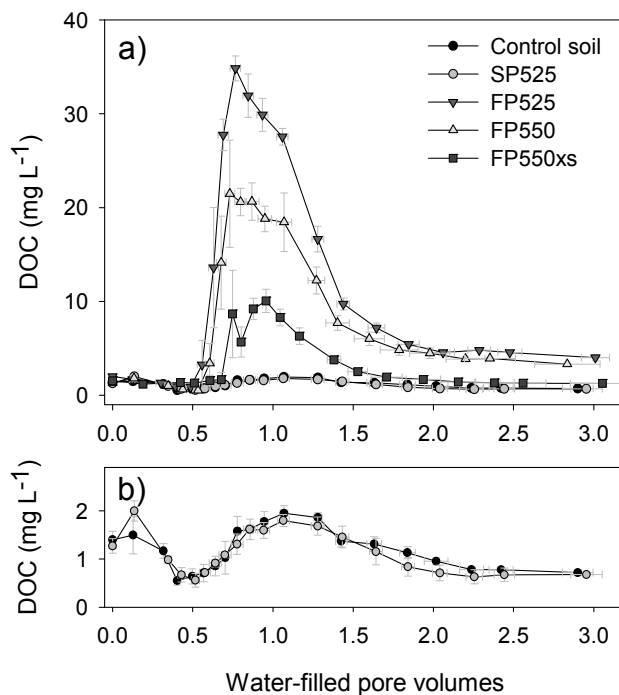


Figure 4. a) The five treatments cumulated effluent DOC concentration. b) Magnification of Fig. 4A showing the close match between the SP525 and the Control soil. All values are shown as mean \pm standard error (n=3).

In order to account for a potential biochar particle transport, the total C content was measured after the experiment in different depth intervals of the bottom layer (Fig. 5). There were no significant differences between the Control soil and the different treatments, except

for the fine FP550 biochar which had slightly higher C-content at 1-3 cm's depth. There was virtually no nitrogen in the bottom layer (< 0.002 %) after the experiment.

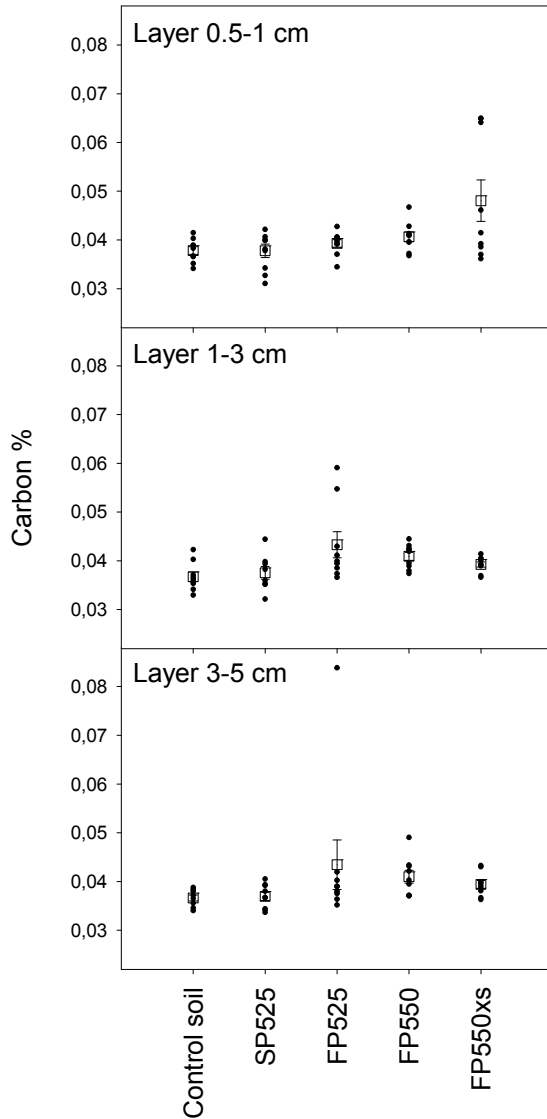


Figure 5. Replicate C values of the upper bottom layer layers (0.5-1, 1-3, 3-5 cm) in the different treatments. Open squares are the mean (n=9) ± standard error.

Discussion

The infiltration of water

The water movement was expected to peak around one WFPV due to the homogeneously packed sand bottom layer. However, somewhat earlier peaks of the bromide tracer (0.80-0.88 WFPVs) were observed in all columns indicating preferential flow, most likely along the sides of the columns (Fig. 3a). Macropore transport is not likely in these repacked sandy

columns, which is also supported by the fact that no black biochar particles were visible on the filters below the bottom layer after the experiment. Nevertheless, it was evident e.g. from the bromide tracer curves and the water budget that the columns had similar water movement and that biochar thus apparently did not affect the flow of water. Biochar have in previous studies been shown to increase water retention in sandy soils and sand mixtures (Brockhoff et al., 2010), but also to decrease moisture content in clayey soils (Verheijen et al., 2010). Yet, expected effects of biochar on the water retention in the present experiment would probably not be manifested, due to the columns very thin top layer (3 cm) with only 2 wt% biochar relative to the thick bottom layer (45 cm).

