CHALLENGING THE CLAIMS ON THE POTENTIAL OF BIOCHAR TO MITIGATE CLIMATE CHANGE | TERRA PRETA PROGRAM Tatiana Francischinelli Rittl

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TERRA PRETA PROGRAM

Tatiana Francischinelli Rittl

INVITATION

YOU ARE CORDIALLY INVITED TO
ATTEND THE PUBLIC DEFENSE
OF MY PHD THESIS ENTITLED:

CHALLENGING THE CLAIMS ON
THE POTENTIAL OF BIOCHAR TO
MITIGATE CLIMATE CHANGE

ON WEDNESDAY JULY 1ST 2015
AT 11:00 IN THE AULA OF
WAGENINGEN UNIVERSITY,
GENERAAL FOULKESWEG 1A,
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Challenging the claims on the potential of biochar to mitigate climate change

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This research was conducted under the auspices of the C.T. de Wit Graduate School for Production Ecology and Resource Conservation

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Thesis
submitted in fulfilment of the requirements for the degree of doctor
at Wageningen University
by the authority of the Academic Board,
in the presence of the
Thesis Committee appointed by the Academic Board
to be defended in public
on Wednesday 1 July 2015
at 11 a.m. in the Aula.

T.F. Rittl
Challenging the claims on the potential of biochar to mitigate climate change
145 pages.

PhD thesis, Wageningen University, Wageningen, NL (2015)
With references, with summaries in English and Dutch

ISBN: 978-94-6257325-3

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Chapter 1

General Introduction

Tatiana F. Rittl

1.1 Introduction

The aim of this thesis is to evaluate the potential of biochar for carbon (C) sequestration in soils, and to describe the policy arrangement related to it in Brazil. Biochar is the charcoal deliberately produced and applied to the soil. The intentional production and application of biochar in soil differs it from other carbonized materials, such as pyrogenic organic materials, charcoal and pyrogenic carbon. Essentially, biochar, charcoal, pyrogenic organic materials and pyrogenic carbon refer to the material derived from incomplete biomass combustion. The general idea of biochar drew its inspiration from Amazonian practices that led to the creation of Amazonian Dark Earth (ADE; also known as *Terra Preta de Índio*), fertile soils rich in soil organic carbon (SOC) and millennial charcoal. Inspired by the charcoal found in ADE, the current production of biochar and its addition into soil is claimed to sequester C for thousands of years. However, little is known about biochar stability in tropical sandy soils, where the lack of C protection and warm-dry conditions can enhance biochar decomposition. This chapter provides a general introduction to the study. First, it presents the contextual framework of Terra Preta Programme (1.2) where this thesis is a part of. Second, it specifies the relevance of biochar for climate change mitigation (1.3). Then, it outlines: (1.4) the multi-potentials of biochar use, (1.5) the decomposition of biochar, (1.6) its interaction with native soil organic carbon, (1.7) and reviews the quantification methods for biochar. Finally, it identifies (1.8) the specific research objectives and explains (1.9) the overall research design and methods.

1.2 Contextual Framework: Terra Preta Programme

The Terra Preta Programme (http://www.terrapretaprogram.org/) is an integrated research programme in which social and natural sciences come together to address the recreation of ADE, locally known as *Terra Preta de Índio* (Figure 1.1).

The suggestion has been made to recreate such soils (New ADE - *Terra Preta Nova*) where soil fertility can be combined with soil C sequestration. The proposal to (re-)

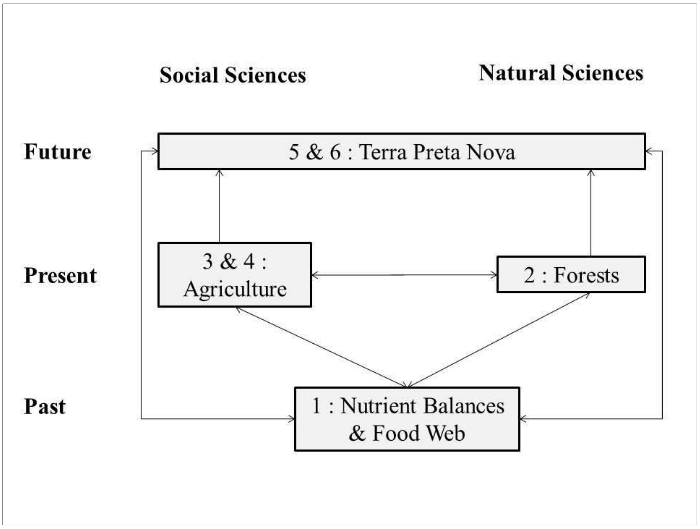

Figure 1.1 Interrelationships between the individual PhD projects in the Terra Preta Programme, arranged along a temporal axis (past, present and future). Numbers assigned to the projects refer to individual PhD projects.

create such soils is a challenge, which requires an interdisciplinary and historical approach that links the natural and social sciences. First, the understanding of the ADE genesis is a source of information for the current practice of their re-creation. Second, the understanding of the present use of ADE for various agricultural purposes improves the designs of more sustainable cropping systems. Third, the understanding of institutional and policy dimensions related to the potential future use of New ADE are paramount for scaling up the recreation of these soils.

This PhD project is part of the Terra Preta Programme, which consists of six multi- or interdisciplinary PhD projects. The Terra Preta Programme aims to lead to the improvement of the livelihood of smallholders living in Amazonia, through information on the sustainable use, conservation and re-creation of Terra Preta soil. This thesis corresponds to the project number five in the Terra Preta Programme framework (Figure 1.1), and it focuses on the future of ADE, specifically to mitigate climate change by the creation of New ADE for C sequestration.

1.3 Relevance

Climate change is one of the biggest challenges at present. Since the Industrial Revolution, global atmospheric concentrations of greenhouse gases (GHG) have risen as a result of human activities (IPCC, 2007; Raupach *et al*., 2007). The concentration of CO_2 in the atmosphere increased from 280 ppm before the Industrial Revolution to 400 ppm in 2014 (NASA, 2014). While GHG emissions from human activities in many countries result mostly from industry, energy consumption and transport (FAO, 2008), in Brazil the majority (~80%) originates from land use change (Lapola *et al*., 2013). Emissions due to land use change include those by deforestation, biomass burning, conversion of natural to agricultural ecosystems, drainage of wetlands and soil cultivation (Lal, 2004). Policymakers react to the climate change threat with policies that minimize GHG emission to atmosphere and maximize retention of carbon and nitrogen in the biosphere and lithosphere (UNFCCC, 2007).

Experts have recommended the addition of organic C to soil as a way to sequester C, and improve soil fertility at the same time (Cerri *et al*., 2010; Neto *et al*., 2010). However, there is a question whether the capacity of C sequestration through increasing the SOC pool is finite or infinite. The global potential of SOC sequestration through conversion of marginal lands into restorative land uses or adoption of no-tillage systems (Conservation Agriculture) corresponds only to one-fourth to one-third of the estimated annual increase in atmospheric CO_2 (Lal, 2004). The potential of soil to sequester C is mainly dependent on the environmental conditions in the soil and the quality of the added residues, which can be a food source for soil organisms (Brady & Weil, 2008). Although tropical soils can have a natural high C content, their C concentration decreases quickly when cultivated. After conversion from forest to pasture, the C concentration in tropical soils decreased around 73% compared to their initial SOC concentration (Cadisch *et al*., 1996). On the other hand, cultivated soils with high fertility and C content had been described in the Amazon basin.

Amazonian Dark Earths are fertile soils with high carbon levels. These soils are mainly a result of additions of charcoal, ceramics, excrements and animal carcasses by the pre-Colombian indigenous population of the Amazon. The charcoal found in these soils was dated older than thousands of years (Pessenda *et al*., 2001) and rich in carboxylic groups (Novotny *et al*., 2009a), which retains the nutrients on the surface of chracoal. These charcoal-containing soils have high nutrient (e.g. phosphorus, calcium and potassium) and SOC levels. The SOC content in ADE was eight times higher than in the surrounding soils (Glaser & Balashov, 2000). Based on these indications, the current production of biochar from residues and its addition to soil has been claimed simultaneously to sequester C in soil, enhance soil fertility, produce energy and reduce solid waste (Laird, 2008).

1.4 Multi-potentials of biochar

Biochar advocates claim that biochar technology offers potent ways to meet pressing challenges across food production, climate change, waste management and bioenergy, attracting the attention of different sectors of the society. Inspired by the aged charcoal found in the fertile ADE, biochar advocates promote biochar application as an important C sink (Reeves *et al*., 2008; Whitman & Lehmann, 2009; Woolf *et al*., 2010), soil conditioner (Lehmann *et al*., 2003a; Rondon *et al*., 2006; Steiner *et al*., 2007), waste management technology (Kwapinski *et al*., 2010), and bioenergy (Lehmann & Joseph, 2009).

Biochar is claimed to have a high potential to mitigate climate change. The biochar climate change mitigation potential is strongly based on the idea that the C present in the biochar will be sequestered in soil for hundreds to thousands of years (Kuzyakov *et al*., 2009). Claims on biochar suggested that the biochar potential to sequester C ranges from 5.5 to 9.5 Gt C / year by 2100 (Lehmann *et al*., 2006). Although the optimistic claims seek the use of biochar, the proposal to submit biochar under Clean Development Mechanisms (CDM) projects failed at Conference of Parties to the United Nations Framework Convention on Climate Change (UNFCCC) in Copenhagen (Leach *et al*., 2011). The reduction of atmospheric CO_2 by stabilization of

C in soil was not eligible for carbon credits under the CDM (Sohi *et al*., 2010). Despite that, an increasing number of actors have been engaged in the biochar climate change mitigation debate. Private organizations, research institutes, pyrolysis companies and venture capitals acknowledge the potential of biochar to mitigate climate change and expand into the carbon market.

Biochar is also claimed to enhance soil fertility, thereby increasing food productivity. Agricultural productivity is the second large potential use of biochar. Based on the high productivity of the ADEs, the current biochar addition to soils is supposed to increase crop yields significantly. A meta-analysis by Jeffery *et al*. 2011 showed that biochar may increase crop production. However, other studies reported no significant improvement by biochar application on crop growth (Güereña *et al*., 2012; Sagrilo, 2014; Carvalho, 2015). Less prominent than the climate change discourse, the use of biochar as an enhancement for soil fertility has attracted only a small number of actors. The potential of biochar to increase food production attracts the interest of few agronomic institutions and universities (e.g. Embrapa and Cornell University), while private organizations, NGO and policymakers seem to be outside of this debate.

Furthermore, biochar production can reduce solid waste. Biochar can be produced from residues, reducing the quantity of solid waste, and leaving less residue that needs to be handled/disposed. Theoretically, biochar may be produced from a large range of materials as crop and forestry residues and domestic wastes. Although the increasing production of solid waste is a serious environmental problem, the potential of biochar to reduce solid waste attracts the attention of a small number of stakeholders. The reasons for the low interest of stakeholders in the potential of biochar to reduce waste may be due the uncertainties about the life cycle of solid waste management (e.g. availability), the local-specific regulations and the potential toxicity of the feedstock. These uncertainties have even motivated biochar advocates to propose turning forests into biochar plantations (Read, 2009). However, this proposal has been strongly questioned in terms of its technical feasibility and sustainability (Leach *et al*., 2010).

Last, biochar is claimed to have a potential to produce energy. When biomass is carbonized in the absence of oxygen (pyrolysis), it may generate different fractions of oil, gas and (bio-) char. Biochar produced in modern pyrolysis plants could co-produce bio-gas and bio-oil. The bio-oil is a raw material that could be directly burned to produce heat energy or refined into more useful products (Laird, 2008). However, in many countries biochar may be produced in traditional kilns rather than in modern pyrolysis plants. These traditional charring process are not designed to co-produce bio-gas or bio-oil, reducing the viability of the use of biochar to generate energy.

It is the claim of these four potentials simultaneously rather than individually that makes biochar to cater for the needs of a large group of actors. The quadruple-win solution suggests that the four potentials of biochar can be maximized simultaneously under real farming conditions (Laird, 2008). This possibility has pulled policymakers, private institutions, researchers and companies together in the biochar debate. However, there are always trade-offs between the biochar potentials, and negative effects also may occur (Jeffery *et al*., 2015). Furthermore, biochar development is not a purely technical issue only; most options have also political implications that need to be solved. Although countries like Switzerland already sought the use of biochar, it is not clear that biochar technology will be accepted in other countries.

To date, there are no policies and strategic plans to implement the use of biochar in Brazil. Brazil is an important player in the biochar debate. In the last decade, Brazilian scientists established a set of biochar experiments, built up national and international networks with focus on biochar and worked together to understand and promote the use of biochar. However, despite their collective effort, the Brazilian government does not acknowledge the importance and potential of biochar. In this context, **Chapter 2** of this thesis assesses the driving forces behind the biochar debate, and to which ends biochar technology may be used in Brazil, and lists the local legal and policy rules that are relevant to the topic.

1.5 Biochar decomposition

A wide range of stakeholders claims that biochar has great potential to sequester C in soils. When applied to soil, biochar is expected to contribute to the most recalcitrant pool of SOC (Knicker *et al*., 2013). However, biochar is a heterogeneous material composed of multiple components that degrade at different rates. Small molecules as n-alkanoic acids, hydroxy and acetoxy acids, benzoic acids, diols, triols, phenols (Graber *et al*., 2010) and aliphatics are degraded rapidly in the soil, whereas stable polyaromatic compounds in the biochar decompose at a slower rate (Kuzyakov *et al*., 2009; Foereid *et al*., 2011; Zimmerman *et al*., 2011).

Depending on the pyrolysis process, the chemical composition of biochar may vary, affecting its residence time in the soil. It is known that high pyrolysis temperatures increase the proportions of polyaromatic structures, which may enhance the mean residence time of biochar in soil (McBeath *et al*., 2014). When produced under controlled condition (in the laboratory) the pyrolysis temperature can reach up to 1000ºC, increasing the chemical recalcitrance of biochar. However, these conditions are unrealistic in the field, as the Brazilian charcoal is traditionally produced in brick kilns at 400-500ºC, using native woods and crop residues (Duboc *et al*., 2007) or in modern biofuel pyrolysis plants as a by-product of the growing Brazilian biofuel production. Furthermore, the feedstock origin and quality may also affect the composition and hence potentially the decomposition of biochar.

The feedstock can influence the chemical-physical composition of biochar. Oilseed-derived biochar may be richer in aliphatic compounds than those commonly produced from wood and crop residues, which are richer in aromatic compounds. These chemical differences in the biomass may affect the decomposition rate of biochar, because aliphatics are in general more labile than aromatic compounds (Lehmann *et al*., 2003a). These variations in the decomposition rate of the resulting biochar compounds may change the C sequestration efficiency of biochar in soil. The decomposition rate of locally produced biochar was quantified in **Chapter 3**, and the effect of oilseed feedstocks on the decomposition rates of biochar in soil was studied in **Chapter 4**.

1.6 Biochar interaction with native soil organic carbon

Biochar may interact with native SOC, changing its decomposition rate in soil. The addition of biochar may accelerate or decelerate the decomposition of native SOC (Zimmerman *et al*., 2011). Some studies have shown that biochar application can lead to stabilization of SOC (Keith *et al*., 2011). But in other studies it was shown that addition of biochar may promote the decomposition of SOC (Wardle *et al*., 2008). The acceleration of SOC decomposition by biochar addition to soil may be caused by changes in the microbial community due to: (i) an increase in the pH to a near-neutral condition by the ash of biochar; (ii) an improved soil moisture retention through biochar water uptake; (iii) an increase in soil aeration; and (iv) the presence of labile organic compounds in biochar (Luo *et al*., 2011; Zimmerman *et al*., 2011). The mechanisms for the deceleration of SOC decomposition rate by biochar application may be due to: (i) the formation of soil aggregates, as biochar may enhance the formation of microaggregates that physically protect the native SOC against decomposition (Brodowski *et al*., 2006); (ii) the toxicity of biochar; (iii) the sorption of enzymes and native SOC to the biochar surface; (iv) and the preferential utilization of biochar rather than SOC by the microorganisms (Verheijen *et al*., 2009; Liang *et al*., 2010; Zimmerman *et al*., 2011; Whitman *et al*., 2014). As a result of these interactions, a change in the dynamics of C decomposition in soils amended with biochar is expected.

One way to investigate the dynamics of C decomposition in soils is by discriminating whether the decay happens in the SOC or biochar fraction. Studies have mistakenly interpreted the increase in CO_2 emissions in biochar-amended soil as an unique consequence of the acceleration of native SOC decomposition. Biochar, however, also has a labile component that can decompose within days to months, contributing to the emitted CO_2 (Sagrilo *et al*., 2014). To overcome this problem, the use of isotope analysis is recommended. Isotope analysis can be used to discriminate between native

SOC and C from biochar amendment. Furthermore, isotope analysis allows for determining whether native SOC or biochar was the source of CO_2 emission. With the help of this powerful tool, the biochar decomposition (**Chapters 3** and **4)** and the biochar effects on the native SOC decomposition (**Chapters 4**) are investigated.

1.7 Biochar quantification methods

Biochar plays a vital role in SOC, but its quantification still remains a major analytical challenge. If biochar is to become a C sequestration solution in the CDM projects, affordable and high-throughput methods are needed to quantify and monitor its presence over time in the environment where it was applied. Routine methods, such as the widely used acid dichromate oxidation method to quantify total SOC – e.g. Walkley-Black method - do not quantify all SOC. The low (120-130ºC) and short-term peak temperature of the Walkley-Black method are not enough for the complete oxidation of some types of soil C, for example biochar. The mean recovery of organic C using this method is around 76% (Walkley & Black, 1934), and it can performed worse in soils rich in biochar. Since several studies suggested that this method (Skjemstad & Taylor, 1999; Simpson & Hatcher, 2004; De Vos *et al*., 2007) determines only a (small) portion of the biochar present in soil, this method cannot be recommended for soil C stock measurements (Maia *et al*., 2013).

Other methods used to quantify biochar, such as optic (Skjemstad *et al*., 1996; Golchin *et al*., 1997), microscopic (Poirier *et al*., 2000; Skjemstad & Reicosky, 2002), thermal (Gustafsson & Gschwend, 1998), or spectroscopic (Knicker *et al*., 1996; Novotny *et al*., 2006a) are far too complex, time-consuming and expensive to be suitable for assessment of the soil C sequestration potential.

Another approach to quantify biochar is the use of molecular markers. The benzene polycarboxylic (BPCA) method (Glaser *et al*., 1998) quantifies biochar using BPCA as a molecular maker. The BPCA method consists in the oxidation of polycondensate aromatic structures of the biochar into single benzene rings with carboxylic acid groups (Ziolkowski *et al*., 2011), which are then quantified by gas chromatography

(GC). The quantity of benzene rings (BPCA) correspond to the concentration of biochar in the sample. The BPCA method has been used in many publications over the past decade (Glaser *et al*., 2000; Czimczik *et al*., 2003; Glaser & Amelung, 2003; Rodionov *et al*., 2006; Brodowski *et al*., 2007; Hammes *et al*., 2008) and it is well established to quantify biochar in soil and sediments.

Although many studies applied the BPCA method with GC to quantify biochar, a study involving 17 laboratories revealed disparate results (Hammes *et al*., 2007; Schneider *et al*., 2011a). The many steps needed to quantify BPCA though GC resulted in variable measurements. Based on the BPCA methodology Dittmar (2008) determined biochar using high-performance liquid chromatography (HPLC), which omitted the cleaning and derivatization steps necessary in GC analysis in the original method (Glaser *et al*., 1998), decreasing the sources of errors. However, a drawback is that sample analysis takes three times longer (90 min) than the established GC method (30 min). Therefore, a better analytical procedure to quantify BPCA through chromatography is needed. In **Chapter 5**, a new chromatography method to quantify BPCA in biochar was developed.

1.8 Objectives

Given the above research needs, the main objective of this thesis is to contribute to the biochar climate change debate through enhancing our understanding on the dynamics of C decomposition in soils amended with biochar. This information is paramount for policymakers and therefore for policy support to biochar implementation. Thus, the specific objectives are:

1. To discuss the policy arrangement related to biochar use in Brazil (**Chapter 2**).

2. To quantify the changes in the biochar stocks in a tropical sandy soil amended with biochar (**Chapter 3**).

3. To investigate the potential interaction of oilseed-derived biochar with the native SOC and their decomposition (**Chapter 4**).

4. To investigate the suitability of rapid-resolution liquid chromatography (RRLC) technique for quantification of biochar (**Chapter 5**).

1.9 Thesis outline and experimental approach

This thesis consists of six chapters including the General Introduction, four research chapters and a final chapter with conclusions and reflections. Figure 1.2 presents an overview of the structure of thesis.

In **Chapter 2**, I conceptualize biochar as a new and emerging policy arrangement, and investigate it along the four interrelated dimensions (actors, power, discourse and rules) of the policy arrangement approach (PAA), with a focus on Brazil. A policy

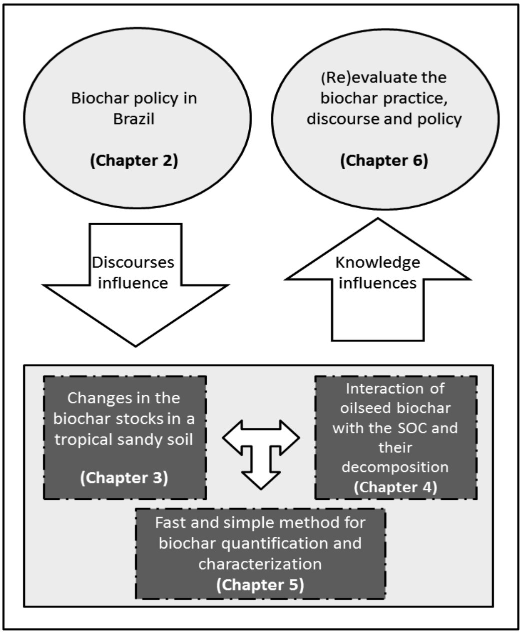

Figure 1.2 Overview of the thesis. Ellipses refer to the chapters where the biochar discourses and claims are (re)evaluated. Arrows refer to the direction of the influence. Boxes refer to the chapters where the biochar claims and methods are tested.

arrangement refers to the way in which a certain policy domain – or an emerging domain such as the multi-potentials of biochar – is temporally shaped in terms of these four dimensions (Arts & Leroy, 2006). Actors can be organizations or individuals involved in a specific policy issue. Power is constituted and exerted by actors in relationships in order to achieve outcomes. Discourse can be defined as ideas, concepts, and categorizations that give meaning to certain physical and social realities. Finally, the rule dimension consists of various instruments and procedures that define responsibilities, access to networks, and interactions among actors. Based upon the PAA, and particularly operationalized by social network analysis, I identify who are the main actors involved in the biochar network, what their power relationships are, how the biochar discourses are progressing in Brazil and whether these have led to rule-making. Furthermore, I explain how the current political context influences the emerging biochar policy arrangement in Brazil.