Effect of biochar on the nitrogen concentration in leachate

In the treatment with biochar only (FP550xs), barely any transformation of the fertilizer ammonium took place during drainage (Fig. 3b). The obvious reason for this was the lack of a well colonised top layer soil to affect the NH_4^+ solution by physicochemical and biological processes. Moreover only limited retention of NH_4^+ by the biochar seemed to take place, as the NH_4^+ breakthrough was observed only few hours later than the breakthrough of bromide and because no NH_4^+ ‘peak tailing’ was observed (Fig. 3b). However, only 78 % of the applied fertilizer N was accounted for in the leachate under FP550xs (Fig. 3g) indicating that some N was adsorbed to biochar particles. Loss of gaseous N via nitrification and denitrification might also occur in FP550xs, as a small NO_3^- peak revealed that nitrification took place despite the lack of top layer (Fig. 3c).

In the Control and biochar amended soils a substantial part of the applied fertilizer ammonium was nitrified rapidly, as shown by the NO_3^- breakthrough curves emerging concurrently with the FP525xs’s NH_4^+ breakthrough (Fig. 3b,c). Relative to the Control, the biochar amended soils had lower leachate NO_3^- peak concentrations. As most of the surface charges on biochars are due to negatively charged carboxylic and phenolic groups, biochar may retain NH_4^+ , but not the anionic NO_3^- (Cheng et al., 2006; Laird et al., 2010). Adsorption of NO_3^- to biochar surfaces can therefore not explain the lower NO_3^- peak concentrations. However, NH_4^+ adsorption might have limited the substrate availability for the nitrifying community and thereby reduced the nitrification. Yet, the lower leachate peaks of NO_3^- in the biochar-soil treatments should probably be explained predominantly by microbial immobilization of nitrogen. As N immobilization is coupled to the quantity of C readily available for microbial assimilation, the application of fresh C-rich biochar with high C/N ratios likely caused short-term N immobilization in the top layer and thus reduced the leaching of NO_3^- .

Moreover, the much higher content of DOC and carbohydrates in the FP-biochars relative to the SP525 biochar (Table 1) probably prolonged the period of N immobilization for these treatments, as also indicated by the lower cumulative NO_3^- leaching from the FP525 and FP550 soils relative to the SP525 and Control soils (Fig. 3f). In an incubation study, using the same biochar and soil batch as the present, Bruun et al., 2011b showed considerable N immobilization in the FP525 biochar soil, and to a lesser degree in the SP525 biochar, when compared to the control soil at Day 14. Inhibition of the nitrification process by microbial toxic biochar substances, as discussed by Deluca et al., 2006, could also explain lower production of NO_3^- . An inhibition, though, would likely occur from the very beginning of the

experiment and thus we would expect NH_4^+ in the leachate concurrently with (or a little later than) the bromide breakthrough.

The several hours later breakthrough of the NH_4^+ relative to the breakthroughs of bromide, nitrate, and DOC in the biochar amended soils and the Control soil was probably due to nitrification of the early 'front' of NH_4^+ percolating down through the top layer, which thereby delayed the NH_4^+ breakthroughs. However, the earlier breakthrough and greater leaching of NH_4^+ in the biochar-soils compared to the Control soil is intriguing (Fig. 3b,e). As mentioned in the introduction biochar has been shown to retain ammonium, but in the present study biochar seemed to increase and speed up the leaching of NH_4^+ relatively to the Control soil. The reason for this was not clear. We consider a potential promotion of preferential flow by the biochar application for unlikely to explain the faster breakthroughs. The lack of more tailing combined with very similar DOC curves of the Control and SP525 (Fig. 4b), as well as the bromide study, strongly support similar flow patterns in the Control and the biochar amended treatments.

It is possible that exposed and (presumably) ion-free biochar surfaces more rapidly adsorbed applied fertilizer ammonium than native soil organic matter and clay minerals, but subsequently also released it faster again, when Ca^{2+} from the irrigation exchanged sites with NH_4^+ . By contrast the soil organic matter might bind NH_4^+ more strongly, due to more complex molecular structures, or NH_4^+ is more biologically available at the fresh biochar surface sites.

It is also possible that a greater microbial respiration in the biochar amended soils (due to the added biochar pool of easy-degradable carbohydrates) caused oxygen depletion in microsites, which in turn reduced the nitrification and consequently resulted in an earlier and greater leaching of NH_4^+ .