In **Chapter 3**, I study the biochar decomposition under field conditions. There is a lack of long-term biochar field experiments with isotope data. To date, most of the results of biochar decomposition are from incubation studies in the laboratory. Although these studies are important to understand the underlying mechanisms, they are not necessarily appropriate to recommend biochar application at large scale. To upscale biochar application, experiments need to be conducted on the desired region of application, because of the specificity of the environmental conditions. The region selected for the field study is one of the poorest in Brazil, with increasing demand for arable land for crops such as soybean. In this field study I evaluate the effects of different amounts of biochar on the stocks and decomposition rates of biochar over four soybean cropping cycles (1.5 years). In this experiment, biochar was applied at different rates and discriminated from the native SOC by ^{13}C stable isotope. The biochar was derived from native wood residues (C_3-plant) pyrolysed in a traditional kiln. The soil in the field experiment is a sandy soil with SOC derived from C_4-plants, and with low C content and protection. This approach allowed us: to quantify the decomposition rate of biochar under savannah environments.

In **Chapter 4**, I investigate how the quality of the biomass (and hence the biochar quality) affects its potential - directly and indirectly – to sequester C in soil. For that, I use biochar derived from oilseed crops. There is an increasing availability of oilseed-derived biochar in Brazil, however, little is known about its potential to sequester C in soil and its impact on the native SOC decomposition. To address these questions, I perform an incubation experiment using C_4-plant derived sandy soil and three C_3-oilseed biochar (castor bean, jatropha and soybean) rich in aliphatic compounds. I use the elemental composition (CHN) and the ^{13}C NMR spectroscopy to characterize the chemical compounds in the biochars. To study their impact on native SOC, I apply them in sandy soil with low SOC content and protection. For one month, I measure the CO_2 efflux from a mixture of the biochar and SOC as a proxy for the C decomposition rate. Later, I use ^{13}C stable isotope data from the biochar, the soil and the CO_2 released to distinguish between the CO_2 sources. From this experiment, I address the influence of biomass quality on the decomposition rates of biochar and its impact on SOC decomposition.

In **Chapter 5**, I develop a new chromatography method to quantify and characterize BPCA in different biochars. Chromatography is a collective term for a set of laboratory techniques for the separation of the compounds from the mixture. This separation occurs based on the interactions of each compound with the mobile (gas or liquid) and stationary (column) phases, which results in different retention times of each compound in the system. There are many stationary/mobile phase combinations that can be employed to separate compounds from the mixture, and therefore there are several different types of chromatography. The best known are gas (GC) and liquid (LC) chromatography. In the GC the mobile phase is a chemically inert gas that serves to carry the mixture through the heated column, while in the LC the mobile phase is liquid. In the end of both systems there is a detector which provides a quantitative measurement of each component of the mixture. In **Chapter 5** a new chromatographic method is presented to quantify BPCAs in the biochars. Later, the optimized method and ^{13}C-NMR are used to quantify the proportion of C structures and condensation degree of different biochar sources, i.e. from different biomass sources and produced at different final pyrolysis temperatures (350-550ºC).

In **Chapter 6** (General Discussion), I analyse how the biochar discourses influence the biochar practices in Brazil, and how the new insights on biochar decomposition rate affects the current debate on the potential of biochar to mitigate climate change. The chapter ends with a general conclusion to the thesis, brief reflection on interdisciplinary research and a discussion on the policy implications of the findings of this thesis.

Chapter 2

Biochar: an emerging policy arrangement in Brazil?

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Published as

Rittl, T. F.; Arts, B.; Kuyper, T. W. (2015). Biochar: an emerging policy arrangement in Brazil? Environmental Science & Policy, v. 51, pp. 45-55.

Abstract

Biochar, the solid product of pyrolysis, has emerged as a new technology and policy tool to address various environmental challenges (climate change, food production and agricultural waste management). The concept of biochar drew its inspiration from Amazonian practices that had led to the creation of *Amazonian Dark Earth* (ADE): fertile soils rich in (bio)char and human artefacts. In this article, we conceptualize biochar as an emerging policy arrangement, and examine it along the four dimensions of the *Policy Arrangement Approach* (PAA), which are actors, discourse, power and rules. We focus on Brazil as an important player in the international biochar debate. Our analysis shows that science experts are the predominant players in the network, while policymakers, businessmen and farmers are marginally positioned. Experts from *Embrapa* occupy central positions and thus exercise most power in the network. Moreover, experts linked to ADE have lost prominence in the network. The reason for this is to be found in the shift from the ADE/biochar to the biochar/technology discourse. The latter discourse includes different coalitions such as 'climate change mitigation', the 'improvement of soil fertility' and 'improving crop residue management'. Although the biochar/climate coalition is dominant at the international level, it is far less prominent in Brazil. Nationally, it is particularly the discourses of 'improvement of soil fertility' and 'improving crop residue management' which have prompted actors' relationships and practices. However, the biochar/technology discourse has not (yet) been formally institutionalized in Brazil. As a consequence, the country lacks an established biochar policy field.

2.1 Introduction

Recently, both scientists and policy makers have promoted *biochar* as a policy mechanism (Heffernan, 2009; Lehmann, 2012). Biochar is a solid material obtained from the carbonisation of biomass (IBI, 2014). When applied to soil, biochar may increase soil fertility and the soil carbon (C) stock. The use of biochar as a soil amendment was inspired by *Amazonian Dark Earths* (ADE), also known as *Terra Preta de Índio*. The high fertility and C levels of those soils are likely a result of the presence of (bio)char and additions of excrements and animal carcasses. It has been claimed that the current use of biochar enhances carbon sequestration, improves soil fertility, provides an alternative for crop residue management and aids pollution remediation, thereby offering options for solving specific environmental policy problems (i.e. climate change, sustainable land use, agricultural waste management, and pollution remediation) (Lehmann *et al*., 2006; Gaunt & Lehmann, 2008; Lehmann & Joseph, 2009; Kwapinski *et al*., 2010; Maia *et al*., 2011). In this paper, we conceptualize biochar as a new and emerging ‘policy arrangement’ to address issues within different policy fields for Brazil – this involves actor networks and their power relations, discourse coalitions, and institutional settings (Hajer, 1995; Arts *et al*., 2006; Arts & Buizer, 2009). The possibility of multiple uses of biochar in different policy fields has created various alliances amongst stakeholders including scholars, policy makers, businessmen, and (non-) governmental organisations (Leach *et al*., 2012). In the past, actors credited ADE for the recognition of biochar potentialities, whereas now actors see it as an advantage to claim biochar as a technology in itself. They find common purposes in promoting biochar as a mechanism for climate change mitigation, enhancing food production, rehabilitation of degraded land, and waste management (Leach *et al*., 2012). However, these options are neither formally accepted in the climate change and agriculture regimes, nor are they uncontested topics in policy debates. Advocates suggest that biochar can be produced from any kind of biomass residue and its application may sequester carbon and concurrently increase soil fertility, thereby contributing to policy solutions. In turn, critics argue (Biofuelwatch *et al*., 2011) that carbon sequestration through biochar is not applicable to current climate change policies and its agronomic benefits still need to be confirmed. Such discourse coalitions strive for hegemony and seek to have their views and solutions formally accepted.

The proposal to submit biochar under the *Clean Development Mechanism* (CDM) projects was rejected at the *Conference of Parties to the United Nations Framework Convention on Climate Change* (UNFCCC) in Copenhagen (Leach *et al*., 2012). The reduction of emissions by stabilizing carbon in soils was not considered eligible for carbon credits under the CDM (Sohi *et al*., 2010). Furthermore, agricultural solutions for climate change are not part of the REDD+ framework (Reducing Emissions from Deforestation and Forest Degradation). However, the increased emphasis on "no climate security without food security" in UNFCCC negotiations did raise expectations that biochar use for soil fertility enhancement may be recognized as a climate mitigation and adaptation technology in the future (Leach *et al*., 2012). Effective agricultural management is increasingly being recognized as part of the solution in international climate change negotiations, with biochar included as one of the agricultural solutions proposed for "climate-smart agriculture" (Ernsting, 2011). Biochar has also been a theme within the *United Nations Convention to Combat Desertification* (UNCCD), where it has been posited as a means of combating land degradation, improving farmland and mitigating climate change (Sohi *et al*., 2010). The UNCCD has therefore promoted biochar as a valuable tool for countering land degradation, and many other bodies have enthusiastically backed its use (Barrow, 2012).

Policy discourses and discourse coalitions are part of broader, emerging policy arrangements that include rules (legislation, measures, etc.), resources (money, information, instruments, etc.), and consequently also power relations (*who* is getting *what, when* and *how*?) (Arts & Leroy, 2006). International advocates of biochar have been encouraged by the development of large-scale industrial biochar technology, hence making it an even more promising policy option for the future (Bjerregaard & Georg, 2011; Shackley *et al*., 2011). Dominant among them is the *International*

Biochar Initiative (IBI), a non-profit organization concerned with promoting biochar use foremost as a tool to mitigate climate change.

Despite its high international policy relevance, the international climate change / biochar debate is dominated by scientists and commercial enterprises from the global North. However, tropical countries, especially Brazil, are important players in the international biochar debate. Brazil is a pioneer in research on ADE and 'new ADE' (locally known as *Terra Preta Nova*, which is the (re)creation of ADE), as well as the world's largest producer of charcoal and a well-known actor in biochar research. Therefore, the national discourse in Brazil may have an impact on the channels through which biochar policy will be arranged.

In this context, the identification and characterization of the emerging biochar policy arrangement in Brazil may help to clarify the nature of the discourse, identify which groups and networks of actors are involved, list the legal and policy rules relevant to this topic, and also assess the resources that have already been mobilized. Consequently, the objectives of this article are as follows: (i) to identify who is driving biochar policy forward in Brazil; (ii) to describe how the biochar policy discourses, and their discourse coalitions, are progressing in Brazil; (iii) to explain how the current institutional context influences the emerging biochar policy arrangement, as well as to assess whether new rules are being generated from it. In order to integrate all these dimensions, *Policy Arrangement Approach* (PAA) (Liefferink, 2006; Arts & Buizer, 2009; Veenman *et al*., 2009) was used and operationalized with the tools of social network analysis (Borgatti *et al*., 2009; Vignola *et al*., 2013).

2.2 Methods

Theoretical framework: Policy Arrangement Approach

Biochar is a policy arrangement consisting of different policy fields (including climate change, food production and agricultural waste management), which is driven by distinct groups of actors and their interests. For this reason due to its ability to incorporate a multiplicity of perspectives, PAA may provide insights into the historical and current networks, ideas and (informal) (dis)agreements on biochar arrangements in Brazil, and how they affect national policy fields. A policy arrangement is defined as the way in which the organization and contents of a certain policy field are temporarily moulded in terms of discourses, actors, resources, rules and their relationships (Liefferink, 2006; Arts & Buizer, 2009; Veenman *et al*., 2009). Four interrelated dimensions are used to describe a policy arrangement: (1) Actors and their networks involved in a policy field; (2) Discourses that capture the views and positions of the actors – or coalitions of actors – involved; (3) Resources (e.g. money, knowledge, facilities), and their division of among actors and the power relations they imply; and (4) Rules and regulations (both formal and informal) that shape both the arrangement and the policy it produces (Liefferink, 2006).

Methodologically, this paper commences the policy arrangement analysis by determining who is involved in the emerging biochar policy arrangement in Brazil, and then proceeds to analyse the institutional context in which they operate, as well as the power relations between these actors. For this purpose, three types of sources were consulted and triangulated (Yin, 1991): written sources, interviews and a focus group. The written sources included non-academic and academic literature, i.e. articles, policy documents and websites. The second source of information consisted of ten in-depth, semi-structured interviews with *key* actors of the Brazilian biochar field. These Brazilian biochar actors were previously identified in the written sources. The *key* actors were strategically selected through snowball and respondent-driven samplings. After saturation, the search for the *key* actors was stopped. The third source of data consisted of a focus group conducted with participants of the Third Workshop of the *Terra Preta de Índio Programme* in 2013. This was done to gather additional data, and to check the data already obtained from the other two sources. After that, we validated our findings with two well-informed Brazilian biochar actors.

Actors, their relationships and power were identified by social network analysis (Freeman, 1979). To provide an historical overview of the actors in the network, we analysed three periods: 2001-2005; 2006-2010 and 2011-2013. The historical analysis started in 2001, when a series of meetings were initiated to define and consolidate the biochar community (Shackley *et al*., 2011). For all periods, actors were identified and their influence assessed through their relationships (quantity and intensity). An undirected graph of the network (network analytic software Gephi 8.2) was developed for each period. We used the Lattes Platform specifically for selecting actors involved in the biochar network. The Lattes Platform (CNPq, 2014) is an information system (i.e. integrated database) maintained by the Brazilian Government to manage information on science, technology, and innovation related to individual experts and institutions in Brazil. Since all researchers and institutions are required to keep their records up to date, the Lattes Platform can be used to obtain primary information on individual actors. The following key words were used in the Lattes Platform: *Terra Preta de Índio Nova*, *pyrogenic carbon*, *biochar* and *biocarvão*. In addition to that, we also added in the network actors identified in the written sources and the interviews. The relationships among actors were established when the presence of co-authorship of papers, co-partnership in projects, project sponsorships and historical cooperation data could be identified.

Having identified the most important actors and their relationships, we added the second dimension of the PAA to our analysis, discourses and the coalitions organized around them. Because of data availability, the discourse analysis was only applied to the last period of the actors network analysis (2011- 2013). We chose to use discourse analysis as it “allows for a better understanding of controversies, not in terms of rational-analytical argumentation, but in terms of argumentative rationality that actors bring to a discussion” (Hajer, 2006:68). Discourse is defined as “a specific ensemble of ideas, concepts, and categorizations that are produced, reproduced and transformed in a particular set of practices and through which meaning is given to physical and social realities” (Hajer, 1995:44). Discourse plays an important role in the organization of a network because it influences how actors become positioned vis-a-vis each other in the network. Since this positioning often leads to the creation of ‘like-minded’ groups, we also adopt the concept of “discourse coalition”, which, according to Hajer

(2006:70), refers to a group of actors that share a particular set of storylines over a particular period of time. The concept of "storyline" refers to a "condensed statement summarizing complex narratives, used by actors as a '*short hand'* in discussions" (Hajer, 2006:69). Given these theoretical considerations, our discursive analysis consists of three steps: (1) the identification of the discourses of biochar (e.g. 'mitigation of climate change') in Brazil; (2) the identification, within each discourse, of (key) storylines (e.g. 'stability of biochar', 'recalcitrance'); and (3) the identification of discourse coalitions in the network. For the purpose of our analysis, websites, written documents (articles, reports, projects, etc), interviews and focus group were used to reconstruct the discourses, storylines and coalitions around biochar.

The third dimension, power, was determined by the presence/absence, intensity and number of actor relationships in the policy arrangement. Relationships were categorically determined as: co-authorship of papers, co-partnership in projects, project sponsorships and historical cooperation data. Each relationship was weighed as binary data. The sum of the weights determined the intensity of the relationship. Because power is assessed in terms of location in the network, which is temporal, we measured the importance of each actor and their power for the last period (2011-2013). We used the following network indexes to measure power: centrality (closeness, and betweenness) and eigenvector (Freeman, 1977, 1979). The values of these indexes are dependent on the pattern of connections that an actor is embedded in. Closeness measures how easily an actor can access the rest of the network, and it is estimated by the minimal path distance between actors. Betweenness measures the control an actor has over what flows in the network, and is determined by the length and number of shortest paths between all actors and the sum of all actors - dependencies. An eigenvector measures how well an actor is connected to other well-connected actors. The eigenvector is a relative score of the connections of the actor, where connections to high-scoring actors contribute more to the score of the actor in question than equal connections to low-scoring actors. Where an actor himself has easy access to others while at the same time controlling the access of other actors in the network through their connections, a high measure of power is revealed.

The last dimension of the PAA, *Rules of the Game*, consists of informal and formal rules. Informal rules refer to the conventions that shape the interactions of actors in the network. Informal rules were assessed by analyzing who, over time, has gained access to the Brazilian biochar network, in other words who is allowed in, and who is not. The formal rules refer to the existent law, programmes and policies that may influence the biochar practices in Brazil. Formal rules were assessed by understanding how the current institutional context influences the emerging biochar policy arrangement, and whether it develops new rules for itself. For this end, we analyzed the network rules of the arrangements as well as the current Brazilian policy programs and laws – particularly on climate change and agricultural development – in which biochar could be an important mechanism.

2.3 Results and Discussion

The emerging biochar arrangement in Brazil

The Brazilian biochar policy arrangement was investigated through the PAA and social network analysis. The four analyzed dimensions (Actors, Discourse, Power and Rules) are shown and discussed in the next four sections. In the first section the relevant actors and actor coalitions are mapped and interpreted. The second section shows the discourses and discourse coalitions around biochar in the last years (2011-2013) in Brazil. The third section shows how actor power relations are measured. The final section examines the current rules of interaction among actors and formal procedures.

Who drives the biochar policy forward in Brazil?

We used social network analysis (Freeman, 1979) to represent the structure of relationships between actors and organizations in the Brazilian biochar context. Nodes represent actors (experts, companies, policymakers, farmers), ties represent their relationships (co-authorship of papers, co-partnership in projects, project sponsorships and historical cooperation), and location represents their power relations (the more central in the network, the more powerful). Actors are organized in clusters. A cluster is a tightly knit, highly bonded, subgroup of actors (Hoppe & Reinelt, 2010). Each cluster consists of a number of actors who share resources and/or interpretations of biochar mechanisms (such as for soil fertility, climate change mitigation and agricultural waste management). As a consequence, each cluster identifies its own goals, and is engaged in the network to achieve those goals. Clusters are dynamic in the sense that an actor may create new interactions with new or existing actors. The resulting update of the network may not only generate new clusters, but can also dissolve existing clusters. These changes concern shifts in power relations, redefining the predominant actors in the network. A historical view (2001-2013) of the development of the Brazilian biochar network is consequently provided (Figure 2.1 a, b and c).

In the first period (2001-2005; Figure 2.1a), two well-defined and independent clusters are visible (Figure 2.1a). One cluster consists of six actors who are mainly linked to the national institutes. The other cluster is mainly composed of international actors. Both aimed to achieve their respective objectives, which at that time were scientific, although the ADE (re)creation debate also suggested policy goals (Sombroek *et al*., 2003; Marris & Feature, 2006). The goal of the first cluster was to understand the fertility of ADE, while the second cluster was more concerned with the agronomic benefits of the (re)creation of ADE. These two clusters together included soil scientist, archaeologist and agronomists, who saw in the ADE the possibility to understand the Amazonian rural livelihoods and recreate the ADE fertility. In this period, soil scientist and agronomists performed some exploratory experiments with charcoal, subsequently called biochar. Each group of scientists also looked for partners (experts, national and international institutes) with whom an acceptable consensus on the study and recreation of ADE could be reached. The only actor not directly linked to the network was the incipient biochar company *Bioware*, which focused on biochar production and product development.

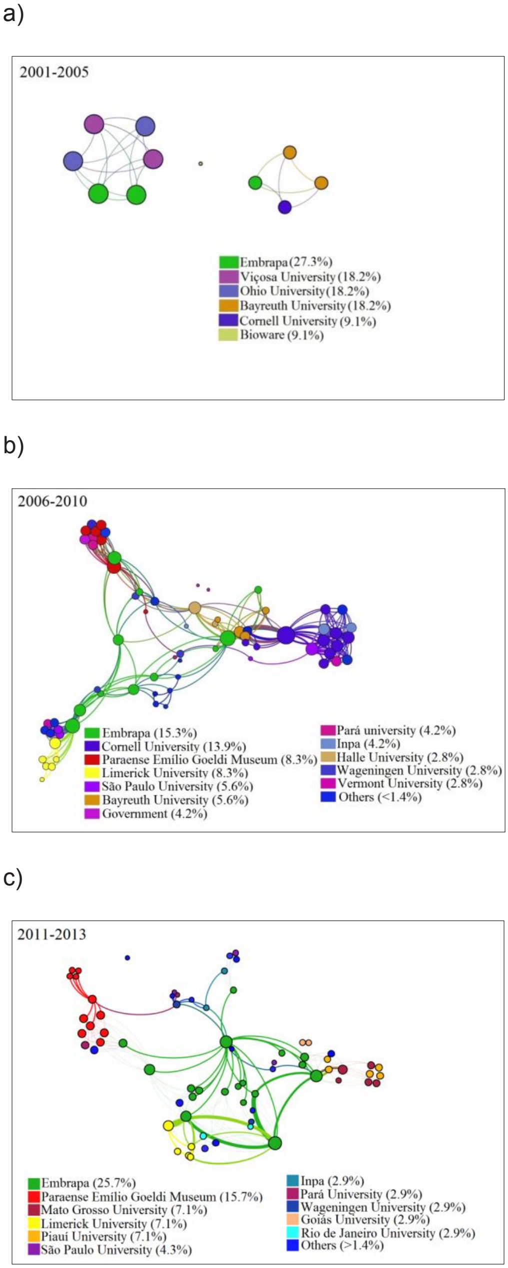

Figure 2.1 Historical development (2001-2013) of the Brazilian biochar network. Individual actors (experts, companies, policymakers) are represented by the nodes and tight relationships by the edges. Size of nodes indicate the number of connections (degree) and length of edges indicates how strong the connection is. The larger the node, the more influential the actor is in the overall network. Actors of the same colour belong to the same institute. Each colour represents one institute, and percentages (%) indicate the participation of each institution in the network.

The second period (2006-2010; Figure 2.1b) was characterized by the development and consolidation of the biochar network in Brazil. New actors joined the network and interactions intensified. During this period, biochar experts could be arranged in three clusters, each interested in one aspect of biochar: (i) the relationship between *Amazonian Dark Earth* and biochar; (ii) the use of biochar for climate change mitigation; and (iii) the use of biochar for soil fertility enhancement and agricultural waste management. Despite vast differences in interest among clusters, the high density of relations between actors placed all three clusters together. At the core of these three clusters, *Embrapa* experts were dominant. Due to this position, they enabled possible collaboration between clusters, and allowed the flux of resources (in the form of money, influence, knowledge) to those connected to them. As a consequence of these collaborations, two research networks were formalized: the *New Dark Earth Soil of Central Amazonia* under the coordination of the *National Institute of Amazonian Research* (INPA), which was mainly focused on the (re)creation of ADE; and the *National Research Network of Biochar at Embrapa* which was more concerned with applications of biochar. Simultaneously, *Embrapa* and the IBI organized the *3rd International Biochar Conference* in Brazil in 2010. On one hand, these coalitions and events connected all national and international experts with an interest in biochar in the Brazilian context, either directly or indirectly. On the other hand, they did not attract other potentially interested actors into the network, such as policymakers. Although one policymaker showed interest in the biochar initiative in Brazil (Galli, 2009), he did not become embedded in the network; policymakers remained outsiders in the Brazilian biochar debate during this period.

The third period (2011-2013; Figure 2.1c) of the Brazilian biochar network enabled efficient sharing of resources. However, it did not include new alliances from different societal actors. After the formalization of the three research networks in the previous period, national collaboration among biochar experts was consolidated. Brazilian experts started to work together, developing their own biochar production and analytical protocols and experiments. National research on biochar became more robust and independent from the international research community. The first studies on biochar under tropical conditions started to be published (Petter & Madari, 2012; Petter *et al*., 2012). For the first time in 2013, the *Brazilian Soil Conference* included a symposium dedicated to biochar studies (Madari & Novotny, 2013). Furthermore, the *National Biochar Research Network* consolidated in October of 2013 at the 10th Meeting of the Brazilian Chapter of the *International Humic Substance Society*. Their strong internal organization sets Brazilian biochar research apart from the rest of the world. As a consequence, the number of international experts directly involved with actors in Brazil decreased. However, it was not only international actors who were excluded from the network, but other sectors of society also remained disconnected. As such, policymakers, businessmen and farmers were not absorbed into the emergent *National Biochar Network*.

The Brazilian government seems to be relatively unacquainted with the biochar debates. Other countries have already been seeking to include biochar as a potential climate mitigation and adaptation tool in the post-Kyoto climate agreement, such as Swaziland, Zambia, Australia, etc. (IBI, 2014). In the United States, the IBI succeeded in having biochar research and development included in the *United States Farm Bill* (Leach *et al*., 2010). The Brazilian government is still not as enthusiastic about biochar as these governments; it maintains distance from the biochar debates in the network. As a result, the Brazilian biochar network remains strongly embedded in science. This science-oriented character of the Brazilian network differs from those international biochar networks that are more science-policy-market oriented (Leach *et al*., 2011)

Biochar policy discourses and related discourse coalitions in Brazil

In order to understand and realize biochar's potential, as well as to design possible biochar mechanisms, actors draw on both scientific and popular discourses. On the basis of this definition (Hajer, 1995:44), we assessed discourses through the actors' points of view and their practices (either preferred or actualized). It is important to note that actor clusters differ from discourse coalition. The discourses are spread over the entire network and are not concentrated in a specific actor's cluster. Furthermore, due the multiple potentialities of biochar, some clusters of actors make use of one, two or three discourses at the same time (Figure 2.2). In this section, we examine how discourses around biochar generate new practices (agendas, events, formal agreements, etc) in the Brazilian context. For this purpose, we used the last period of the Brazilian biochar network to better visualize the current actor clusters and discourse coalitions (Figure 2.2). The biochar discourse coalitions and their characteristics are presented below. After the characterization of discourse coalitions, we explain how these influenced biochar policies and practices in Brazil.

First, taking all periods together, we observed a general discursive shift from ADE/biochar (Figure 2.1 and number 1 in Figure 2.2) to biochar/technology (numbers 2 and 3; Figure 2.2). *Amazonian Dark Earths* are rich in (bio)char, which was dated as being at least thousands of years old (Pessenda *et al*., 2001). This, together with the input of excrements and animal carcasses, is considered the main explanation for the high nutrient content of these soils. Consequently, based on the existence of ADE (Glaser *et al*., 2000; Sombroek *et al*., 2003), biochar has been considered as a successful solution on three levels: as an important soil fertility enhancer (Lehmann *et al*., 2003b; Rondon *et al*., 2006; Steiner *et al*., 2007), an alternative for agricultural waste management (Maia *et al*., 2011), and a C sink (Whitman & Lehmann, 2009; Woolf *et al*., 2010). Despite the historical importance of *Amazonian Dark Earths* in the recognition of the potentialities of biochar (Novotny *et al*., 2009a), the relationship between ADE and biochar has been reconfigured over time (Figure 2.1 and Figure 2.2). In the past, biochar was predominantly understood as an important component of ADE, responsible for their high fertility and carbon content. Presently, biochar has become increasingly disconnected from ADE and has become a product on its own. This discourse disconnection translates also into disconnection among actors. The Brazilian actors (number 1; Figure 2.2) who still credit ADE's importance to biochar potentialities are currently located in a margin of the network with little connection to other discourse coalitions.

Second, part of the network - which we conceptualize as a discourse coalition (number 2; Figure 2.2) - focuses on biochar as a 'soil fertility enhancer' by 'agricultural waste management'. These discourses are combined by the Brazilian actors in the network (number 2; Figure 2.2). Biochar application to soil may increase: (i) plant growth and nutrition (Steiner *et al*., 2007); (ii) the efficacy of nitrogen fertilizers (Steiner *et al*., 2008) and (iii) the microbial biomass in soil (Warnock *et al*., 2007; Birk *et al*., 2009), which might also increase biological nitrogen fixation (Rondon *et al*., 2006; Mia *et al*., 2014). All these improvements may bring benefits for food production as well as possibilities for rehabilitation of degraded lands. Furthermore, if biochar is produced from crop residues, it can become an agricultural waste management technology (Maia *et al*., 2011). Biochar can be produced from different sources of biomass, i.e. crop residues, manure and animal carcass. Alcohol production from sugarcane, the main feedstock in Brazil's renewable energy matrix, as well as emergent biofuel (biodiesel) industries generate thousands of tons of residues that could be pyrolysed and reused in the soil (Maia *et al*., 2011). In this context, biochar can offer economic opportunities to reuse crop residues as a means to enhance soil fertility and reduce the volume of waste material.

Third, biochar has been touted by some Brazilian actors as a potential tool for mitigating climate change - which is a dominant worldwide discourse and the third discourse coalition (number 3; Figure 2.2) in the network. These actors, who are strongly linked to international institutions, are pushing for biochar to become part of the emerging carbon market (Leach *et al*., 2012). Biochar climate change actors are quite confident that biochar will deliver on its promises and become part of the package that will ultimately address the climate change problem. Advocates are convinced that biochar can become a long-term and readily measurable sequestration product. The C present in the biochar is claimed to be sequestered in the soil for many decades, if not centuries.

Internationally, the potential of biochar as a soil C sequestration mechanism is superseding its agronomic relevance (Leach *et al*., 2012) and agricultural waste management potentials by far. The alleged high potential of biochar to mitigate climate change is bringing together international research institutes, NGOs and private companies, which will benefit from the biochar carbon market. However, this hope for a strong biochar market, compounded by the international emerging industry around it, might threaten local interests. Some international advocates suggest that millions of hectares could be turned into biochar plantations, with the possibility of large pyrolysis plants being constructed (Leach *et al*., 2010). However, such large scale biochar production might have social and environmental consequences such as land-grabbing (Leach *et al*., 2011). Given the international focus on climate change, the improvement of soil fertility through biochar derived from residues may not be sufficient to bring international organisations together (Leach *et al*., 2010). At the same time however, they may be sufficient to mobilize local actors within Brazil.

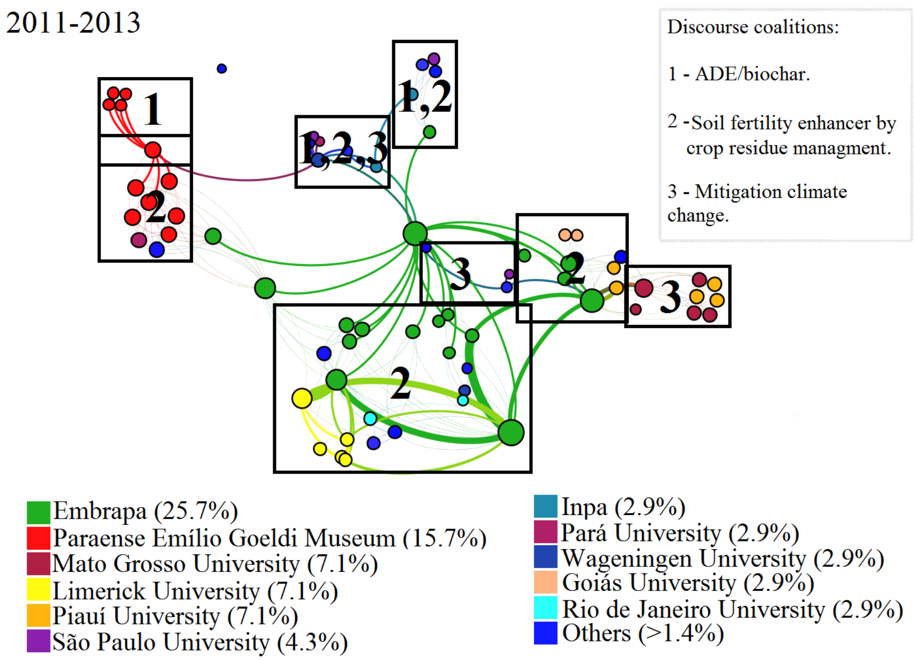

Figure 2.2 Actors and discourse coalitions in the Brazilian biochar network in 2011-2013. Individual actors (experts, companies, policymakers) are represented by the nodes and tight relationships by the edges. Size of nodes indicates the number of connections (degree) and length of edges indicates the strength of the connection. The larger the node, the more influential the actor is in the overall network. Actors of the same colour belong to the same institute. Each colour represents one institute, and percentages (%) indicate the participation of each institution in the network. Numbers correspond to the identified discourses in the Brazilian network. Discourses were based on reconstructing storylines, arguments and assumptions used by identified actors in the network analysis.

The potential of biochar as a tool to mitigate climate change has not been translated into real practices in Brazil, thereby making it more of an echo, or even an imposition of the international discourse. Crop residue management and agronomic effects seem to be the main discourses behind the current biochar practices in Brazil. *Embrapa* has already included the agronomic use of biochar in its strategic agenda (IBI, 2014). Furthermore, in the article "Advances in Biochar Research in Brazil" (Maia *et al*., 2011) , the authors discussed the potential to convert crop residues into biochar and its effects on agriculture and soil C stocks. However, it is important to note that in tropical soils, increasing C stock is seen more as an agronomic practice than a climate change solution. Enhancing or maintaining high levels of soil organic C is important to sustain the productivity of tropical soils (Lal, 2006). Furthermore, the Brazilian agenda for climate change mitigation is far more focused on decreasing deforestation than on increasing C stock in soil.

While the agricultural use of biochar seems an obvious solution for addressing urgent problems in Brazil (Maia *et al*., 2011), experts are not yet confident about its benefits in practice. When asked whether they were ready to recommend and develop rules for biochar application in Brazil, scientists were doubtful and argued that more research was needed (in the form of data from interviews and focus groups). The question remains whether other non-desirable biochar effects, such as the introduction of contaminants into the soil and decreases in crop productivity, might persist in soil as long as the biochar residence time. Many actors seem to uncritically embrace the national soil fertility discourse, despite the many uncertainties that remain as to whether this option would actually work. These uncertainties contrast with the international biochar climate change discourse, where proponents are quite confident that biochar will deliver on its promises and consequently become part of the package that will tackle the climate change problem.

These differences between international and Brazilian discourses have reconfigured alliances between international and domestic actors. After the 3rd *International Biochar Conference* (2010), which was jointly organized by *Embrap*a and the IBI, a new IBI chairman for the *Brazilian Biochar Chapter* was appointed. Up until then, the position had been occupied by a soil scientist from *Embrapa*, whereas now it has been filled by a member of the *Brazilian Panel on Climate Change* (IBI, 2014). Conversely, the Brazilian government seems to be unaware of the submission of biochar to the UNFCCC (IBI, 2014). All in all, it appears that the international discourse may gain power with the new alliances. It is, however, too early to judge whether this might change the dominant discourse and current practices in Brazil.

Power network analysis

Power is constituted and exerted by actors in relationships. To define how much power each actor has, we used the actor's location and relationships in the network as parameters (Dahl, 2007). Location was determined by actors relations (centrality indexes: closeness, betweenness) and the relations with others surrounding actors (eigenvector). Three indexes - closeness, betweenness and eigenvector – are particularly revealing of an actor's advantageous or constrained location in the network. The combination of where an actor has easy access to others, while controlling the access of other actors in the network, reveals a high position of power within the network (Figure 2.3).

Embrapa experts are the most powerful actors in the Brazilian network (Figure 2.3). They are the most sought after connection to exchange resources with (closeness; Figure 2.3a), they are critical to collaboration across clusters and they maintain the spread of resources through the entire network (betweenness; Figure 3b). Furthermore, they are often public figures, playing roles of key opinion leaders and shaping public perception (eigenvector; Figure 2.3c). *Museu Paraense Emílio Goeldi* in Belém (Figure 2.1) forms a clearly distinct cluster in the network. It also has an obvious internal sub-division (Figure 2.2). This sub-division within the *Museu Paraense Emílio Goeldi* experts' cluster is a break between four ADE/biochar (Discourse coalition 1; Figure 2.2) actors on the upside, and eight biochar/technology (Discourse coalition 2; Figure 2.2) actors on the downside; their only connection is a key actor who shares expertise across both coalitions. Four ADE/biochar actors are distant from the whole network (closeness), and because they are connected only with one actor (betweenness) from the entire network, they could be easily cut-off. Consequently, due their marginal position and lack of connections, they are not central actors to the Brazilian biochar network (eigenvector). On the other hand, the eight biochar/technology actors have a higher density of connections with the network (closeness; Figure 2.3a). These connections place them in a better position, with more actors being able to access them (betweenness; Figure 2.3b). Even so, these are not

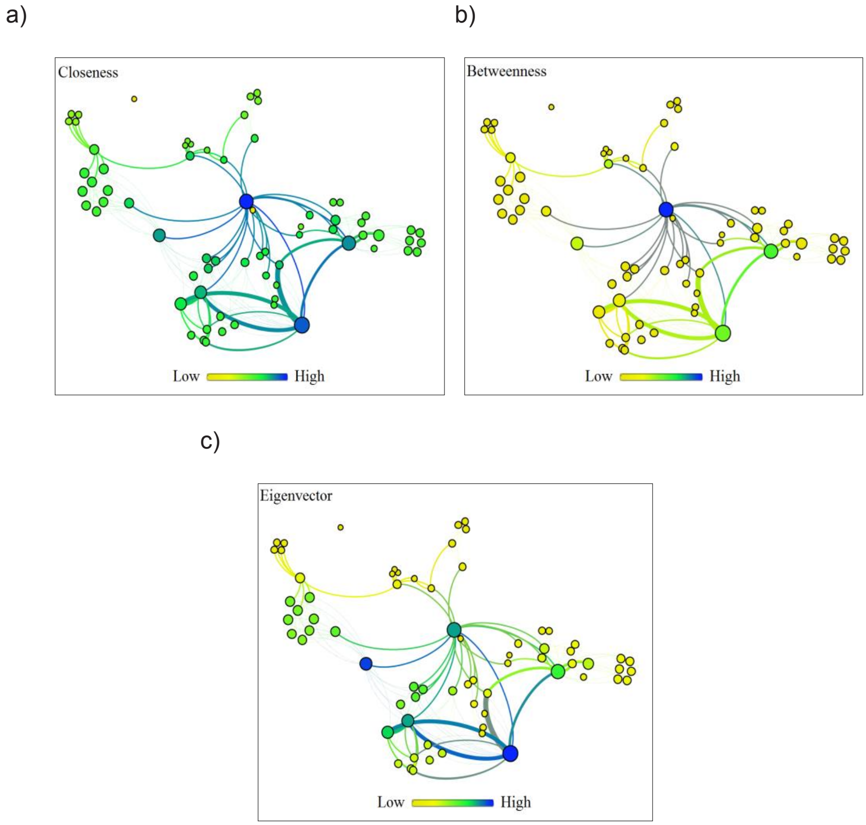

Figure 2.3 Indexes maps for actors' power in the Brazilian Biochar Network in 2011-2013. Individual actors (experts, companies, policymakers) are represented by the nodes and tight relationships by the edges. Size of nodes indicates the number of connections (degree) and length of edges indicates the strength of the connection. The larger the node, the more influential the actor is in the overall network. A = Closeness: actors who are highly connected to others will have a high closeness centrality. B = Betweenness: those who act as bridges between clusters in the network have high betweenness centrality. C = Eigenvector: highly connected actors to other high-profile actor have high eigenvector centrality.

key actors in the network (eigenvector; Figure 2.3c). *Mato Grosso* and *Piauí University* experts are closely associated with each other. Both clusters can be characterized as having a high possibility of exchange with each other, and a lower possibility of exchange with the rest of the network (closeness; Figure 2.3a). They have little influence on the flow of resources inside the network (betweenness; Figure 2.3b), and their importance to the entire network is relatively low. They are only relevant actors for their neighbour cluster (eigenvector; Figure 2.3c).

While *Embrapa* experts are able to mobilize and allocate resources, it is also evident that these resources are unequally divided among actors. Actors who have more marginal positions have consequently less resources and power in the network (Figure 2.3). This is shown by the relations of autonomy and dependency between actors. Actors with little or no power belong to organizations that entered in the network in the last period, such as *Inmetro*, or organizations that have a topic not closely related to the biochar research; for example the *Museu Paraense Emílio Goeldi* and INPA, which focus on *Amazonia Dark Earth* soils. On one hand, *Inmetro* tends to increase the number of connections in the network by developing biochar standards. On the other hand, organizations linked to *Amazonian Dark Earth* soils are likely to have less power in the coming years due to the shifting general discourse from ADE/biochar to biochar/technology (more details are given in section: *who drives the biochar forward in Brazil?*).

Our analysis of the emerging Brazilian biochar network suggests that a powerful expert network is developing which facilitates a more comprehensive study of biochar issues. The end result should be an enhanced ability to understand how biochar works, and which policy aspects should be considered to ensure its effective implementation. Whether effective policy for managing biochar and its potential benefits can be drawn up is dependent on the development of alliances with other sectors in society. These alliances are needed to validate such policy and to bring biochar's potentials to the market.

Institutional context and new rules in the making

Rules are the mutually agreed informal routines of interaction within organizations and formal procedures (Liefferink, 2006). As such, rules define those agents who are the ‘right’ ones to be involved, and those who are not. They define the interrelations between them, and thereby delineate the boundaries of actor coalitions or networks: who is ‘in’ and who is ‘out’; how one can gain access; what constitutes the relationship with outsiders. These rules describe how the game should be played: how issues may be raised, agendas set, interests articulated, policies formulates, decisions made and measures implemented.

In this context, no substantial change can be observed in the access rules of the Brazilian biochar network over the last 13 years. Since its inception, access has been open to all interested and concerned experts in biochar, but other potential stakeholders, such as farmers, companies and policy-makers, did not have direct access to the network; they seemed to remain outsiders or were not aware of the emerging biochar network. Policy-makers and companies had an interest in biochar arrangements, but the network did not embrace them. Likewise, farmers appear not to be aware of the debate surrounding biochar and its developments. This absence of potentially relevant parties can create barriers and delay the application of biochar in Brazil in the future. However, interaction rules *have* changed over time to some extent, because of a discursive shift and the sequential emergence of new discourse coalitions. While the discourse shifted from ADE/biochar to biochar/technology (see above), coalitions were reconfigured and reshaped. In particular, this shift enabled an increase in the number of experts. ADE/biochar is mainly studied by archaeologists and soil scientists, while biochar/technology is examined by a wider range of scientists, from soil and climate change scientists to pyrolysis and waste management experts. The biochar/technology discourse is therefore creating a new structure of social relations, in which knowledge is a powerful driver. Knowledge seems to discipline the social relations in the network. In other words, to have access to and enjoy interactions in the network one must possess knowledge and expertise to contribute to biochar development in a technical sense.

Rules as formal procedures consist of legislation, policies and programmes. Due to the multiple uses of biochar, a larger number of laws, programmes and procedures may affect the interaction between involved actors and biochar development as an agent for change. Based on the identification of the dominant discourses in the Brazilian context in the above section, the existing rules on climate change and agricultural waste are the most relevant ones to potentially impact the biochar policy arrangement. In this context, greenhouse gases reduction targets, low-carbon agriculture programmes and solid waste policies are therefore amongst the formal procedures that may have a primary importance for the current biochar arrangement.

In 2008, Brazil launched a *National Climate Change Policy* and, in 2009, the Brazilian government announced a voluntary target of a 36.1-38.9% reduction of total greenhouse gases (GHG) emission by 2020. A large part of GHG reduction is predicted to come from the agricultural sector. For this purpose, in December 2009 the Brazilian government announced "The Low-Carbon Agriculture Programme" as part of its commitment to cut projected carbon emissions. This programme aims to achieve CO_2 sequestration and a reduction in GHG emissions while also ensuring agricultural efficiency and food security.

In 2010, Brazil finalized its *National Solid Waste Policy*; this is a policy that intends to reduce the volume of agricultural waste produced nationally and increase the sustainability of solid waste management. This policy covers actors in many sectors, such as public, domestic, industrial, mining, agroforestry. Opportunities for new technologies or increased deployment of technology include used electronics recovery, compactors, organic waste digesters and composting, and organic packaging. Brazilian biochar experts are already examining the possibility of producing biochar from different solid waste, such as coconut shells, sugarcane bagasse and agroforestry residues. If they succeed, biochar may become a technology for reducing the volume of solid waste and increasing the sustainability of the agricultural and forestry sector.

These are agreements and policies introduced by the Brazilian government, which have been embraced, developed and reinforced by new coalitions of government, private enterprise and civil society. The support for all these goals might ultimately lead to the development of biochar-specific rules in Brazil in the near future.

2.4 Conclusion

We have linked the policy arrangement approach with social network analysis to analyze the emergent biochar policy arrangement in Brazil. This approach takes advantage of the four dimensions (actors, discourse, power and rules) of the policy arrangement approach, and the tools of network data analysis. Up until now, the Brazilian biochar debate has been driven by science experts. Policymakers, companies and farmers have so far remained marginal in the biochar network. Despite the homogeneity of clusters of actors in the network, relations of power are unbalanced. Experts from *Embrapa* occupy more prestigious and powerful positions than experts from other organizations. Even experts from the pioneer institute on *Amazonian Dark Earth* and biochar research *Museu Paraense Emílio Goeldi* currently remain in more marginal positions, without much influence on the whole biochar network. The main reason for this marginalization may be the discourse shift from ADE/ biochar to biochar/ technology.

The national discourse and discourse coalitions reveal the processes that have shaped biochar, and how this impacts on future developments and potentialities. First, ADEs has been reframed as biochar technology. Second, the understanding that biochar produced from crop residue can bring fertility to the soil has motivated Brazilian actors to engage with it, rather than only seeing biochar as a major solution for climate change mitigation. Third, the international discourse that equates biochar with the carbon market shows its emerging influence on the national discourse, and has created some ambiguity among Brazilian actors.

The last dimension consists of rules of the game, including informal routines of interaction and formal procedures. This analysis shows that knowledge disciplines informal routines of interaction in the network. To have access to and get involved in the network actors must have knowledge to contribute to a more comprehensive understanding of biochar. However, no formal biochar procedures exist as of yet. Therefore, established procedures and policies on climate change and solid waste management are of primary importance to the current biochar arrangement. Together they may lead to the development of biochar-specific rules in Brazil in the near future.

Chapter 3

Rapid decomposition of traditionally produced biochar in a sandy savannah soil

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Abstract

Soil amendment with pyrogenic organic materials (PyOM; biochar) has been claimed as an option for carbon (C) sequestration in agricultural soils. Most studies on PyOM/soil organic carbon (SOC) interactions were executed under laboratory conditions. Here we tested the stability of PyOM produced in a traditional kiln and its effects on the stocks of native SOC under field conditions. The PyOM was characterized using pyrolysis - gas chromatography - mass spectrometry, and then added to a sandy Ferralsol under savannah climate. This soil was amended with 0, 5, 10, 20 and 40 Mg ha^{-1} of PyOM in a randomized complete block design with four replications and cultivated with soybean over four cropping seasons (CS; 120 days each). Soil samples from the 0-10 cm top layer were collected at the end of the first and fourth CS and analysed for CO_2 emissions, isotopic C abundance ($^{13}C/^{12}C$ ratio) and enzymatic activity (fluorescein diacetate and dehydrogenase). The PyOM showed a low degree of thermal modification. Its relative decomposition rate was higher (0.32-1.00 year^{-1}) than generally claimed (0.005-0.0005 year^{-1}), and higher than the decomposition of native SOC (0.22 year^{-1}). Addition of PyOM did not affect the stocks of native SOC. Our findings highlight the need for critically reviewing the potential of locally produced PyOM to sequester C.