The small particle sizes and hydrophobic nature of the biochar could also potentially facilitate a faster transport of cat-ions sorbed on biochar with the percolating water. Although the QMA filter prevents leaching of biochar particles above 2.2 μm from entering the collection beaker, smaller (negatively charged) biochar constituents or molecules would readily pass. However, if such a transport occurred we would expect to see NH_4^+ in leachate concurrently with DOC breakthroughs, which we did not (Fig. 3b and 4a). We therefore consider colloidal transport of NH_4^+ with biochar for unlikely in the present study.

All in all, application of biochar caused no extra retention of the mineral N or delay in the N leaching relative to the Control soil (Fig. 3g). The relatively low amount of biochar applied (2 wt%) could probably blur potential biochar effects on the N retention. However, the SP525 biochar even increased the leaching of N (in the form of more NH_4^+) within the investigated time span. The reason for the different retentions of the biochars was not clear, but the much lower content of labile C of the SP525 relative to the FP-biochars probably played a key-role. As discussed above the labile fraction of the FP-biochars may have caused oxygen depletion due to increased respiration and furthermore caused microbial immobilization of N, thereby resulting in lower nitrification rates in these treatments relative to the Control soil and SP-biochar soil.

The above results, together with the low surface area, suggest that the fresh biochars used in the present study probably were not suitable as soil conditioners, if immediate N retention in

the topsoil was an important priority. However, the repacked column study was performed with high infiltration rates, and extrapolations to field conditions should therefore be made with great caution.

Effect of biochar on the Carbon concentration in leachate

The different pyrolysis methods used to produce the biochars highly influence the leached amount of C (Fig. 4a). Analyses revealed considerably amounts of DOC in the leachate from the FP-biochar treatments, which increased with increasing amounts of extractable C content in the biochar (Table 1).

The SP525 with no leaching generally consists of larger particle than the FP biochars. Hence, it is possible that transport of colloids from this product was completely prevented by pore size exclusion, contrary to transport of some minor colloid particles from the FP products. Size exclusion effects may further give rise to acceleration of mobile organic colloids from the FP's and hence explain the relatively fast break-through observed in columns with these products (e.g. Sirivithayapakorn and Keller, 2003). The lower peak concentration of the FP550xs relative to the FP550 amended soil was due to the lower amount of biochar applied initially (2.00 g vs. 6.00 g). The DOC originated almost exclusively from the labile carbon contained in these biochars as shown by the much lower DOC content in the leachate from the Control soil. Moreover, the DOC pool was shown to be highly mobile since breakthroughs and peaks were similar to the bromide tracer (Fig. 3a). By contrast, only a small peak was observed in the leachate from the SP525 treatment being almost identical to the Control soil (Fig. 4b). Hence, most of the traces of DOC observed in leachate from the SP525 treatment most likely originated from the original topsoil.

From the above it is evident that labile C pools from the FP-biochars made on PCR equipment readily leach to deeper soil layers and perhaps groundwater levels in sandy subsoils. This underscores the importance of knowing the chemical composition of these labile components, which potentially could include contaminants such as heavy metals, PAHs and dioxins (Verheijen et al., 2010). Moreover this labile C pool may facilitate the transport of nutrients attached to biochar components out of the top-soil, as hypothesized. Such a facilitated transport could explain higher loss of $\text{NH}_4^+\text{-N}$ in the FP-biochars (FP525, FP550, and FP550xs), however as discussed above, due to the lack of NH_4^+ in the leachate concurrently with DOC breakthroughs we consider this for unlikely. Movement of biochar particles within the soil could not be concluded on basis of the total C analysis of sections in the bottom layer after the experiment, as all measured C levels were very low and not different from the C content of the pure sand (Table 1, Fig. 5). However, there was a tendency of slightly higher C contents in the upper 5 cm of the treatments with the FP biochars relative to the Control soil (Fig. 5). With more water passing through the column (in the long run), this could potentially constitute a minor risk of biochar particles translocation.

Conclusion

The overall N retention was not improved by the application of biochar produced from wheat straw, and was even increased by the application of slow pyrolysis biochar. The reason for this was not clear, but low adsorption capacity of the biochars used is part of the explanation. Furthermore, our study demonstrated a high mobility of labile C components (DOC)

originating from the fine grained fast pyrolysis biochar. The mobility of DOC from FP-biochar highlights the risk of leaching of contaminants originating from the biochar and of other contaminant (or nutrients) adsorbed to the biochar. By contrast, all components from slow pyrolysis biochar (made on the same feedstock batch as the FP-biochars) were retained in the topsoil. This illustrates the great influence of the pyrolysis type and settings used for the resulting biochars properties. It is crucial to get a better understanding of the mobility of all components of the biochar before large-scale field applications of the products in agriculture should be recommended.

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