3.1 Introduction

Pyrogenic organic matter (PyOM), also named biochar, is the solid product of biomass combustion at low oxygen concentration. Soil amendment with biochar has been advocated as a climate-smart solution for agriculture, reducing atmospheric concentrations of carbon (C) dioxide (Woolf *et al*., 2010), thereby attracting the interest of the carbon market (Lehmann, 2007). When incorporated into the soil, PyOM is expected to contribute to the recalcitrant soil organic carbon (SOC) pool (Lehmann *et al*., 2006; Knicker *et al*., 2013). The decomposition rate of PyOM depends on the soil environment to which PyOM is applied. PyOM decomposes faster under warmer and drier than under cooler and moister conditions (Glaser & Amelung, 2003; Nguyen & Lehmann, 2009). In well-aerated tropical sandy soils PyOM can be degraded in decades (Bird *et al*., 1999; Zimmermann *et al*., 2012). These decomposition studies used PyOM (charcoal) produced by fire events (Bird *et al*., 1999; Glaser & Amelung, 2003; Nguyen *et al*., 2008; Zimmermann *et al*., 2012). It is not immediately evident that findings on charcoal degradation are relevant for the biochar debate. Findings of PyOM produced and incubated under controlled conditions cannot be easily extrapolated to field conditions. In order to apply and to scale up PyOM use to mitigate climate change, PyOM produced by traditional methods (e.g. in brick kilns) will have to be tested under field conditions. This is especially relevant in countries like Brazil, where such charring methods still predominate (Duboc *et al*., 2007). Currently, there is a lack of field data on decomposition rates of PyOM produced in traditional kilns.

Increases in CO_2 emission following PyOM additions in soils may result from the decomposition of part of the PyOM (Hilscher *et al*., 2009; Smith *et al*., 2010; Cross & Sohi, 2011; Jones *et al*., 2011; Zimmerman *et al*., 2011; Méndez *et al*., 2013; Sagrilo *et al*., 2014), suggesting that some PyOM may be less recalcitrant than expected (Knicker *et al*., 2013). In most studies however, it is not possible to distinguish whether the increased production of CO_2 after PyOM addition is due to degradation of PyOM and / or of SOC. Isotope analysis is an effective way to identify the origin of the C in PyOM-amended soils. Only few studies (Smith *et al*., 2010; Cross & Sohi, 2011; Hilscher & Knicker, 2011; Luo *et al*., 2011; Zimmerman *et al*., 2011; Méndez *et al*., 2013) used it to distinguish the origin of evolved CO_2 from PyOM-amended soils or the nature of the remaining C in the soil. However, these studies were performed predominantly under laboratory conditions and for short periods.

There is a lack of data from field experiments lasting for more than one cropping cycle. In our field study, we aimed to quantify changes in the PyOM and SOC stocks over four soybean cropping seasons (CS) in a C_4 sandy Ferralsol amended with different rates of PyOM. The PyOM was produced from C_3 woody species using traditional local charring methods. The PyOM was characterized using pyrolysis - gas chromatography - mass spectrometry (Py-GC-MS). Changes in soil microbial activity were determined by changes in enzyme activity of fluorescein diacetate (FDA) and dehydrogenase (DHG). We used ^{13}C isotopic analysis to discriminate between SOC and PyOM as the source of CO_2 and to quantify the decomposition rates of native SOC and PyOM.

3.2 Materials and methods

Study site

An experiment was carried out at the field station of Embrapa Mid-North in Parnaiba (UEP-Parnaiba), Brazil (3°05’18’’S; 41°47’00’’W; 52 m altitude). Regional climate is ‘Aw’ type (tropical with a dry season), according to Köppen classification. Local annual mean temperature is 27°C, mean precipitation is 1,079 mm and relative humidity is 76.5% (Andrade Junior *et al*., 2005). Potential evapotranspiration (PET) was calculated using the software LocClim 1.10 (Figure 3.1). Crops are generally planted in February-March under natural rainfall conditions and harvested in June or July. The soil was a Ferralsol (Oxisol in the USDA Soil Taxonomy), overlaid by around 40 cm of sand, in which most plants rooted. The textural distribution of the topsoil was 886 g kg^{-1} of sand and 86 g kg^{-1} of clay dominated by kaolinite (1:1). The native vegetation was a Caatinga-coastal phase (Melo *et al*., 2004). From 1995 to 2007

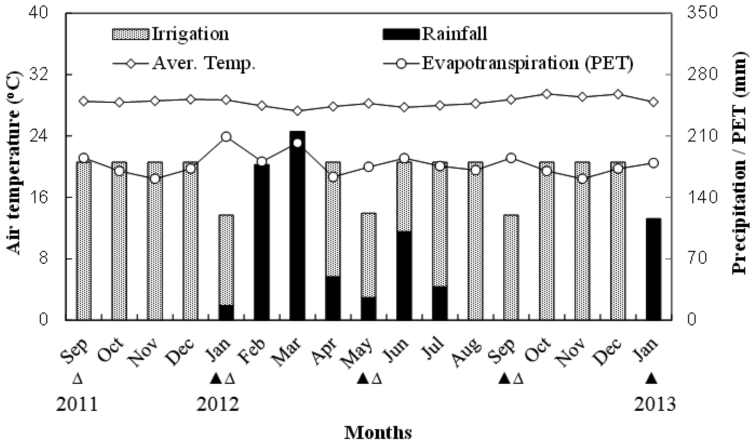

Figure 3.1 Monthly average temperatures and total monthly precipitation from rainfall and irrigation during the experimental period. Δ indicates the sowing events; ▲ indicates the harvest events.

an experiment with tropical grass species had been set up. From 2007 to the beginning of this experiment (September 2011), the area remained under fallow, with grass-dominated spontaneous vegetation, which was cut once per year. The residues were left on the soil surface.

In early September 2011, the soil was harrowed twice with a heavy harrow. Four blocks were distinguished in which experimental plots of 2.0 x 3.0 m were established allowing sprinkler lines between blocks 1-2 and 3-4. Additional sprinkler lines were maintained at each side of the experimental area. Coarse residues of grass on the plots were removed from the top 10 cm with hoes and rake in order to facilitate the PyOM mixing with soil and opening of furrows for planting. Seeds of soybean cultivar BRS-Tracajá, inoculated with a commercial *Bradyrhizobium japonicum* product were planted at a density of 14 plants m^{-1}, in five rows spaced 0.40 m from each other. Plots were 2.0 m apart. Soybean sowing took place at each 4-month interval (120 days), for four successive cropping seasons (CS1-4), which was made possible due to irrigation. Potassium (KCl) was applied each CS, and micronutrients were applied in CS3 and CS4. The year 2012 was unusually dry, with total rainfall of 625 mm - much lower than the average of 1,079 mm - and for this reason, even in the rainy season, irrigation took place regularly, except in February and March (Figure 3.1). Plant traits and management were done according to Sfredo (2008). After harvest of plants in each CS, soybean crop residues were removed from the plots.

Pyrogenic C production

The PyOM was produced from native woody savannah C_3 plants (eg. *Curatella americana*, *Tabebuia* spp., *Parkia platycephala*, *Caryocar brasiliense*) using a slow charring process (~48 h) in regionally used traditional kilns. Chemical properties of PyOM are provided in Table 3.1. These kilns (approximately 2.8 m high, 4 - 6 m diameter) are made from mud bricks and have a loading capacity of around 18 m^3 of feedstock.

Table 3.1 Chemical properties of the pyrogenic organic matter applied to the experimental site

...... pH		Ca	Mg	Al	H+Al	$P_{(Mehlich\ 1)}$	Exchangeable K	Cu
H_2O	KCl(1M)	.... g kg^{-1}				.... mg kg^{-1}		
7.2	6.15	1.86	0.37	0	0	126.5	1547	0.39

Zn	Fe	Mn	C_{tot}	N_{tot}	NH_4^+	NO_3^-	EC*
.... mg kg^{-1}...........			.... %		.... mg kg^{-1}		µs cm^{-1}
2.94	25.20	4.50	74.3	1.18	17.4	0	3573

* EC= Electrical conductivity (micro siemens cm^{-1})

Pyrogenic C characterization

Pyrolysis-GC-MS of the PyOM was performed at 750ºC for 10 s, with a heating rate of 10ºC ms^{-1}. This relatively high analytical pyrolysis temperature is the most suitable for PyC analysis using Py-GC-MS (Kaal *et al*., 2009). Briefly, a PyOM sample of 1–1.5 mg was placed in fire-polished quartz tubes with quartz wool on both ends and pyrolysed using a resistive heating Pt-filament CDS Pyroprobe 5250 Autosampler. The pyrolysis products were transferred into a 6890N gas chromatograph (Agilent Technologies) by He (1 ml min^{-1}) separated on a HP-5MS polysiloxane-based column (temperature program 60 – 325ºC at 20ºC min^{-1}, 5 min dwell time) and identified using an Agilent 5975B mass spectrometer operating in 70 eV electron impact mode.

The main peaks in the pyrolysis chromatograms (‘pyrograms’) were identified on the basis of Py-GC-MS literature of pyrogenic C and NIST’05 library, and quantified using their primary ion fragment or fragments (m/z). Relative proportions of each pyrolysis product are expressed as percentage (%) of total quantified peak area (TQPA).

Experimental design and characteristics of treatments

Five rates of PyOM (0, 5, 10, 20 and 40 Mg ha^{-1}) were applied once (in September 2011) to the respective plots sorted out in a randomized complete block design with four replications. Prior to its application, PyOM was crushed into small pieces and forced to pass through a 2 mm sieve. During field application, plastic canvases were used as wind barriers to prevent dispersion. PyOM was immediately incorporated into the top 10 cm of soil with hoes prior to soybean sowing. Also the control plots (0 Mg ha^{-1} PyOM) were hoed.

Soil sampling

After soybean harvest at CS1 and CS4, soil samples were collected from the 0 - 10 cm layer with an auger. From the three central planting lines within each plot, twelve soil cores were collected and pooled to form a composite sample for each treatment plot. These samples were sieved through a 2 mm screen to remove soybean roots, air-dried and stored at room temperature prior to chemical analyses. Undisturbed soil samples were also taken after CS4 from the 0-10 cm layer in order to determine soil bulk density as described by Sisti *et al*. (2004) for the calculation of SOC stocks.

Enzymatic activity

Fluorescein diacetate hydrolysis was determined according to the method of Swisher & Carroll (1980). Dehydrogenase activity was determined using the method described in Casida *et al*. (1964), which is based on the spectrophotometric determination of triphenyltetrazoliumformazan (TTF) released by 5 g of soil during 24 h at 37°C.

Field CO_2 emission measurements using IRGA

To quantify the soil CO_2 flux in the field, 10.3 cm-diameter and 6 cm-high PVC collars were inserted 2 cm into the soil in each field plot. Collars were inserted monthly from October-2012 to January-2013 (CS4) on the day before measurements to ensure that no overestimation of CO_2 emissions would occur due to recent soil disturbance. Irrigation of the plots ceased always on the afternoon of the same day of collars insertion, in order to ensure similar water content at every measurement. CO_2 flux measurements were performed always from 6:00 to 9:00 o'clock in the morning, to avoid large fluctuations in soil temperature. A portable infrared gas analyser (IRGA) LI-6400/LI-6400XT Version 6 (LI-COR, Lincoln, NE, USA) coupled to a Soil CO_2 Flux Chamber was used to quantify soil CO_2 emissions (Norman & Kucharik, 1997) at 15, 43, 71 and 106 days after plant emergence throughout CS4. At each measurement, values were corrected for ambient CO_2 concentration.

Carbon isotope analysis

After removing soybean plant fragments coarser than 2 mm by sieving, bulk soil samples were oven-dried at 65ºC, ground in a ball mill, and analysed for C content and ^{13}C abundance. The C contents and ^{13}C abundance of the soil samples was determined on aliquots containing between 200 and 400 μg total C using an elemental analyser coupled to a mass spectrometer Finnigan Mat Model delta-E. Results of natural abundance of ^{13}C were expressed in delta units, calculated as $\delta^{13}C$ $[(R_{sample}/R_{standard})-1]$ X 1000 (‰), where R_{sample} and $R_{standard}$ are the ratios of $^{13}C/^{12}C$ of the study sample and the reference standard, respectively.

We used the control treatments for the calculating the turnover in the SOC stock. We use the ^{13}C signature of the controls at CSW1 and CS4 for calculations of the PyOM stocks and decomposition rate. The relative contribution (%) of C derived from native SOC (C_{SOC}) and pyrogenic C (PyC) derived from PyOM was estimated from the ^{13}C abundance of the soil samples with the following formula (Balesdent & Mariotti, 1996):

$$C_{SOC} = (\delta^{13}C_M - \delta^{13}PyC)/(\delta^{13}C_{SOC} - \delta^{13}PyC)$$

where C_{SOC} is the proportion of C derived from the native SOC, $\delta^{13}C_M$ is the ^{13}C abundance of the PyOM-amended soil, $\delta^{13}PyC$ is the ^{13}C abundance of PyC and $\delta^{13}C_{SOC}$ is the ^{13}C abundance of the soil with soybean crop in CS1 (January 2012) or CS4 (January 2013).

We also calculated the stock of native SOC (0 - 10 cm) by the following formula:

$$S_{C4} = S_T \times C_{SOC}$$

where S_{C4} is the stock of C_4-derived carbon (Mg ha^{-1}), S_T the total C stock (Mg ha^{-1}).

Statistical analyses and calculations

Statistical analyses were performed using SAS 9.2 (SAS Institute, 2009). The stocks of native SOC and PyC (Mg ha^{-1}) across the different PyOM treatments and for both cropping cycles were analysed using a two-way ANOVA with the PROC GLM (α= 0.05). The relative decomposition rate of PyOM was estimated using the formula $k = -(ln\ S_{CS4} - ln\ S_{CS1})/(t_4 - t_1)$, where S_{CS4} is the PyOM-C stock after CS4, S_{CS1} is the PyOM-C stock after CS1 and t_4-t_1 is the time passed between the two sampling moments (one year). For the CO_2 emissions, an average value was calculated across the measurements. Emissions of CO_2 were expressed taking the total of soil organic matter (native SOC plus PyOM) in the control and treatments into account.

3.3 Results

Properties of PyOM

The major pyrolysis products and their relative abundances (% of TQPA) are provided in Table 3.2. Phenols were the most abundant compound group (28.6%) in the PyOM, representing primarily demethoxylated lignin. The second most abundant group was composed by monocyclic aromatic hydrocarbons (MAHs) – benzene, toluene, C2-benzenes and C3-benzenes –, which accounted for 13.7%. Polycyclic aromatic hydrocarbons (PAHs), including naphthalene, indenes, benzofurans, biphenyl, fluorene, phenanthrene and anthracene, accounted for 3.3%. The relatively large fractions of simple carbohydrates (13.0%) and lignin moieties (17.0%) indicated a low degree of thermal alteration.

Table 3.2 Pyrolysis product obtained from the quantification of major peaks in the pyrograms of locally produced PyOM . The relative proportions of the major groups are expressed as % total quantified peak (TQPA), average of two replicates

Pyrolysis product	% of TQPA
Acetic Acid	15.1
Benzofurans	2.4
Carbohydrates	13.0
Guaiacyl lignin	13.2
Syringyl lignin	3.8
Monocyclic aromatic hydrocarbon	13.7
Methylene chain compound	2.3
Nitrogen-containing compound	2.1
Polycyclic aromatic hydrocarbon	3.3
Phenol (including catechol)	28.5
Unidentified compounds	2.6

Native SOC and PyC stocks

The control soil collected at the end of CS1 and CS4 showed a ^{13}C abundance, respectively, of -18.51‰ (SE±0.2‰) and -20.31‰ (SE±0.2‰). Soybean showed a ^{13}C abundance of -26.50‰ (unpublished results) and PyOM of -28.66‰. Soybean productivity was not affected by PyOM treatments (Table S3.1; Supplementary information), and therefore, we assumed that soybean did not affect ^{13}C abundance differently among treatments.

Stocks of native SOC did not change significantly ($P = 0.6$) across the cropping seasons. Stocks of native SOC were also not significantly ($P = 0.138$) affected by PyOM addition rates. Stocks of PyC significantly increased ($P < 0.01$) with PyOM additions rates in both cropping seasons (Figure 3.2). They significantly ($P < 0.05$) decreased from CS1 to CS4 at all PyOM application rates. There was no significant PyOM x CS interaction ($P > 0.05$).

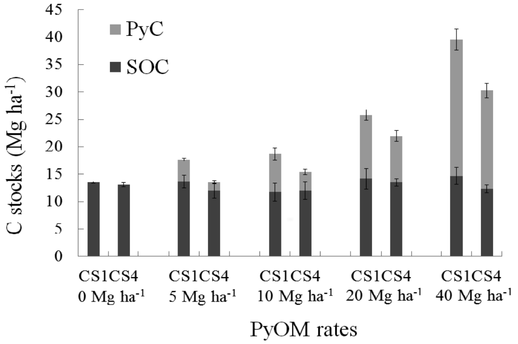

Figure 3.2 Soil organic carbon (SOC) and pyrogenic carbon (PyC) stocks at 1st and 4th cropping seasons (CS) in soil amended with different rates of pyrogenic organic matter (PyOM). Vertical bars are standard error of the mean (n=4).

Native SOC and PyOM decomposition rates

On the basis of the changes in ^{13}C signature of the controls, we calculated a relative decomposition rate for native SOC of 0.22 year^{-1}. PyOM decomposition tended to

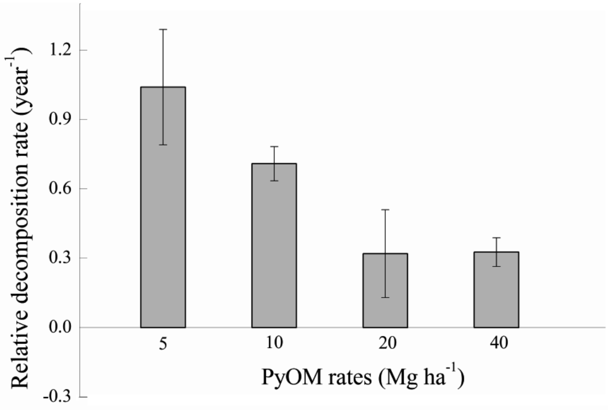

Figure 3.3 Relative decomposition rate (-k) between the 1st and 4th cropping cycle of pyrogenic organic matter (PyOM) in soils amended with different rates of PyOM. Vertical bars are standard error of the mean (*n=4*).

decrease with higher amounts of PyOM added to the soil (Figure 3.3), however the differences between the treatments were statistically not significant (P = 0.136). The relative decomposition rate, average over all PyOM treatments, was 0.32-1.00 year^{-1}, which is higher than that of native SOC.

CO_2 emissions from PyOM-amended soils

There were no significant differences in CO_2 emission between the different treatments. On a relative scale, therefore, the amount of CO_2 emitted per unit of soil C

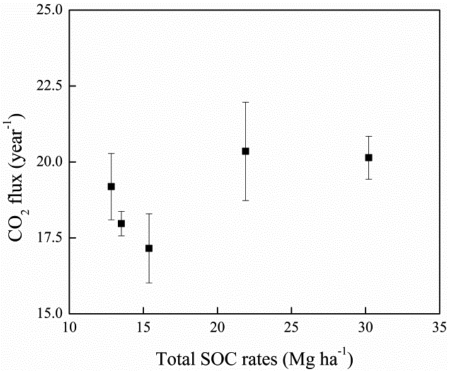

Figure 3.4 The CO_2 flux from soil organic carbon (SOC) amended with different rates of pyrogenic organic matter (PyOM) one year after application. Vertical bars represent the standard error of the mean (*n=4*).

(native SOC plus PyOM) declined (Figure 3.4), suggesting that the PyOM that was present at CS4 was degraded more slowly than the native SOC.

Enzymatic activity

There was no significant effect of PyOM rates, CS or their interaction on DHG activity (Figure 3.5a). For FDA, there was a significant (*$P<0.01$*) effect of the CS only (Figure 3.5b). The FDA activity was higher at the end of the CS1, compared to the CS4. No significant effects of PyOM or the PyOM x CS interaction were observed.

3.4 Discussion

The PyOM that was produced in a local traditional kiln was much less thermally altered than has generally been claimed for biochar. It is assumed (Swami *et al*., 2009) that such local kilns char material at around 500 °C. However, the characteristics of the material (Table 3.2) are similar to those of PyOM pyrolysed at 400ºC (Kaal *et al*., 2012). The proportion of MAHs (13.7% of TQPA; Table 3.2) is low for a PyOM produced at 500ºC (Kaal *et al*., 2012). The presence of lignin, including guaiacyls with an intact C3-side chain, is a further strong indication that a significant part of the lignin had undergone very little thermal rearrangement. PyOM produced in traditional kilns

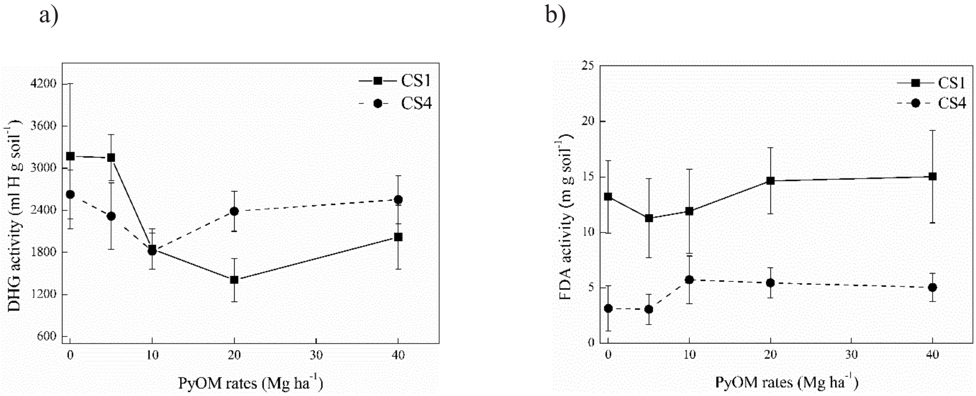

Figure 3.5 Enzymatic activity at different PyOM rates in the 1st and 4th cropping seasons. a= Dehydrogenase (DHG); b= Fluorescein diacetate (FDA). Vertical bars are standard error of the mean (*n= 4*).

is assumed to be similar to PyOM produced under optimal pyrolysis conditions in the laboratory (Lehmann *et al*., 2006). Our results show that PyOM produced in traditional kilns is not equivalent to that produced under laboratory conditions at similar pyrolysis temperatures, with major consequences for the assessment of its climate change mitigation potential.

The decay rate of PyOM was larger (0.32-1.0 year^{-1}) than the decay of the native SOC (0.22 year^{-1}; Figure 3.3). These results are in line with other field studies that also reported a high decomposition rate (0.01 to 0.38 year^{-1}) of PyOM (Bird *et al*., 1999; Nguyen *et al*., 2008; Major *et al*., 2010). These losses are much higher than the 10 to 20% within 5 - 10 years as proposed by Lehmann *et al*. (2006) and the decay rate (0.005 – 0.0005 year^{-1}) suggested by Kuzyakov *et al*. 2009 that were used to argue that PyOM (biochar) application sequesters substantial amounts of carbon.

It is an important issue how these large discrepancies in decomposition rate of biochar can be explained. Major *et al*. (2010) suggested that the large PyOM loss in their study was due to physical movement (leaching, run off) rather than biological degradation. In a two-year field experiment, they found a loss of PyOM ranging from 53% with low PyOM application rates (11.6 Mg ha^{-1}) to 20% with high application rates (116.1 Mg ha^{-1}), resulting in k values of 0.38 and 0.11 year^{-1} respectively. A small fraction of these losses was attributed to leaching (up to 1%). Surface runoff was suggested as the main explanation for PyOM loss, however the authors did not measure the runoff intensity.

In our study, decomposition was the most likely cause for the observed decrease in PyOM stocks (Figure 3.2). The experimental period was unusually dry, and except for 2 months (February and March 2012), water supply was complemented by irrigation (Figure 3.1). Irrigation avoided both excess water (and PyOM) leaching and surface runoff, as only enough water to meet crop requirements was applied. The absence of leaching is confirmed by potential evapotranspiration rates similar to the amount of water available to the crop (Figure 3.1). It is also unlikely that decreases in the PyOM stocks were caused by PyOM effects on soil bulk density, as this variable was not affected by the treatments (Table S3.1).

In addition to the quality of PyOM, its decomposition rate will depend on ecosystem properties, as suggested for SOC (Schmidt *et al*., 2011). In our field conditions, soil temperatures were high, there was no water limitation, and the soil was sandy with very low amounts of clay. In such environments, the decomposition of PyOM is likely fast. Bird *et al*. (1999) estimated PyOM half-life (for large particles, i.e > 2000 µm) in sandy soils as < 50 yr (equivalent to $k > 0.01$ year^{-1}). Zimmermann *et al*. (2012) estimated a half-life of 46 years (equivalent to $k > 0.01$ year^{-1}) for PyOM applied in tropical savannah environments. These estimates refer to fire-derived charcoal, however these estimates are comparable to ours on the long-term. PyOM tends to decompose faster in unsaturated and warmer environments than in saturated and colder environments (Glaser & Amelung, 2003; Nguyen *et al.,* 2008). Furthermore, in fine-textured soils, PyOM may be chemically and physically protected against decomposition similar to SOC (Schmidt *et al*., 2011), through interactions with mineral surfaces and aggregate formation. Pessenda *et al*. (2001) estimated a residence time of thousands of years for PyOM in fine-textured fossil soils. Therefore, lack of protection in sandy soils may have further enhanced the decomposition rates of PyOM in our study.

Our data highlight the rapid decomposition of a large fraction of PyOM produced under traditional methods. Data from Figure 3.4 suggest that after 1.5 years the remaining PyOM is composed of a recalcitrant fraction, as the emissions of CO_2 do not change with increasing amounts of applied PyOM.

Stocks of SOC were not affected by addition of PyOM, suggesting that PyOM addition unlikely causes loss of native SOC through priming. Negative priming was also not observed. These data are consistent with the absence of effects of PyOM addition on enzyme activities (Figure 3.5).

Both the study of Major *et al*. (2010) and our study suggest a decline in PyOM decomposition rates with increasing amounts added; however, in both cases the differences were not statistically significant. This possible effect merits further study, the more so because a meta-analysis by Sagrilo *et al*. (2015) provided evidence that the PyOM: SOC ratio was the major determinant in affecting the magnitude of the increase in CO_2 emissions of soil amended with PyOC. However, the estimates of the decomposition rate should be evaluated carefully. The ^{13}C isotopic differences between controls and PyOM treatments, where low amounts of PyOM (5 and 10 Mg ha^{-1}) were added, were relatively small, compared to the analytical error in ^{13}C measurements (c.v. = 2%, based on 12 measurements of the same standard sample), resulting in large confidence intervals in the estimate of PyOM decomposition.

In conclusion, we demonstrated, under field conditions, that locally produced PyOM can have high decomposition rates, comparable to or even higher than that of native SOC. We further conclude that in order to scale-up biochar projects for soil carbon sequestration, there is a need for further data from field experiments, in which locally produced PyOM is tested. This is especially relevant considering that such materials may be the most abundant form of PyOM in many countries like Brazil. Scaling up carbon sequestration potential of PyOM based on materials produced under controlled conditions and tested in the lab, may result in unwarranted confidence in biochar as a major contribution to climate change mitigation.

Supplementary Information (SI)

Table S3.1 Averages and P-values of plant (shoot dry mass and grain yield) and soil variables (bulk density) as affected by PyOM addition rates in the first and fourth cropping cycle

PyOM application rates (Mg ha^{-1})	Shoot dry mass (Mg ha^{-1})		Grain yield (Mg ha^{-1})		Bulk density (g cm^{-3})
	CS1	CS4	CS1	CS4	After CS4
0	2.05 a	1.89 a	1.35 a	2.52 a	1.49 a
5	1.58 a	1.84 a	1.26 a	2.17 a	1.50 a
10	1.75 a	1.75 a	1.80 a	1.85 a	1.54 a
20	1.12 a	2.08 a	1.29 a	2.08 a	1.46 a
40	1.41 a	1.96 a	1.37 a	1.87 a	1.50 a
P-values	0.32	0.06	0.36	0.19	0.27

Means followed by the same letters in columns do not differ by the Tukey test ($p>0.05$).

Chapter 4

Negative priming of native soil organic carbon by oilseed biochars of contrasting quality

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Rittl, T.F.; Novotny, E.H.; Balieiro, F.C.; Hoffland, E.; Alves, B.J.R; Kuyper, T.W. (2015). Negative priming of native soil organic carbon mineralization by oilseed biochars of contrasting quality. European Journal of Soil Science, doi: 10.1111/ejss.12257.

Abstract

Oilseed-derived biochar, a by-product of pyrolysis for biodiesel production, is richer in aliphatic compounds than commonly studied wood-derived biochar, affecting both its mineralization in soil and its interaction with native soil organic carbon (nSOC). Here, we investigated the soil C sequestration potential of three different oilseed biochars derived from C_3 plant material: soybean, castor bean and jatropha cake. The chemical composition of these biochars was determined through elemental analysis (CHN) and ^{13}C NMR spectroscopy. The cumulative CO_2 efflux from 30-day laboratory incubations of biochar mixed with a sandy soil containing nSOC from C_4 plants was measured as a proxy for mineralization rate. The relative contribution of each source to CO_2 production was calculated based on the ^{13}C-signatures of total CO_2 efflux and the source materials (soil and biochars). Our results showed that (i) castor bean biochar contained relatively high levels of aliphatic compounds, resulting in a higher mineralization rate compared to soybean and jatropha biochars; (ii) CO_2 efflux from the soil-biochar mixtures originated mostly from the biochars, suggesting that these biochars contain rapidly decomposable compounds; (iii) All three oilseed biochars decelerated nSOC mineralization. This negative priming effect appeared to be due to different factors. We conclude that oilseed biochars have the potential to directly raise soil C stocks and indirectly increase soil C sequestration in the short-term through negative priming of nSOC mineralization.

4.1 Introduction

The expanding production of biodiesel from oilseed by low temperature pyrolysis (below 400ºC) generates increasing amounts of by-product in the form of oilseed biochar. In Brazil, biodiesel production has increased from 70,000 m^3 in 2006 to 2.9 million m^3 in 2013 (ANP, 2014). Today, Brazilian biodiesel is mainly produced from soybean (*Glycine max* (L.) Merrill) (71%) and other oilseeds (9%) such as jatropha (*Jatropha curcas* L.) and castor bean (*Ricinus communis* L.), as well as from animal fat (20%). Despite the increased availability of oilseed-derived biochar, its potential to sequester soil C and its possible interactions with native soil organic C (nSOC) have not yet been investigated.

Biochar is the solid product of charring biomass, i.e. heating biomass with little or no oxygen at relatively low temperatures. Biochar is intentionally produced to be used as a soil amendment, which distinguishes it from other charring products, such as charcoal, pyrogenic carbon and black carbon produced for other purposes (Lehmann & Joseph, 2009). The charring process increases the quantity of aromatic compounds and aromatic ring condensation, such that the resulting biochar has a lower H:C molar ratio than the original biomass. These aromatic structures are more resistant to microbial and inorganic degradation than labile carbon compounds, and therefore biochar is claimed to be more recalcitrant than nSOC (Schmidt *et al*., 2011) and to have a greater potential than regular SOC to sequester C in soils. The charcoal found in the fertile Amazonian dark earths has been dated thousands of years old (Pessenda *et al*., 2001), suggesting that degradation of biochars currently added to soils may also be slow, contributing to carbon sequestration. Furthermore, the Amazonian dark earths have been found to contain higher levels of nSOC (i.e. native soil organic carbon not originating from charcoal) than adjacent charcoal-poor soils, which suggests that charcoal-amended soils support higher biomass production and hence greater soil organic matter input, and/or that charcoal addition to soils may decelerate nSOC mineralization, leading to enhanced nSOC preservation (Glaser *et al*., 2000).

Amending soils with organic materials may change the turnover rate of nSOC (Zimmerman *et al*., 2011), a non-additive effect known as 'priming' (Bingeman *et al*., 1953). This priming effect is called positive when addition of organic material accelerates nSOC mineralization, and negative when it decelerates nSOC mineralization. Biochars have been found to have positive priming effects (Luo *et al*., 2011; Farrell *et al*., 2013), as well as negative priming effects (Keith *et al*., 2011; Knicker *et al*., 2013), positive *and* negative priming effects (Zimmerman *et al*., 2011), and no effect on nSOC mineralization (Jones *et al*., 2012). These variable results are likely due to the different types and chemical qualities of the biochars investigated, as well as differences in soil characteristics, incubation conditions, and biochar application rates in these studies (Sagrilo et al., 2014).

The positive priming effect of biochar on nSOC mineralization has been attributed to the labile organic compounds left in biochar after pyrolysis (Cross & Sohi, 2011; Luo et al., 2011). Labile organic compounds have been found to enhance soil microbial activity, giving rise to increased mineralization of nSOC (Luo *et al*., 2011; Zimmerman *et al*., 2011; Bamminger *et al*., 2014; Watzinger *et al*., 2014). Negative priming effects, on the other hand, have been attributed to various factors, including (i) enhanced soil aggregate formation; (ii) microbial toxicity of biochars; (iii) sorption of enzymes and nSOC to biochar surfaces; and (iv) preferential mineralization of biochar over nSOC (Verheijen *et al*., 2009; Liang *et al*., 2010; Zimmerman *et al*., 2011; Bamminger *et al*., 2014; Whitman *et al*., 2014). Therefore, the chemical composition of biochar is expected to influence both the direction and magnitude of its priming effect (Fontaine *et al*., 2003), as well as its potential to sequester C in soils.

Oilseed-derived biochars may have a different effect on soil C sequestration than other types of biochars studied so far. Oilseeds are rich in lipids, which during pyrolysis may be decarboxylated to form aliphatic compounds (Chornet & Overend, 1985). Our hypothesis is that low temperature pyrolysis does not extract all fatty acids from the oilseeds, and hence produces biochar rich in aliphatics. As aliphatics are generally more labile than aromatics (Lehmann *et al*., 2003a), these compounds could influence the direction and magnitude of the priming effect of oilseed biochars. Furthermore, oilseeds may also contain toxic compounds; for example, jatropha biomass is rich in phorbol esters, which are known to be toxic to microorganisms and animals (Devappa *et al*., 2010a, 2010b). If these compounds are not degraded during low temperature pyrolysis, jatropha-derived biochar could inhibit the activity of soil microorganisms and hence affect mineralization processes.

In this paper we examine the short-term priming effects of three different oilseed biochars on nSOC mineralization: soybean, castor bean and jatropha. For this purpose we incubated these biochars during 30 days in air-tight jars with a sandy soil from a pasture area. We used the isotope ^{13}C signature technique (Pausch & Kuzyakov, 2012) to separate the CO_2-C efflux from these incubations into carbon originating from mineralization of nSOC (from C_4 plants) and carbon originating from mineralization of the added biochar (from C_3 plants).

4.2 Materials and methods

Biochars and Soil

Three types of oilseed (*Glycine max* – soybean seed; *Ricinus communis* – castor bean seed; and *Jatropha curcas* – jatropha cake; all C_3 plants) were subjected to low-temperature conversion (LTC) pyrolysis to produce biofuel and biochar. Details on process parameters have been presented elsewhere (Figueiredo *et al*., 2009; Vieira *et al*., 2009). In short, oilseeds and jatropha cake were dried at 75ºC in an oven for 24 h until constant weight, and then pyrolyzed under an N_2 atmosphere in an LTC reactor, in which the temperature was increased by 10ºC min^{-1} until reaching 380ºC, where it was kept for 3 h (Vieira *et al*., 2009).

Soil was collected at the experimental station of Embrapa Agrobiologia (Seropédica, Rio de Janeiro state, Brazil), from a pasture area grown with native C_4 grasses for (at least) the past 15 years. The natural vegetation of the region is Atlantic Forest. The soil was a Haplic Planosol (FAO Soil Taxonomy), with a sandy topsoil (~90% sand) with low CEC, SOC, clay and nutrient levels. For the experiment, soil was collected from the 0-20 cm layer and characterized as follows: pH_{water} 5.7; exchangeable Al, Ca and Mg: 0.23, 1.2 and 1.1 $cmol_c kg^{-1}$, respectively; available P (Mehlich 1) and K 20.6 and 35.0 mg kg^{-1}, respectively; and SOC 5 g kg^{-1}.

Chemical analyses

Elemental composition (CHN) of soil and biochar samples (5.0 ± 0.1 mg) was determined by the Dumas combustion method, using an elemental analyzer (PerkinElmer 2400). Acetanilide was used as reference material.

Mass spectrometry was used for determining the ^{13}C isotope signatures of the biochars, soil organic matter (nSOC) and CO_2-efflux (trapped in NaOH and precipitated as $CaCO_3$, see below) from the incubations. The ^{13}C natural abundances were determined using an elemental analyser coupled to a Finnigan Mat Model Delta-E mass spectrometer. Results were expressed in delta units, calculated as:

$$\delta^{13}C = [(Rsample / Rstandard) - 1] \times 1000\ (‰) \qquad (1)$$

where Rsample and Rstandard are the ^{13}C:^{12}C ratios of the analyzed sample and the standard of the analysis system, respectively (Sisti *et al*., 2004).

Solid-state ^{13}C NMR spectra of the three biochar types were measured with a VARIAN INOVA (11.74 T) spectrometer at ^{13}C and ^{1}H frequencies of 125.7 and 500.0 MHz, respectively. Samples were packed in 5 mm diameter cylindrical zirconia rotors with Kel-F rotor end caps. The employed pulse sequence was Variable-Amplitude Cross-Polarization. In this technique, protons (^{1}H nuclei) are polarized, after which this polarization is transferred to nearby C nuclei during the cross polarization time. Measurements were carried out using a Magic-Angle Spinning (MAS) of 15 kHz, a cross-polarization time of 1 ms, an acquisition time of 15 ms, a recycle delay of 500 ms and higher-power Two-Pulse Phase Modulation (TPPM) proton decoupling of 70 kHz. The cross-polarization time was chosen after variable contact time experiments, and the recycle delays were chosen to be five times longer than the longest ^{1}H spin–lattice relaxation time (T_1H) as determined by inversion-recovery experiments (Novotny *et al*., 2006a). For quantification, the spectra were deconvoluted (Wiedemeier *et al*., 2015) into 11 individual signals, using Voigt functions. The positions of the fitted bands were determined using second derivative methods. The fitted peaks were grouped into an alkyl region (peaks centred at 15, 24, 31 and 40 ppm) and an aryl region (peaks centred at 128; 143 and 157 ppm) (Novotny *et al*., 2006b). In this procedure, the partial overlap of residual di-O-alkyl groups and/or olefinic C (alkene sp^{2} C) in the 90-120 ppm region can be properly taken into account since the fitted peak around 106 ppm is not grouped with the aryl groups. The peak areas within each region were summed to calculate the relative contribution of each functional group (region) to total C as a percentage of the total spectrum area.

Design of incubation experiment

Two-litre incubation jars were filled with 100 g of sieved (<2 mm), air-dried soil (amounting to 0.5 g nSOC per jar). To each jar (except the controls) the equivalent of 32 Mg biochar ha^{-1} (~1.04 g of biochar per 100 g soil) was added and mixed with the soil. Treatments (soil + soybean biochar, soil + castor bean biochar, soil + jatropha biochar) and controls (unamended soil) were in triplicates. The moisture of the soil (or soil-biochar mixture) in the jars was adjusted to 60% field capacity and maintained at that level throughout the experiment. Prior to incubation, to avoid CO_2 contamination from the atmosphere, the jars were sealed using a lid with a rubber ring fitted into its inside rim. Treatments and controls were incubated in a Biochemical Oxygen Demand incubator at 28 °C during 30 days (700 hours) in the dark. To evaluate the mineralization rate in the biochar-soil mixtures, the CO_2 efflux and its ^{13}C isotopic signature were measured and compared to the controls without biochar addition.

Biochar and nSOC mineralization

The CO_2-C efflux from each jar was measured on day 0, 1, 2, 5, 9, 16, 23 and 30, using the alkali-trapping method (Schweizer *et al*., 1999). To this end, each jar was permanently connected to an external trap containing 20 mL of 0.31 M sodium hydroxide (NaOH). On each sampling date, each trap was emptied and the NaOH solution divided into two samples: 5 mL for quantifying CO_2 respiration through back-titration with HCl after carbonate precipitation with $BaCl_2$; and 15 mL for ^{13}C analyses. For ^{13}C analyses, CO_2-C trapped in NaOH was precipitated as $CaCO_3$ with 1 mL of 5.5 M $CaCl_2$, and this was bulked into one sample (all sampling dates together) per treatment for ^{13}C analysis. After each sampling all traps were refilled with fresh NaOH solution and soil moisture in all jars adjusted to 60% field capacity (see above).

Calculations

The relative contributions of biochar mineralization (f_b) and nSOC mineralization (f_{SOC}) to the CO_2 efflux from the incubated jars over 30 days were calculated using a two-component isotopic mixing model (Cheng *et al*., 2008; Liang *et al*., 2008; Zimmerman *et al*., 2011) and the measured $\delta^{13}C$ values of the CO_2 efflux and source materials (i.e. C_4 nSOC and C_3 biochar):

$$f_b = (\delta^{13}C_{mixture}\, CO_2 - \delta^{13}C_{SOC}CO_2)/(\delta^{13}\, C_{biochar} - \delta^{13}C_{SOC}CO_2) \quad (2)$$

and

$$f_b + f_{SOC} = 1 \quad (3)$$

where $\delta^{13}\, C_{biochar}$, $\delta^{13}\, C_{mixture}\, CO_2$, and $\delta^{13}C_{SOC}CO_2$ are the C stable isotopic ratios of, respectively, the biochar, the CO_2 efflux from biochar-soil mixtures and the CO_2 efflux from unamended soil (control).

The direction and magnitude of the priming effect of biochar on nSOC mineralization was calculated as the difference between the CO_2 efflux from soil-only incubations and the $CO_{2\text{-}nSOC}$ efflux from soil-biochar mixtures, estimated with the two-component isotopic mixing model as $CO_{2\text{-}nSOC} = f_{SOC} * CO_{2\text{-}mixture}$.

Because of carbon fractionation during mineralization, the ^{13}C abundance of the CO_2 emitted by the treatments may differ from that of the original plant material (Werth & Kuzyakov, 2010). To account for this effect on the mineralization rate of biochar, we first calculated the level of fractionation in the control treatment based on the difference between the ^{13}C signature of the soil (nSOC) and the ^{13}C signature of the product of its mineralization (i.e. the CO_2 efflux from control jars). The resulting figure was used to calculate the potential fractionation of the three oilseed biochars. Next, we calculated the relative contribution of the two sources of CO_2 in the soil-biochar mixtures using two models, assuming either 1) no fractionation of biochar-C during mineralization or 2) fractionation of biochar-C to the same extent as calculated for nSOC.

The relative mineralization rate of the oilseed biochars was estimated using a first order single component exponential decay equation:

$$k = (\ln \text{biochar}_0 - \ln \text{biochar}_{30})/(t_{30}-t_0) \qquad (4)$$

where biochar_0 is the C content of the biochar; biochar_{30} is biochar_0 minus the total amount of CO_2-C released from biochar mineralization over 30 days (f_b * $CO_{2\text{-mixture}}$); and t_{30}-t_0 is the incubation time expressed in days.

Statistics

Measurements and derived data (CO_2 efflux, priming effect and relative mineralization rate) were subjected to multivariate analysis of variance (MANOVA). The Newman-Keuls test was used for comparing the means when the multivariate F ratio was significant ($P \leq 0.05$).

4.3 Results

Chemical characterization

The C contents of the biochar samples ranged from 50.2 to 59.7% (Table 4.1). The C:N ratio was lowest in soybean biochar and highest in castor bean biochar. The H:C ratio, which reflects the degree of thermal modification of the biochar and is an indirect measurement of aromatic polycondensation (Keiluweit *et al*., 2010) was highest in castor bean biochar and lowest in soybean biochar. Chemical analysis of the soil showed low contents of C, H, and N, a C:N ratio of 7.7 and a H:C ratio of 2.0. The ^{13}C signature of soil C (nSOC) was -15‰, which confirms that the organic matter mainly originated from C_4-plants. The ^{13}C signature of the biochar samples ranged from -26.5 to -27.0‰, which is typical for C_3 plants (Table 4.1).

Table 4.1 Elemental composition and ^{13}C signatures of biochars and soil used in the experiment

Source	C%	H%	H:C	N%	C:N	δ‰ ^{13}C
Castor bean biochar	57.58	5.27	1.10	4.18	13.78	-26.6
Jatropha biochar	50.21	3.76	0.89	3.75	13.39	-27.0
Soybean biochar	59.68	4.18	0.84	6.29	9.48	-26.5
Soil only	0.54	0.09	2.00	0.07	7.71	-15.1

The solid-state ^{13}C NMR spectra of the three oilseed-derived biochars investigated in this study are presented in Figure 4.1. In all cases, the spectra were dominated by a featureless broad band from aromatic (aryl) groups centred at 128 ppm, and a band from alkyl groups (45-0 ppm) with a dominant peak at 31 ppm, typical of amorphous poly(m)ethylene-like chains (Hu *et al*., 2000). Jatropha biochar contained more aromatic carbon (64%) than soybean (54%) and castor bean (48%) biochars, whereas castor bean biochar contained the most alkyl carbon (37%). The relatively high levels of amorphous alkyl groups in the oilseed biochars suggest that at a significant amount of fatty acids were decarboxylated during pyrolysis, indicating that pyrolysis is not very efficient in extracting fatty acids from soybean, castor bean and jatropha cake.

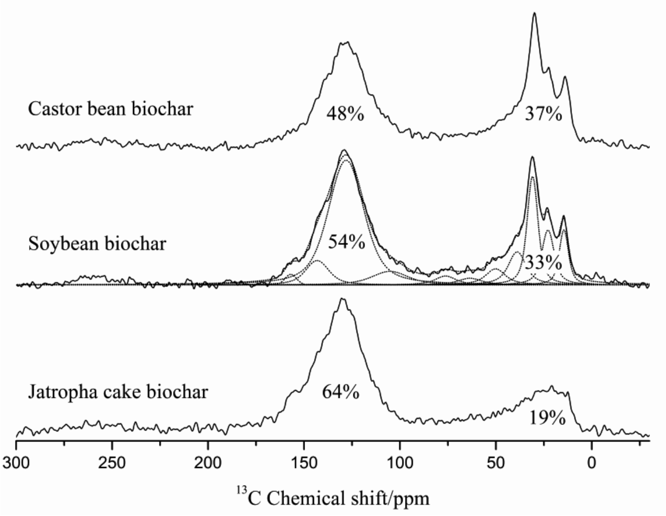

Figure 4.1 Solid-state ^{13}C NMR spectra of three oilseed biochars produced by low temperature pyrolysis (380ºC) of castor bean, soybean and jatropha cake. The spectra show two broad bands, representing aromatic (160-100 ppm) and aliphatic (50-0 ppm) compounds. The dotted lines indicate the fitted peaks used for quantification of chemical groups. Percentages (%) refer to the relative contribution of aromatic and aliphatic areas to total spectrum area.

Total carbon mineralization

Total cumulative CO_2 efflux over 30 days from the biochar treatments ranged from 26 (jatropha biochar) to 112 µg C (castor bean biochar) (Figure 4.2). While the soybean biochar treatment showed a similar CO_2 efflux pattern and cumulative soil respiration as the control treatment, castor bean biochar increased cumulative soil respiration by 46 µg C, whereas jatropha biochar decreased soil respiration by 40 µg C. In the latter, soil respiration was extremely low until day 16 of the incubation, after which CO_2 efflux slowly increased, at a lower rate than in the other treatments including the control (Figure 4.2).

Biochar-derived versus soil-derived CO_2

The ^{13}C signature of the CO_2-C emitted from soil-biochar mixtures over 30 days (Table 4.2) was more similar to the ^{13}C signature of the original biochar material than of the unamended soil (Table 4.1); for all soil-biochar mixtures the ^{13}C signature of the CO_2-C efflux was around -22‰, despite the significant differences in total respiration between treatments. Depending on which fractionation model was used for calculating the contribution of the two sources in the mixture (nSOC + biochar), biochar contributed 52 - 65% (castor bean), 44 - 55% (jatropha) or 47 - 59% (soybean) to total respiration, while nSOC contributed 35 - 56%.

Priming effect

Addition of biochar to the soil reduced the amount of CO_2 emitted from nSOC mineralization compared to the control (Figure 4.3). This negative priming effect was found for all three oilseed biochars tested, although the magnitude of the effect varied significantly between biochars (Figure 4.3). The same pattern emerges from the relative mineralization rate (-k) of nSOC, which was significantly lower in the biochar-amended soils compared to the control soils (Figure 4.4). Jatropha biochar had the strongest negative priming effect on nSOC mineralization rate ($2.43\ 10^{-4}$ year^{-1}; a reduction of 82% compared to the control), followed by soybean biochar ($7.03\ 10^{-4}$ year^{-1}; 58%) and castor bean ($1\ 10^{-3}$ year^{-1}; 40%). Figure 4.4 also shows that the relative mineralization rates of the biochars themselves differed significantly from each other, with the lowest rate found for jatropha ($3.81\ 10^{-4}$ year^{-1}) and the highest for castor bean biochar ($1.65\ 10^{-3}$ year^{-1}). Furthermore, the mineralization rates of both soybean ($8.66\ 10^{-4}$ year^{-1}) and jatropha biochars were significantly lower than found for nSOC (in soil-only controls: $1.69\ 10^{-3}$ year^{-1}), while the mineralization rate of castor bean biochar was similar to nSOC.

Table 4.2 ^{13}C signatures of total CO_2-C efflux over 30 days from each treatment, and the relative contribution of each source (soil versus biochar) to total CO_2-C efflux

Treatments	δ‰ ^{13}C	Relative contribution to total CO_2-C efflux (%)	
	CO_2-C efflux	Biochar	Native SOC
Castor bean biochar + soil	-23.0	52-65	48-35
Jatropha biochar + soil	-22.2	44-55	56-45
Soybean biochar + soil	-22.4	47-59	53-41
Soil only	-16.5	___________	100

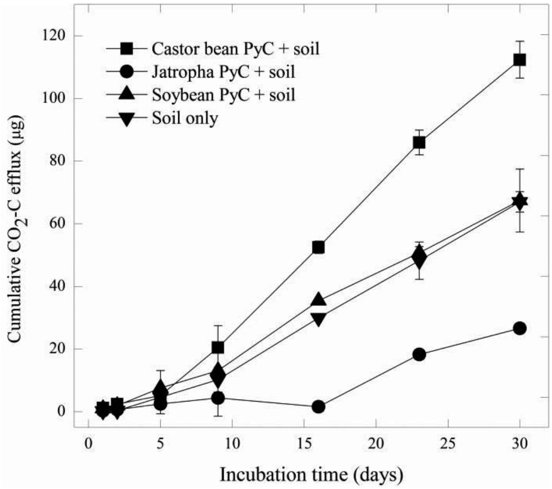

Figure 4.2 Cumulative CO_2-C efflux from 30-day laboratory incubations of sandy soil and three oilseed biochars (castor bean, soybean and jatropha cake). Vertical bars are standard errors of the means (n=3).

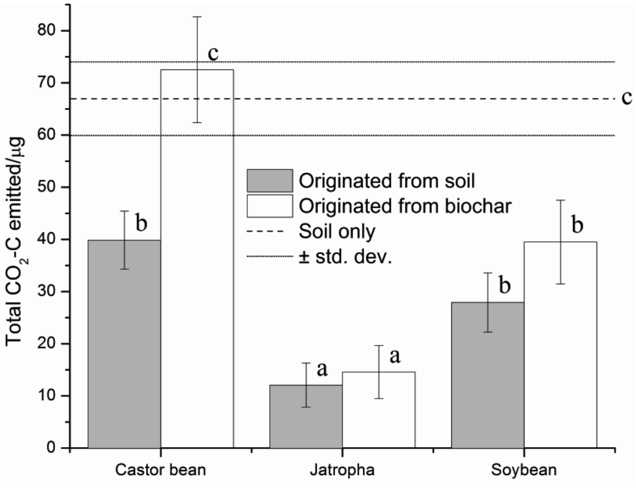

Figure 4.3 Total CO_2-C efflux from 30-day laboratory incubations of sandy soil and oilseed biochars (castor bean, soybean and jatropha cake), divided by CO_2 source (nSOC versus and biochar), assuming fractionation of nSOC only. The dashed line indicates total CO_2-C efflux from the control (soil only). Vertical bars are standard errors of the means (*n=3*). Dashed line and columns with the same letters do not differ at p=0.05 by the Newman-Keuls test.

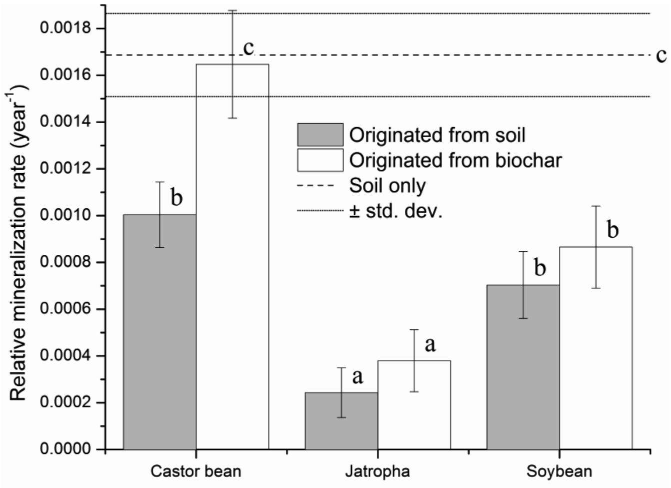

Figure 4.4 Relative mineralization rate (-k) of oilseed biochars (castor bean, soybean and jatropha cake) and nSOC in 30-day laboratory incubations. The dashed line indicates the relative mineralization rate of nSOC (soil-only control). Vertical bars are standard errors of the means (*n=3*). Dashed line and columns with the same letters do not differ at p=0.05 by the Newman-Keuls test.

4.4 Discussion

Negative priming effect

All three oilseed biochars decelerated the mineralization of nSOC (Figures 4.3 and 4.4). This negative priming effect was strongest for jatropha biochar, followed by soybean biochar and weakest for castor bean biochar. In the jatropha treatment, nSOC mineralization (cumulative CO_2-C efflux from nSOC over 30 days) was reduced by 82% compared to nSOC mineralization in unamended soil (Figure 4.3). Even though total CO_2 efflux increased considerably after addition of castor bean biochar (Figure 4.2), this biochar slowed down nSOC mineralization (Figure 4.4); the increased CO_2 efflux was entirely due to mineralization of biochar.

Short-term negative priming of nSOC mineralization by oilseed-derived biochars has not been demonstrated before, but is consistent with studies on biochars derived from other materials, such as grass and wood (Keith *et al*., 2011; Zimmerman *et al*., 2011).

Hence, negative priming effects are not limited to a particular type of biochar. Short-term negative priming has been attributed to various factors, including microbial toxicity of biochar (Verheijen *et al*., 2009), sorption of enzymes and nSOC to biochar surfaces (Zimmerman *et al*., 2011), and soil microbial communities switching from nSOC to more labile (Whitman *et al*., 2014) and accessible (Mondini *et al*., 2006) components of biochar.

In the case of the three oilseed-derived biochars investigated in this study, negative priming appears to be caused by various mechanisms. In the jatropha treatment, the suppressed CO_2 efflux during the first 16 days of incubation (Figure 4.2) suggests that toxic compounds were inhibiting microbial activity. Fresh jatropha biomass contains phorbol esters, which are toxic to animals and microorganisms (Giibitz *et al*., 1999; Devappa *et al*., 2010b). These toxins may have withstood LTC pyrolysis and remained in the jatropha biochar. The fact that CO_2 efflux from the jatropha biochar treatment picked up after 16 days (Figure 4.2) is consistent with findings that phorbol ester compounds are biodegraded in soil within 3 weeks (Devappa *et al*., 2010a; Joshi *et al*., 2011).

We did not find indications of microbial toxicity of the other two biochars investigated. The CO_2 efflux from the castor bean and soybean biochar treatments started to increase after 5 days of incubation (Figure 4.2), similar to the unamended soil (control). However, the relatively large contribution of biochar-derived C to total CO_2-C efflux (Figure 4.3) suggests that the soil microbial community preferred biochar over nSOC. Furthermore, we cannot exclude that sorption of enzymes and nSOC to biochar also played a role in suppressing nSOC mineralization.

Biochar quality and mineralization

The C:N and H:C ratios of the oilseed-derived biochars investigated in this study did not appear to be the main drivers of their mineralization. Castor bean and jatropha biochars had similar C:N ratios (Table 4.1), but had significantly different mineralization rates in the soil-biochar mixtures (Figure 4.4), whereas soybean biochar, with the lowest C:N ratio, showed an intermediate mineralization rate. Likewise, jatropha and soybean biochars had similar H:C ratios but differed significantly in their mineralization rates. These findings do not correspond with other studies, which found that, plants residues with low C:N ratio (e.g. Manzoni *et al*., 2008) and biochars with high H:C ratio (e.g. Budai *et al*., 2013) decompose more rapidly. In our experiment, it appears that the relative content of aliphatics in the oilseed biochars (Figure 4.1) was a better predictor of biochar mineralization.

^{13}C NMR spectrum analysis confirmed our hypothesis that oilseed biochars produced by LTC pyrolysis are relatively rich in aliphatic compounds. Although the aliphatic fraction was smaller than the predominant aromatic fraction, it was substantial in all oilseed biochars investigated (19-37%; see Figure 4.1). Aliphatic fractions in non-oilseed-derived biochars (produced by similar low temperature (380ºC) pyrolysis) are usually around 10% (Rutherford *et al*., 2012). The relatively high aliphatics contents of our oilseed biochars may be characteristic of a wider range of oilseed-derived biochars produced by low temperature pyrolysis.

The biochar with the largest aliphatic fraction, i.e. castor bean biochar, decomposed fastest (Figures 4.1, 4.3 and 4.4). In our study it was not possible to distinguish between the CO_2-C efflux from aliphatic versus aromatic fractions. However, we did observe a consistent pattern between aliphatics content and CO_2 efflux: castor bean biochar had both the largest CO_2 efflux (72 μg C; Figure 4.3) and largest aliphatic fraction (37%; Figure 4.1), followed by soybean biochar (40 μg C; 33%) and jatropha biochar, the latter of which had both the lowest CO_2 efflux (15 μg C) and smallest aliphatic fraction (19%).

In terms of relative mineralization rates (Figure 4.4), castor bean biochar and nSOC (control) were found to decompose faster (-k around 1.65 10^{-3} year^{-1}) than jatropha biochar (3.81 10^{-4} year^{-1}) and soybean biochar (8.66 10^{-4} year^{-1}). The k-values for oilseed biochar correspond to a loss of between 0.003% and 0.012% over 30 days under laboratory conditions. This is significantly lower than the values observed by Hamer *et al*. (2004) for non-oilseed biochars in a similar incubation experiment, measuring a loss of 0.53% for maize biochar and 0.46% for rye biochar over a period of 26 days.

Due the short-term nature of our incubation experiment, it is not possible to estimate the mean residence time of oilseed biochars in soils. However, the relatively low mineralization rates found in our experiment suggest that oilseed biochar soil amendments could enhance soil organic matter levels and increase soil carbon sequestration in the short-term.

4.5 Conclusion

Relative content of aliphatic compounds appears to be a better predictor of oilseed biochar mineralization rate than C:N and H:C ratios. Of the three oilseed biochars investigated, castor bean biochar contained the highest levels of aliphatic compounds and mineralized faster than soybean and jatropha biochars. Using stable isotope analysis we demonstrated that the investigated biochars reduced nSOC mineralization (negative priming effect). All three biochars (soybean, castor bean and jatropha cake) were preferentially mineralized over nSOC, resulting in a lower mineralization rate of nSOC in soil-biochar mixtures than in soil-only controls. Therefore, oilseed biochars have the potential to increase soil C sequestration by raising the quantity of C in soil and – at least in the short term – by negative priming of nSOC mineralization.

Chapter 5

Fast method of liquid chromatography for pyrogenic carbon quantification and characterization through BPCA determination

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Abstract

The characterization and quantification of the carbonaceous polyaromatic structure of pyrogenic carbon (PyC) are of paramount importance to evaluate the role of PyC in soil carbon sequestration. Rapid resolution liquid chromatography with UV diode array detection (RRLC-UV-DAD) is proposed as a new method to quantify benzene polycarboxylic acids (BPCAs). BPCAs are considered molecular markers of the polycondensed aromatic structure of PyC. The proportion of aromatic carbon structures and the condensation degree obtained from different PyC, i.e. different biomass pyrolysed at different final temperatures (350-550ºC) were quantified with RRLC-UV-DAD and ^{13}C-NMR. Our results showed that (i) the analysis using RRLC-UV-DAD takes one quarter of the analysis time of conventional HPLC and half of the time of the GC analysis, increasing throughput; (ii) the optimized method showed high overall precision, reproducibility and (iii) plausible PyC values comparable to those obtained using ^{13}C-NMR method spectroscopy assisted by multivariate curve resolution; (iv) PyC produced from different biomasses showed a wide range of BPCA yields and patterns.

5.1 Introduction

Pyrogenic carbon (PyC) is the solid product resulting of incomplete combustion of organic materials. The deliberately application in soil of PyC (known as biochar and produced by pyrolysis) has been suggested as an alternative to increase the carbon stocks of soil. The PyC application in soil can contribute to increase the most recalcitrant component of the soil organic matter (Smernik *et al*., 2000). The potential of PyC for carbon sequestration in soils depend on the concentration of polycondensed aromatic units in PyC (Novotny *et al*., 2009a; Singh *et al*., 2012).This chemical characteristic confers a high recalcitrance (resistance to degradation) to PyC (Novotny *et al*., 2009a; Singh *et al*., 2012), making it more suitable to sequester carbon in soil than ordinary soil organic matter (Maia *et al*., 2011). Therefore, the characterization and quantification of polycondensed aromatic structures is important to assess the chemical quality of PyC, and to infer about PyC persistence in the environment. Furthermore, the quantification of these structures in PyC is an analytical challenge because PyC is not a compound with a defined chemical structure (Masiello, 2004), but rather more a continuum of materials (Preston & Schmidt, 2006) with different proportions of polycondensed aromatic structures.

Depending on pyrolysis temperature and substrate properties, the final concentration of polycondensed aromatic varies (McBeath *et al*., 2014). PyC produced at high temperatures is richer in polycondensed units than PyC produced at low temperatures (Schneider *et al*., 2010; McBeath *et al*., 2011). Although PyC can be produced from different starting materials, it is not clear how the characteristics of starting materials may determine the concentration of polycondensed structures in PyC (McBeath *et al*., 2014).

The polyaromatic structure of PyC is often characterized using solid-state ^{13}C-NMR spectroscopy (Novotny *et al*., 2007; Knicker, 2011; McBeath *et al*., 2011, 2014) that quantifies the aromatic fraction of total PyC (aromaticity) as the concentration of aromatic functionalities (110-145 or 110-160 ppm) relative to the total area under the spectra (Novotny *et al*., 2009b). However, untransformed (non-pyrolysed) compounds from the starting materials containing aromatic groups such as lignin and tannins, that can bias and lead to misinterpretations of PyC data (Novotny *et al*., 2009b). To prevent this problem, mathematical treatments of data, such as multivariate curve resolution (MCR) can be employed (Novotny & Bonagamba, 2009). The MCR determines the number of components that co-exist in the chemical system and extracts their pure spectra for qualitative analysis and concentration profiles of each component for quantitative analysis (Novotny *et al*., 2009b). Even thus, ^{13}C-NMR is considered a semi-quantitative, expensive and time-consuming analytical technique and its use for routine quantification analysis is not recommended.

Another method of characterization and quantification of PyC is based on the determination of the benzene polycarboxylic acids (BPCA) produced after chemical oxidation of the PyC samples. The BPCAs are specific molecular markers of condensed aromatic structures typically occurring in PyC (Glaser *et al*., 1998; Brodowski *et al*., 2005). This method converts polycondensed aromatic structures in PyC to single benzene rings. The single benzene rings contain 3 to 6 carboxylic acid groups (B3CA, B4CA, B5CA and B6CA) derived from the oxidation of adjacent aromatic rings or side chains (Ziolkowski *et al*., 2011). The number of carboxyl groups present in each BPCA is directly related to the condensation degree of PyC. Therefore, the individual contributions of BPCA (Figure S5.1) can be used to determine the aromaticity (proportion of aromatic C) and polyaromatic condensation (size of aromatic C structure) of PyC (Hammes *et al*., 2008; Schneider *et al*., 2010).

The BPCA method originally proposed (Glaser *et al*., 1998) has been employed in the quantification of PyC in charcoals, soils and sediments over the past decade (Glaser *et al*., 2000; Czimczik *et al*., 2003; Glaser & Amelung, 2003; Rodionov *et al*., 2006; Brodowski *et al*., 2007; Hammes *et al*., 2008). However, a study involving 17 laboratories revealed that the many steps need to clean up, transfer and derivatize the BPCA prior to quantification by gas chromatography (GC), may result in disparate results (Hammes *et al*., 2007; Schneider *et al*., 2011a), which may vary from 0 to 43%, depending on the material analysed.

Dittmar (2008) determined PyC in seawater using high-performance liquid chromatography (HPLC) with diode array UV detection (HPLC-UV) to analyze BPCA. This analytical technique avoided the critical cleaning and derivatization steps necessary for GC analysis (Glaser *et al*., 1998). A major advantage of the HPLC-UV method is that minimal sample processing and no derivatization are required, reducing the potential risk of methodological artifacts and errors (Dittmar, 2008). Schneider *et al*., 2011a compared the efficiency of the GC with a flame ionization detector (FID) and HPLC with photodiode array detector (DAD) methods in determination of BPCA. According to them, the HPLC-DAD method is more robust for BPCA quantification than GC-FID, although it is time consuming(Schneider *et al*., 2011a). The best BPCA separation took 90 min and the fastest one 60 min (Dittmar, 2008). In this context, rapid resolution liquid chromatography (RRLC) may be advantageous over HPLC (Mazzeo *et al*., 2005), reducing the analysis time and allowing a more sensitive quantification (de M Ochs *et al*., 2010).

Therefore, this study aimed to: (i) present a new high-throughput method of BPCA quantification using RRLC-UV-DAD; (ii) present its application in the evaluation of the aromatic structure of PyC; and (iii) evaluate the degree to which the initial material and temperature affect the aromaticity and aromatic condensation of PyC. With this purpose, PyC produced from the same starting material at different pyrolysis temperatures and from different starting materials at the same pyrolysis temperature were studied. The aromatic structures were quantified by the new RRLC method through BPCA determination. Finally, the data obtained using RRLC were compared with those obtained by ^{13}C-NMR analysis of the PyC.

5.2 Experimental section

Standards and reagents

Tetrabutylammonium hydroxide, nitric acid and 2-propanol and methanol (HPLC grade, Tedia Brazil, RJ, Brazil), tris(hydroxymethyl)aminomethane hydrochloride (Tris-HCl, Sigma-Aldrich, MO, USA), and sodium acetate, sodium hydroxide and hydrochloric acid (all P.A. grade, Merck, RJ, Brazil) were used. Ultrapure water was prepared using a Simplicity System (Millipore, USA) following reverse osmosis (Rios-DI, Millipore, USA).

Solid BPCA (1,2,3-benzenetricarboxylic acid; 1,2,4-benzenetricarboxylic acid; 1,3,5-benzenetricarboxylic acid; 1,2,4,5-benzenetetracarboxylic acid; 1,2,3,4,5-benzenepentacarboxylic acid and 1,2,3,4,5,6-benzenehexacarboxylic acid) were purchased from Sigma-Aldrich (MO, USA) and used without further purification.

Standard stock solutions of individual BPCA (1000 mg L^{-1}) were prepared by dissolving 10 mg of each standard up to 10 mL of Tris-HCl (0.1 mol L^{-1} at pH 7.5). Standard solutions containing the six BPCA in concentrations of 0.5; 1; 5; 10; 20; 50; 80; and 100 mg L^{-1} were prepared by combining appropriate aliquots of each solution and diluting up to 1.00 mL using the initial proportion of the mobile phase. Stock solutions were stored in amber glass vials at 2-4°C in the dark and discarded one month after preparation, although they were stable for at least 3 months. Working standards were stable for at least one month, but they were discarded after one week.

Pyrogenic C samples and sample treatment

Samples of PyC were obtained from two eucalyptus species *Eucalyptus dunnii* - DUN and *E. urophylla* - URO, and two pine species *Pinus taeda* - TAE and *P. caribaea* - CAR pyrolysed at 350, 450 and 550ºC. PyC from sugarcane bagasse (*Saccharum officinarum* - CAN), coconut (*Cocos nucifera* - COC), water hyacinth (*Eichhornia crassipes* - WAT), candeia submitted before bisabolol extraction (*Vanillosmopsis* *erythropappa* - EXT), Chinese silver grass after acid hydrolysis to recover the carbohydrates (*Miscanthus sinensis* - MIS) and macadamia nut shells (*Macadamia integrifolia* - MAC) were obtained after pyrolysis at 450ºC. The studied samples consisted of at least 100 g of PyC that was powdered and homogenized prior to taking the aliquots used for oxidation and BPCA analysis. The PyC studied were produced in the same pyrolysis plant and under similar conditions, therefore allowing a direct comparison of their chemical characteristics. Biomass was pyrolyzed at a heating rate of 10ºC min^{-1} until reaching the final temperatures (350, 450 or 550ºC) that were maintained for 60 min (Alho *et al*., 2013).

Treatment of PyC samples for BPCA evaluation

Aliquots of 5 ± 0.01 mg of pulverized PyC were weighed and filled into 5 mL glass ampoules, which were sealed after addition of 0.5 mL concentrated HNO_3 (65% m/m). The ampoules were placed into microwave digestion vessels (Dittmar, 2008) and heated up to 170ºC for 8 h (Glaser *et al*., 1998; Brodowski *et al*., 2005; Dittmar, 2008) using a laboratory oven. After oxidation, the ampoules were opened and the excess of nitric acid was evaporated under a gentle N_2 flux until sample dryness. The samples were diluted to 10 mL using the initial composition of the mobile phase composition (see below). Three to five aliquots of each PyC were independently oxidized and analyzed.

Evaluation of UV-Vis absorption spectra

A UV-Visible spectrophotometer (Thermo Scientific Evolution 600, USA) and a quartz cuvette (10 mm) were employed to obtain UV-Vis absorption spectra of solutions (10 mg L^{-1}) of individual BPCA. Solutions were prepared in water, in the mobile phase previously employed for BPCA analysis (sodium acetate 0.1 mol L^{-1}) (Dittmar, 2008) and in the mobile phase proposed in this study (Tris-HCl 0.1 mol L^{-1} at pH 7.5). The spectra obtained allowed selecting the best wavelengths for BPCA detection.

Chromatographic analysis

Qualitative and quantitative chromatographic analyses were performed by RRLC-UV-DAD. The chromatographic system consisted of a vacuum degasser, a binary pump, an autosampler, a column oven and an UV-DAD detector (all Agilent 1200 Series, USA), and was controlled by an Agilent ChemStation. Pre-experiment have shown that the best results were obtained using a detector slit of 4 nm and a response time of 0.1 min. The standard flow cell employed increased the chromatographic signals. The best separation of BPCA was achieved using a Zorbax Eclipse Plus C18 column (4.6 x 50 mm, 1.8 μm). A gradient of an aqueous solution containing Tris-HCl (0.1 mol L^{-1}) + tetrabutylammonium hydroxide (2.5 mmol L^{-1}) (A) and a solution of the same composition prepared in water containing 2-propanol (70:30, v/v) (B) was optimized and applied. The optimized gradient was as follows: it started at 6% of B at a flow rate of 2.1 $ml.min^{-1}$, then a linear gradient of 6% to 14% of B at the same flow rate until 10 minutes, followed by a linear gradient of 14% to 100% of B at a flow rate of 0.5 $ml.min^{-1}$ until 12 minutes and another gradient of 100% to 6% at a flow rate of 2.1 $ml.min^{-1}$ until 16 minutes. The optimized gradient allowed a complete BPCA separation within approximately 8 min. An additional period of 8 min was used to clean the chromatographic system and reestablish the chromatographic conditions, therefore leading to a complete analysis in 16 min. The column temperature was 20 ºC and the injection volume was 10 μL.

BPCA identification and quantification

The determination of BPCA was carried out at 226 nm. The analytes were identified by comparison of retention times of the individual BPCA, elution order and absorption spectra, which were usually simultaneously acquired during BPCA analysis. The detector allowed also simultaneous detection at 234 and 240 nm that were used to improve identification and verify interferences or coelutions.

Analytical curves were obtained after triplicate injections of standard solutions containing the six BPCA in concentrations ranging from 0.5 up to 100 mg L^{-1}. Linear fitting and curve parameters were obtained by the least squares method. The limits of detection (LD) and quantification (LQ) of individual BPCA were estimated by dividing respectively 3 and 10 times the standard deviations of peak areas obtained after 7 subsequent injections of the 0.5 mg L^{-1} standard solution by the angular coefficients of the analytical curves (IUPAC Criteria). The analytical curves were used to estimate the concentration of BPCA in the studied samples. The precision of the entire method (oxidation of PyC and BPCA determination) was evaluated oxidizing 4 aliquots of 5 mg of the same PyC (sugarcane bagasse pyrolysed at 450ºC) and analyzing them under the optimized conditions. The analytical curve obtained for 1,2,4,5-benzenetetracarboxylic acid, the only commercially available isomer, was used for the quantification of the other benzenetetracarboxylic acids (Dittmar, 2008). After quantification, the BPCA isomers containing three and four carboxylic groups were summed and quantified as ∑B3CA and ∑B4CA, respectively.

Solid state ^{13}C-NMR analysis of pyrogenic carbon

All PyC samples were analyzed by solid state ^{13}C-NMR using a VARIAN INOVA (11.74 T) spectrometer operating at frequencies of 125.7 and 500.0 MHz for ^{13}C and ^{1}H, respectively. The pulse sequence employed was Variable-Amplitude Cross-Polarization. The experiments were carried out using a Magic-Angle Spinning (MAS) of 15 kHz, a cross-polarization time of 1 ms, an acquisition time of 15 ms, a recycle delay of 500 ms and a high-power Two-Pulse Phase-Modulation (TPPM) proton decoupling of 70 kHz. The cross-polarization time was chosen after variable contact time experiments, and the recycle delays were chosen to be five times longer than the longest ^{1}H spin–lattice relaxation time (T_1H), as determined by inversion-recovery experiments (Novotny *et al*., 2006a).

To assist the spectra analyses, a MCR procedure was carried out using the software The Unscrambler X® (v10.3, CAMO Software AS, USA). The MCR was preceded by principal component analysis (PCA). First, the PCA estimated the number of components in the mixture. Second, the rotation of the PC was calculated without orthonormality constraints, leading to infinite solutions. New constraints (*e.g*., non-negative concentrations; non-negative spectra; and closure) were adopted to solve the problem. In this way, when the goals of MCR were achieved, it was possible to unravel the "true" underlying sources of data variation, and then the results with physical meaning were easily interpreted (Novotny & Bonagamba, 2009). After the modeling, the pure spectra of the individual components were identified by usual peak assignment.

5.3 Results and discussion

Evaluation of the absorption spectra of the studied BPCA in the analytical conditions

The first step of the method development consisted in the evaluation of the UV-Vis spectra of BPCA solutions and of the mobile phase previously employed for HPLC-UV analysis (sodium acetate solution) of BPCA (Dittmar, 2008). The mobile phase has a strong absorbance in the lowest wavelength region of the spectra (210 – 240 nm) (Figure S5.2), which prevents BPCA detection at wavelengths below 240 nm. Therefore, we had to use 240 nm as a detection wavelength (Dittmar, 2008). Other mobile phases (*e.g.*, phosphate buffer) at the same pH were evaluated but most of them also showed important absorption in that region of the spectra ($\lambda \leq 230$ nm). The mobile phase composed of Tris-HCl (0.1 mol L^{-1}) + tetrabutylammonium hydroxide (2.5 mmol L^{-1} at pH 7.5) was selected because its absorption was practically negligible at $\lambda \geq 226$ nm. The mobile phase of Tris-HCl did not interfere in this region of the spectra, allowing the UV spectra of the BPCA (Figure S5.2) to be obtained. The wavelength of 226 nm and the mobile phase described above were selected for BPCA determination.

Optimization of the RRLC method and evaluation of selected analytical features of the optimized method

The optimization of the chromatographic conditions (column characteristics, mobile phase composition and flow rate, temperature and injection volume) resulted in separation conditions described above and employed in this work. Maximum pressure recommendations of the RRLC system (600 bar) did not allow to use flow rates above 2.1 mL min^{-1}, which could improve separation. The addition of acetonitrile to the mobile phase B resulted not only in lower pressure, but also in poorer separation or coelution of 1,2,3-B3CA and 1,2,4-B3CA. Other buffers (*e.g.*, phosphate) resulted in incomplete separation of BPCAs.

The gradient employed and the optimized method allowed a baseline separation of all BPCAs (Figure 5.1) within 8 min. The time needed for the separation of BPCA using HPLC was previously considered a disadvantage when compared to GC (Schneider *et al*., 2011a). However the chromatographic method presented in this study was almost 4 times faster than the previous HPLC-UV method (Dittmar, 2008), and even faster than the GC method (Brodowski *et al*., 2005). This demonstrated its advantageous throughput when compared to the previous methods.

The chromatographic areas of the BPCA were usually 10 to 20% larger at 226 nm than

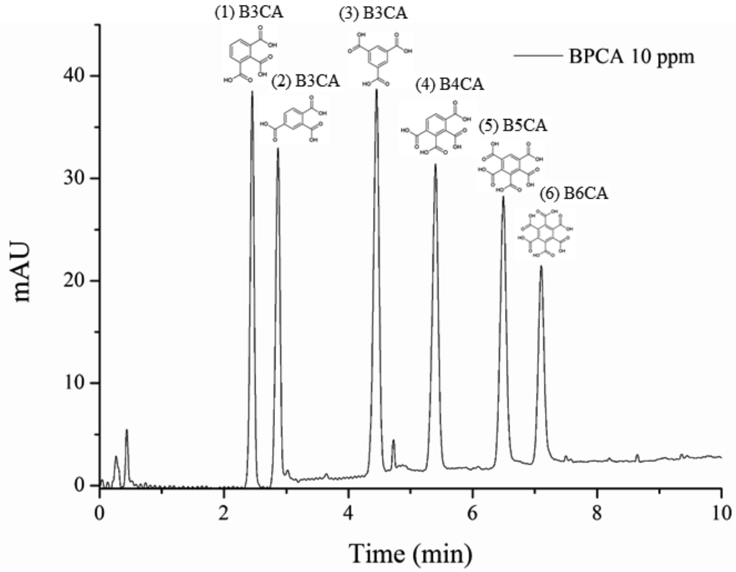


Figure 5.1 Chromatogram of a solution containing all studied BPCA (10 mg L^{-1}) under the optimized conditions. (1) 1,2,3-B3CA; (2) 1,2,4-B3CA; (3) 1,3,5-B3CA; (4) 1,2,4,5-B4CA; (5) B5CA; (6) B6CA.

at 230 or 240 nm. The analytical curves of the BPCA showed very good adherence to linear models, showing excellent correlation coefficients (>0.996) in the studied range (0.5 - 500 mg L^{-1}). This demonstrates that the detector signal was linear up to at least 500 mg L^{-1} for all BPCA.

The analytical curves allowed estimating LD and LQ. LD varied between 0.2 and 0.5 μmol L^{-1} whereas the LQ varied between 0.7 and 1.7 μmol L^{-1}. The LD values were similar to those previously found (0.2 to 0.5 μmol L^{-1}) (Dittmar, 2008), demonstrating the applicability of the proposed method of BPCA determination. Considering the typical sample mass and dilution, LD varied between 0.4 and 1.0 mmol kg^{-1} of PyC, whereas LQ varied from 1.3 to 3.3 mmol kg^{-1} of PyC. Detailed values of LD and LQ are shown in Table S1.

The overall precision of the method was evaluated by the coefficients of variation (CV%) obtained after oxidation of four independent aliquots of PyC obtained from sugarcane bagasse pyrolyzed is at 450ºC (Table 5.1). The CV% were below 2.5% except in the case of 1,2,3-B3CA possibly due to its relatively low concentration.

The chromatographic resolution, the figures of merit and the high throughput of novel RRLC-UV-DAD method demonstrated that, when compared to previous methods, it was advantageous for the evaluation of BPCAs in PyC. As far as we are concerned, this is the first application of RRLC-UV-DAD for the analysis of PyC. This method was considered satisfactory for the evaluation of BPCAs in PyC and allowed us to evaluate different characteristics of PyC, as discussed below.

Table 5.1 Evaluation of the precision (*n* = 4) of the proposed method considering the BPCA produced by oxidation of PyC derived from sugarcane bagasse charred at 450ºC

Benzene polycarboxilic acids (BPCA)	BPCA concentrations (g kg^{-1} of PyC)		Coefficients of variation (%)
	Mean value	Standard deviation	
1,2,3-B3CA	2.56	0.20	7.75
1,2,4-B3CA	6.66	0.14	2.01
1,3,5-B3CA	19.44	0.44	2.30
1,2,4,5-B4CA	26.14	0.28	1.08
B5CA	69.88	0.60	0.85
B6CA	70.22	1.32	1.89

Evaluation of the aromaticity of PyC obtained from the same biomass at different pyrolysis temperatures by BPCA determination

The proposed methodology allowed the determination of individual BPCA concentrations following oxidation of *E. dunnii* (DUN) pyrolysed at different temperatures (350, 400, 450, 500 and 550ºC) and in the original DUN biomass (Figure 5.2). The results obtained were used to evaluate the aromacity of the different PyC.

The total BPCA concentration (ΣBPCA) of DUN biomass was very low (1.26 g BPCA kg^{-1} of PyC). This value is comparable to the sum of the LD of individual BPCA (1.06 g BPCA kg^{-1} of PyC). This demonstrates the selectivity of the method to BPCA obtained after oxidation of PyC, despite the presence of aromatic structures, such as lignin in the original biomass.

The total BPCA concentration (ΣBPCA) increased with charring temperature of DUN, indicating an increased proportion of condensed aromatic structures with temperature. In the lowest charring temperatures 350 and 400ºC, the ΣBPCA increased from 222.5 to 269.1 g BPCA kg^{-1} of PyC. A further increase of ΣBPCA from 301.4 at 450ºC to 303.1 g BPCA kg^{-1} of PyC at 500ºC, and finally up to 306.4 g BPCA kg^{-1} of PyC at 550ºC was observed when the charring temperature was increased from 450 to 550 ºC.

ΣBPCA showed a positive significant correlation with temperature ($R = 0.943$; $p = 0.016$), indicating that higher temperatures produced a larger concentration of ΣBPCA. However, ΣBPCA remained almost invariable with the temperature increase from 500 up to 550ºC. The results are comparable to the ones obtained by ^{13}C-RMN spectra (Alho *et al*., 2013) that showed an increase in the polyaromatic structures of PyC derived of *E. dunnii* pyrolysed 350ºC to 450ºC, and no or little effect in the chemical structure of PyC pyrolysed at 500ºC, showing discrete alteration at temperatures higher than 450ºC (Alho *et al*., 2013). In addition, the ΣBPCA, after pyrolysis of E. *dunnii* at 450ºC, are comparable to previous results obtained for wood charcoal pyrolysed at the same temperature (Schneider *et al*., 2010).

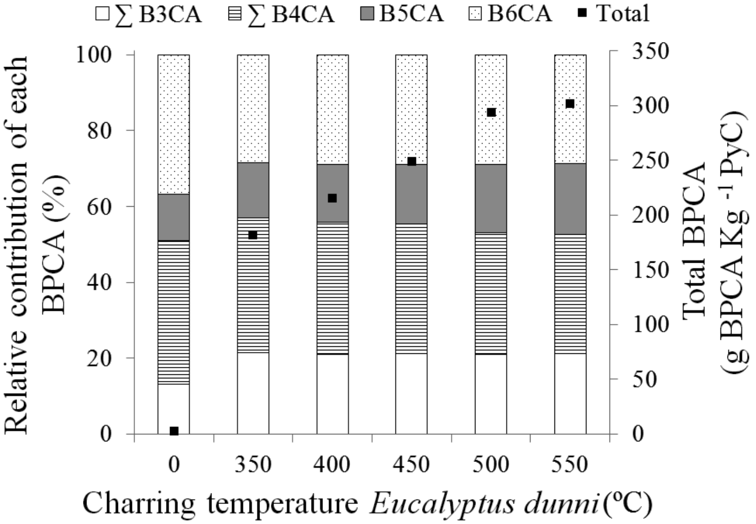


Figure 5.2 Concentrations of BPCA (g BPCA Kg^{-1} of PyC; mean of 3 measurements) of PyC obtained from *Eucalyptus dunnii* (DUN) at increasing charring temperatures.

The charring temperature affected the individual contributions of each BPCA. With increasing temperatures (350 to 450ºC) there is a relative increase in the contributions of all BPCA (Figure 5.2). The concentration of B6CA and B5CA slight increased, while that of B4CA (Σ B4CA) did not change after pyrolysis at 500ºC. Larger proportions of B6CA would reflect higher degrees of condensation of the pyrogenic C and matches earlier observations (Glaser *et al*., 1998; Dittmar, 2008). These results are similar to previous reports of a consistent increase of the B6CA concentration with increasing pyrolysis temperature (Schneider *et al*., 2010). This fact is expected because the highest temperatures favor a high aromatic condensation that leads to B6CA.

Evaluation of aromaticity of PyC obtained from different biomasses at the same pyrolysis temperature

PyC obtained from different biomasses (DUN, TAE, EXT, COC, CAN and WAT) pyrolysed at the same temperature (450ºC) were evaluated to study the effect of the biomass composition upon the BPCA patterns. The ΣBPCA varied from 127.5 g BPCA kg^{-1} PyC (WAT) to 288.8 g BPCA kg^{-1} PyC (TAE). Although our values are higher than the results obtained for wood pyrolysed at 450ºC (161.9 and 155.3 g BPCA kg^{-1} PyC) (Schneider *et al*., 2011a), the results are still comparable.

Variations of individual contributions of each BPCA were observed. Results showed that wood-PyC (DUN and TAE) contained a higher proportion of B5CA and B6CA than PyC produced from other starting materials (CAN, COC, EXT and WAT). PyC obtained at 450ºC produced mainly B6CA that corresponded to around 33% of ΣBPCA, with a somewhat smaller amount for coconut samples (~ 30% of ΣBPCA) and the lowest amount for water hyacinth (~ 22% of ΣBPCA). On the other hand, coconut and water hyacinth produced more B5CA (35.8 and 36.4% of ΣBPCA, respectively) than the other biomass (Figure 5.3).

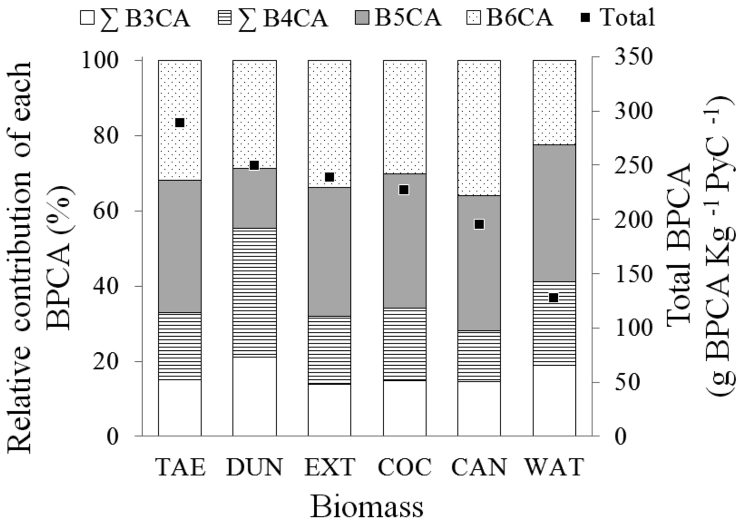


Figure 5.3 Concentrations of BPCA (g BPCA Kg $^{-1}$ of PyC; mean of 3 measurements) of PyC produced at 450°C from different starting biomasses: DUN (*Eucalyptus dunnii*), TAE (*Pinus taeda*), CAN (sugarcane bagasse - *Saccharum officinarum*), EXT (candeia - *Vanillosmopsis erythropappa*), COC (coconut - *Cocos nucifera*) and WAT (water hyacinth - *Eichhornia crassipes*).

Although there are some studies concerning the aromaticity of PyC produced at different temperatures, we are not aware of any study of BPCA produced from PyC obtained from different biomass at the same temperature. PyC derived from DUN and TAE showed a higher proportion of B5CA and B6CA than PyC produced from other starting materials (CAN, COC, EXT and WAT) at the same temperature. This could be caused by a higher lignin content (or the structure of the lignin building blocks) of the biomass of both tree species.

Characterization of the different PyC obtained at different pyrolysis temperatures by ^{13}C-NMR assisted by MCR and BPCA yields obtained by RRLC

The ^{13}C-NMR spectra data set (Figure S5.3) was modelled by MCR as a ternary mixture (Figure 5.4a). The first component of this mixture corresponds to the material least altered by the thermal treatment (the lowest carbonized component) with important signals from lignin: (56; 134; 147; and 154 ppm); cellulose (75 and 112 ppm) and alkyl groups (region of 45-0 ppm). The second component represents the material with intermediary thermal alteration (intermediary carbonized component) with an asymmetric signal in the aryl region (peak center at 130 ppm). This asymmetry, broadness and shoulders in the aryl signal are due to a diversity of aryl groups that persist at intermediary pyrolysis conditions, including O-aryl groups. The last (3rd) component is characterized by a narrow, symmetrical and featureless aryl signal, with an important upfield shift (125 ppm), typical of charred material and attributable to polycyclic aromatic structures produced at more intense pyrolysis conditions (highest carbonized component).

The concentrations of each component depend on the original biomass and pyrolysis temperature. In general, PyC prepared at the lowest temperature (350ºC) presented a higher concentration of residual cellulose and lignin (1st component) and lower

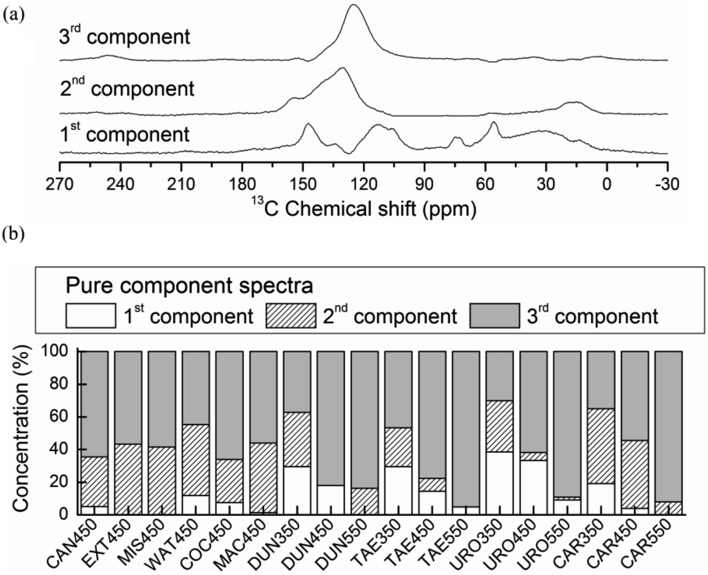


Figure 5.4 Multivariate curve resolution analysis from full ^{13}C-NMR spectra of PyC obtained from different biomass and temperatures (350-550ºC). A) The 1st component refers to the residual lignin and cellulose. The 2nd component mainly relates to aryl and O-aryl groups (130 and 155 ppm, respectively). The 3rd component refers to condensed aryl structures (125 ppm). B) The concentration of each component refers to concentration of the pure spectra extracted from the original data. Pyrogenic carbons analysed: pine (CAR and TAE); eucalyptus (DUN and URO); water hyacinth (WAT); sugarcane bagasse (CAN); coconut (COC); grasses (MIS); candeia (EXT) and macadamia (MAC).

concentration of the polyaromatic structure (3rd component), than the PyC obtained at higher temperatures (450 and 550ºC). PyC obtained at 550ºC showed a predominance of polycyclic aromatic structures that corresponded to more than 80% of the components present in the samples. In general, the increase of pyrolysis temperature increased the proportion of polycyclic aromatic structures at expenses of the lowest and intermediary carbonized components. These results confirm the role of temperature on PyC formation, meaning that the increase of the pyrolysis temperature leads to an increase of the concentration of the polyaromatic structure of PyC at the expense of structures related to lignin and cellulose (Schneider *et al*., 2010; McBeath *et al*., 2011, 2014).

The contributions of each component varied among PyC produced from different starting materials at the same temperature of pyrolysis (450ºC) (Figure 5.4b). PyC derived from DUN, TAE, COC and CAN showed a larger contribution (65-82%) of the polyaromatic structures (3rd component; Figure 5.4b) than PyC derived from the other materials. The concentration of polyaromatic structures was negatively correlated (R = - 0.973) with the ash content, showing that the production of PyC is more efficient with plants that contain lower ash concentration (Yang *et al*., 2011) (Figure S5.4). The concentration of the less-condensed aromatic groups (2nd component) varied from 0 up to 43% among the different PyC. The lowest concentration was observed for the PyC obtained from DUN and URO (0 and 5%, respectively), whereas the PyC derived from CAR, MAC, WAT, MIS and EXT showed the highest concentration (around 43%). The concentration of residual cellulose and lignin (1st component) was higher among PyC derived from URO, DUN, TAE and WAT, ranging from 12-33%, than those PyC derived from EXT, MIS (both 0%) and MAC (1%). The pre-treatments of EXT and MIS would explain the low contents of thermo-labile compounds in the PyC (component 1st) obtained from them. Furthermore, arboreous species (*Pinus* and *Eucalyptus*) showed a high content of low altered original biopolymers (lignin and cellulose), indicating a presence of plant tissues, possibly of lignin structures more resistant to the thermal treatment (Yang *et al*., 2007).

Table 5.2 Correlation matrix obtained by carbonized components (^{13}C-NMR) versus BPCA (g Kg^{-1}) obtained by RRLC. Marked correlations (∗) are significant at $p<0.05$

Variable	Low (L)	Med (M)	High (H)	Sum M+H
∑B3CA	0.63	**-0.92∗**	**0.91∗**	-0.63
∑B4CA	0.62	**-0.81∗**	0.77	-0.62
B5CA	-0.38	0.01	0.17	0.38
B6CA	-0.11	-0.51	0.72	0.11
∑B3CA +∑B4CA	0.16	-0.68	**0.83∗**	-0.16
Total	0.63	**-0.86∗**	**0.83∗**	-0.63

n=6

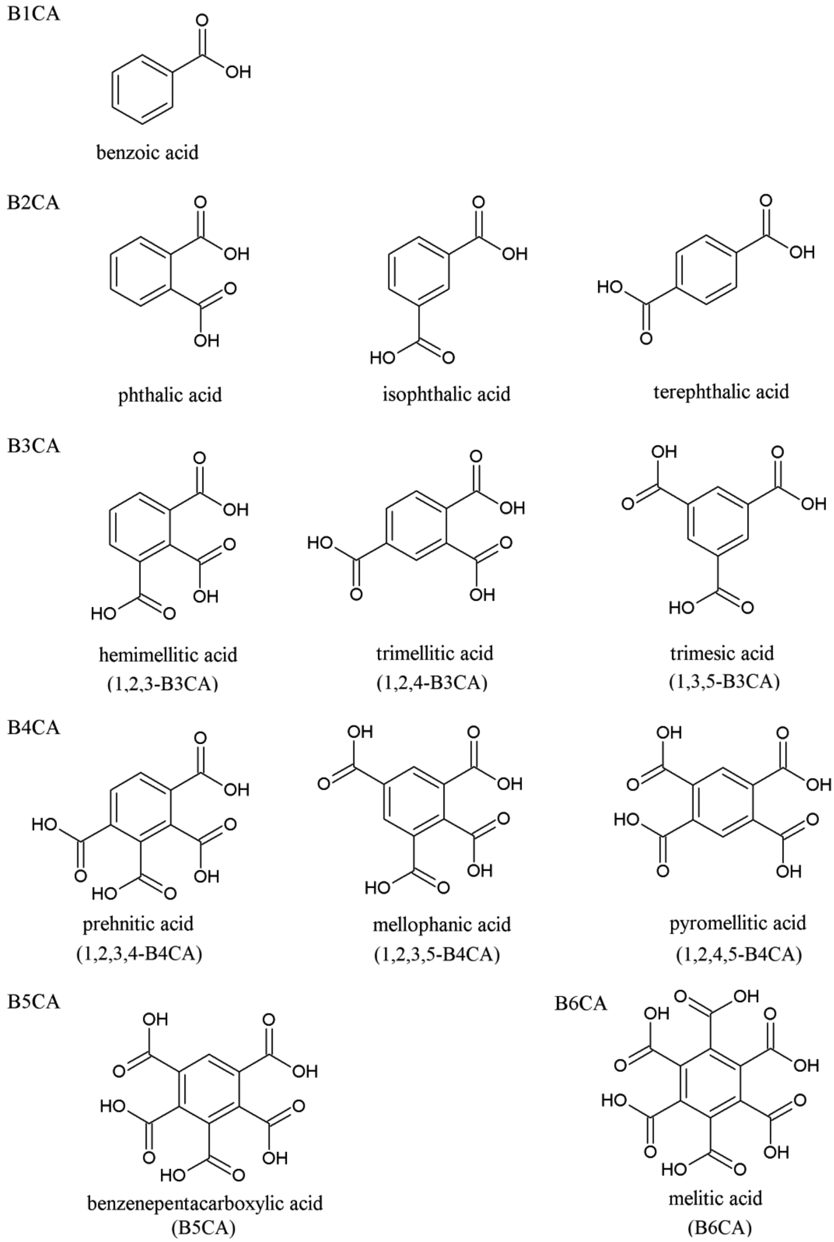
The concentration of each carbonized component (^{13}C-NMR) was correlated with the individual BPCA yields. The best correlation was found between intermediary and highest carbonized component, and ∑B3CA and ∑B4CA (Table 5.2). This suggests that ^{13}C-NMR, assisted by MCR, detected better the less-polycondensed clusters that resulted in ∑B3CA or ∑B4CA than the large polycondensed clusters that result in B5CA or B6CA, after oxidation. These results corroborate previous obtained ones (Freitas *et al*., 1999, 2001) that described the limitation of the use of cross-polarization to detect polycondensed structures poor in hydrogen. Although a previous study already compared ^{13}C-NMR measurements with the relative proportion of B6CA (McBeath *et al*., 2011), only the similar trends of the methods were discussed.

We suggest our novel method of oxidation to be used with the purpose of evaluating the polyaromatic structure of PyC. With this regard, our work presents an improved, high-throughput and simple method for PyC quantification and characterization following PyC oxidation and BPCA production that certainly shows application for routine purposes.

Supporting Information

Table S5.1 Limits of detection and quantification for the individual BPCA obtained under optimized chromatographic conditions

BPCA	**Limits of detection (LD)**			**Limits of quantification (LQ)**		
	µmol L^{-1}	mmol kg^{-1}	g kg^{-1}	µmol L^{-1}	mmol kg^{-1}	g kg^{-1}
1,2,3-B3CA	0.3	0.6	0.13	1.0	2.0	0.43
1,2,4-B3CA	0.4	0.8	0.17	1.3	2.7	0.56
1,3,5 B3CA	0.3	0.6	0.13	1.0	2.0	0.43
1,2,4,5-B4CA	0.4	0.8	0.20	1.3	2.7	0.66
B5CA	0.5	1.0	0.30	1.7	3.3	1.00
B6CA	0.2	0.4	0.14	0.7	1.3	0.47



benzoic acid

phthalic acid

isophthalic acid

terephthalic acid

hemimellitic acid
(1,2,3-B3CA)

trimellitic acid
(1,2,4-B3CA)

trimesic acid
(1,3,5-B3CA)

prehnitic acid
(1,2,3,4-B4CA)

mellophanic acid
(1,2,3,5-B4CA)

pyromellitic acid
(1,2,4,5-B4CA)

benzenepentacarboxylic acid
(B5CA)

melitic acid
(B6CA)

Figure S5.1. Chemical structures, names and acronyms of BPCA studied. Redrawn from Glaser *et al.* (1998).

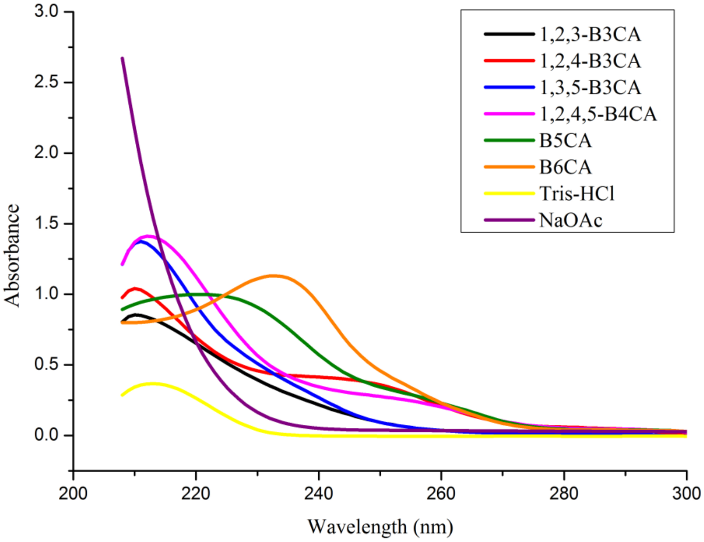


Figure S5.2 Absorbance spectra of sodium acetate solution (0.1 mol L^{-1}), Tris-HCl solution (0.1 mol L^{-1} at pH 7.5) and individual BPCA (10 mg L^{-1}) in the mobile phase.

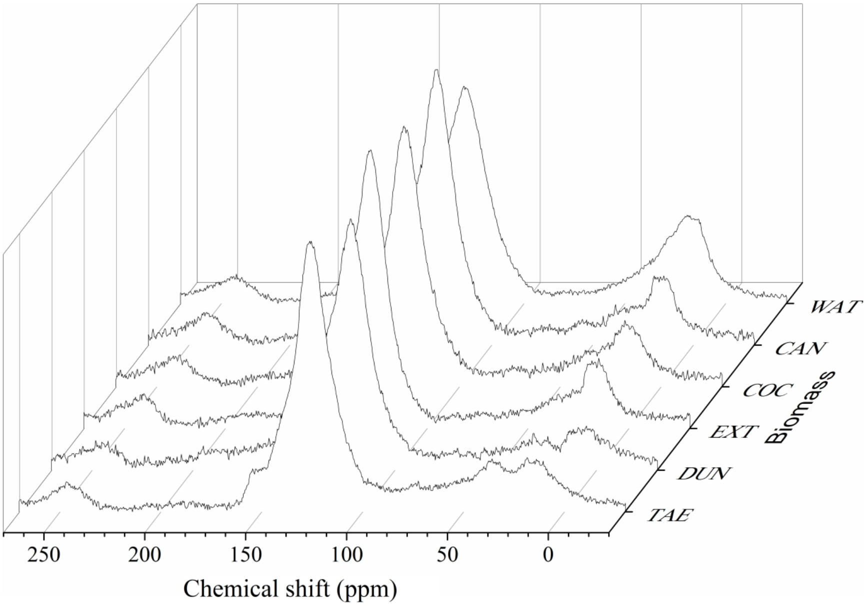


Figure S5.3 Solid state ^{13}C-NMR spectra of pyrogenic carbons prepared from different biomasses pyrolysed at 450º C. Pyrogenic carbons analysed: pine (TAE); eucalyptus (DUN); water hyacinth (WAT); sugarcane bagasse (CAN); coconut (COC); and candeia (EXT).

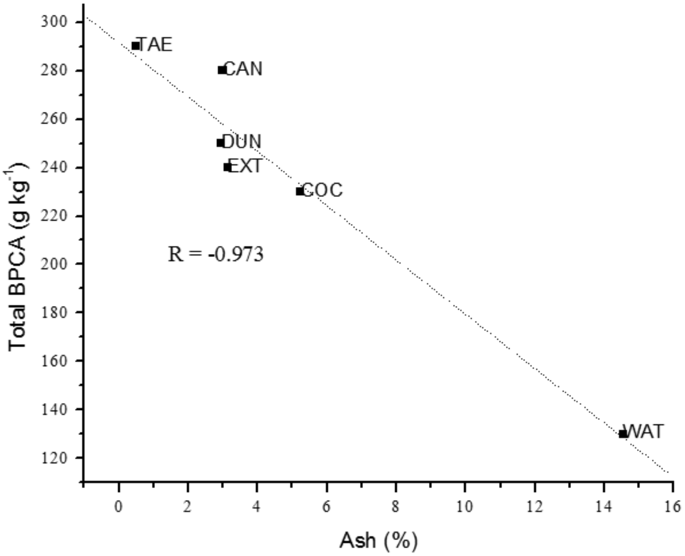


Figure S5.4 Total of BPCA and ash content. Pyrogenic carbons analysed: pine (TAE); eucalyptus (DUN); water hyacinth (WAT); sugarcane bagasse (CAN); coconut (COC); and candeia (EXT).

Chapter 6

General Discussion

Tatiana F. Rittl

6.1 Background

In this PhD thesis, I studied the influence of biochar discourses on the political practices in Brazil and the potential of biochar to sequester carbon (C) in soil, thus contributing to the current debate on the potential of biochar to mitigate climate change. In this final chapter, I contextualize how these findings fit with the existing literature on the following topics: (i) biochar use in Brazil; (ii) biochar decomposition; (iii) biochar priming effect; and (iv) biochar quantification methods. Later, I discuss the impact of my findings on: the contribution of biochar to sequester C in sandy savannah soils, where soil texture and the warm-dry conditions of savannah environments may impact the decomposition rate of biochar. This also has implications for the biochar climate change discourse and policy. The chapter ends with brief reflections on interdisciplinary research, and the main conclusions of the thesis.

6.2 Main findings

The use of biochar in Brazil

Biochar is the solid product of carbonization of organic materials, intentionally produced to be applied in the soil. The deliberative production and addition of biochar in soil distinguishes it from other carbonized products like charcoal, pyrogenic organic materials, black carbon and pyrogenic carbon (Lehmann & Joseph, 2009). Essentially, the production process of biochar is similar to the production of charcoal. The use of the prefix ‘bio’ in front of char suggests that biochar is more environmentally friendly than other biochar-like materials. Thus, to rename charcoal as biochar is a smart marketing decision, especially in Brazil where charcoal production is often associated with deforestation in Amazon (Greenpeace, 2013) and slave labour (Kato *et al*., 2005). Therefore, the use of biochar rather than charcoal has been recognized as a technology for solving environmental and social policy problems (e.g. mitigation of climate change, waste management, energy production and food production). Biochar attracts the interest of actors from different sectors of society, who have particular ideas and concepts of biochar that translate in different discourses about the use of biochar.

Worldwide, the biochar climate change discourse is dominant among the multiple biochar discourses (food production, bioenergy and waste control). It has been claimed that biochar has a great potential: to mitigate climate change by increasing the C stock in soils; to increase food production by improving soil quality; to co-produce bioenergy by slow pyrolysis production; and to decrease solid agricultural waste by using available crop residues as a feedstock for biochar production. The simultaneous use of these potentials in a real farming system has been called win-win-win-win situation (Laird, 2008; Lehmann & Joseph, 2009; Kwapinski *et al*., 2010). However, there are always trade-offs between these four uses (Jeffery *et al*., 2015), leading to the dominance of that one that is more adequate to the demand. Internationally, the biochar climate change discourse is dominant (Leach *et al*., 2010), however in Brazil that discourse is only emerging (**Chapter 2**).

The development of the biochar network/discourse in Brazil occurred at the expenses of the Amazonian Dark Earth (ADE) network/discourse. As elaborated in **Chapter 2**, in Brazil the shift between the once dominant ADE/Biochar discourse to the current discourse of biochar as a technology by itself was shaped by the interplay of actors and their interests. Before 2006, ADE actors interested in understanding the genesis and fertility of ADE dominated the network in Brazil. After 2006, when a large and diverse group of actors joined the network, the Brazilian network became more interested in biochar technology than in ADE. Embrapa researchers became the most powerful actors in the Brazilian Biochar Network, occupying strategic positions in the network. Empraba actors were interested in the potential of biochar to increase food production and to increase residual biomass cycling. They drove the Brazilian Biochar Network in the direction of Embrapa's own interest. Embrapa actors drove the incipient network to study the application of biochar derived from crop residues as a way to improve soil fertility (food productivity) by increasing C stocks. In Brazil, to increase C stock is considered more as an agronomic practice than a climate change solution. In order to sustain the productivity of tropical soils it is important to enhance or maintain high contents of soil organic carbon (Lal, 2006).

The low C stock of soils is a challenge that limits agricultural production in Brazil. For decades, Brazilian researchers have been searching for alternatives to increase C stocks in degraded and arable soils. For example, non-tillage (as practiced in Conservation Agriculture) and the use of green manure are common practices used in Brazil to increase / maintain the soil C stocks and soil fertility. However, the C added to soil by these practices disappears quickly, potentially still resulting in lower C stocks and reduced soil fertility in the long-term. One way to overcome the fast degradation of the residue in soil is to carbonize it as biochar. The carbonization increases the chemical recalcitrance of the residue (**Chapter 5**). Furthermore, biochar can be produced by the carbonization of a large range of solid materials, such as crop residues and solid waste. In this context, biochar could be a feasible solution to increase the C stocks in soil, the fertility of soil, and to promote the recycling of biomass. Consequently, biochar could be produced from crop residues and its application in soil could increase the soil C content and sustain these higher amounts for thousands of years (Kuzyakov *et al*., 2009). Therefore, biochar could sequester C in soil over long periods, decreasing CO_2 in the atmosphere, increasing soil fertility and reducing solid waste.

Although the prospects of using biochar as a way to sequester carbon, increase soil fertility and reduce waste seem good, biochar is not part of any program dealing with the reduction of GHG emissions or management of solid waste or use of organic compost in Brazil. In order to control GHG emissions, the Brazilian government launched the National Climate Change program in 2008, which had the declared goal to reduce total GHG emissions by 37%. Furthermore, in order to reduce solid waste production, Brazil started a new program on National Solid Waste Policies in 2010. One of the objectives of the National Solid Waste Policies is to transform the solid waste in organic compost, which will increase the C content of the soil. However, neither program considered biochar an option to tackle the respective problems in Brazil.

The Brazilian Biochar Network has not recommended the biochar technology as a policy yet. Brazilian actors argue that there are risks associated with biochar application, and claim that more research needs to be done. Under Brazilian conditions, biochar showed very little, if any, effect on crop yield (Sagrilo, 2014; Carvalho, 2015). This lack of effects after the use of biochar in real farming systems contrasts with the optimistic discourse of win-win-win-win situation. Under Brazilian conditions, the potential uses of biochar are being (re)evaluated. This thesis is embedded in the current practices of biochar in Brazil, and here the potential of biochar to mitigate climate change at Brazilian conditions was reassessed. Our findings highlight the need for revising the potential of biochar to sequester C in soil for long term in different geographical regions.

Biochar decomposition

Literature often suggests that biochar is recalcitrant material with a residence time in soil of thousands of years, which would make it a suitable candidate to sequester C (Cheng *et al*., 2008; Laird, 2008; Liang *et al*., 2008; Kuzyakov *et al*., 2009; Major *et al*., 2010; Novak *et al*., 2010). This assumption is based on the idea that biochar would not be decomposed in the short-term due its high proportion of polycondensed aromatic structures. Indeed, the charcoal found in the ADE (Amazonian Dark Earth; *Terra Preta de Índio*) and current biochar produced and incubated under controlled conditions (**Chapter 4**), which are rich in polycondensed aromatic structures, showed a millennial residence time in soil. However, these observations are not evidence that every biochar produced and applied in the field will not degrade in the soil. Biochar produced in traditional kilns may challenge the claim that all biochars are rich in polycondensed aromatic structures. Biochar produced in a traditional kiln was shown to be poorer in polycondensed aromatic structures than biochar produced in 'industrial' kilns, therefore decomposing fast (**Chapter 3**). Furthermore, quantitative studies of biochar and charcoal decomposition under field conditions might challenge the claims about the intrinsic recalcitrance of biochar and its high potential to mitigate climate change.

In **Chapter 3**, I found that a substantial portion of the biochar degraded within months under savannah conditions in a sandy soil. Biochar decomposed at a higher rate than native SOC in a biochar-amended soil. Within one and a half year, between 25 to 60% of the biochar was lost (**Chapter 3**). Our results are in line with other field studies, which determined the apparent loss of charcoal or biochar *in situ* under savannah conditions (Table 6.1). A chronosequence study (2, 3, 5, 20, 30, 50, 80 and 100 years) in western Kenya revealed an initial phase of rapid charcoal decomposition, during which 70 to 84% of the charcoal was lost depending on the quantification method applied (Nguyen *et al*., 2008). Other field studies on biochar decomposition in savannah soils reported initial losses of 20 – 53% within 2 years (Major *et al*., 2010), and losses of 50% over a period of 51 years (Bird *et al*., 1999). With the exception of the study of Schneider *et al*. (2011) who did not find a decline in charcoal stocks over 100 years, all other studies reported a high biochar or charcoal loss in savannah environments. Only Major *et al*. (2010) speculated that the major cause of biochar loss is surface runoff (although they did not measure it) rather than biochar decomposition. Therefore, a large part of biochar might decompose relatively fast before the remainder stabilizes in the environment.

Table 6.1 Biochar and charcoal loss under field conditions

Biochar/Charcoal loss (%)	Time years	Location, soil	Reference
50	51	Zimbabwe, sandy savannah soil	Bird *et al.* (1999)
58	22	France, sandy soil	Quénéa *et al.* (2006)
18	11	Florida, Spodic Quartzipsamment	Alexis *et al.* (2006)
70 – 84	30	Western Kenya, Humic Nitosols	Nguyen *et al.* (2008)
20 – 53	2	Colombia, Oxisol savannah soil	Major *et al.* (2010)
0	100	Western Kenya, Humic Nitosols	Schneider *et al.* (2011b)
25 – 60	1.5	Brazil, Sandy savannah soil	**Chapter 3**

The fraction of biochar that will decompose quickly in the environment may include both labile (aliphatic) and recalcitrant (aromatic) C fractions. It is not only the chemically labile fraction of biochar that may degraded relatively rapidly, but also part of the high condensed (H:C < 0.4; molar ratio) part of biochar that is considered the stable fraction of biochar (Budai *et al*., 2013). Recent studies show that even a substantial part of the chemically recalcitrant fraction of biochar can be degraded within a short time. Studies reported an increase in the number of smaller clusters of polyaromatic structures at the expense of the degradation of more condensed aromatic structures in biochar (Abiven *et al*., 2011; Singh *et al*., 2014). Thus, the remaining fraction of biochar that is claimed to persist in soils for thousands of years (Budai *et al*., 2013) is hardly the dominant fraction of the biochar. This stable fraction may be only a small portion of biochar, implying that the contribution of biochar to mitigate climate change is substantially less than often claimed.

Biochar priming effect

Priming refers to changes in the decomposition rate of the native SOC stock after the addition of organic compounds (Bingeman *et al*., 1953). Priming can be positive or negative. Positive priming refers to an acceleration of the decomposition rate of native SOC, while negative priming refers to a deceleration of that rate. As demonstrated in **Chapter 4**, biochar can even negatively prime native SOC, which would result in a lower decomposition rate of native SOC. In this experiment biochar decomposed faster than the native SOC, showing that biochar is an important source of energy for the microorganisms in soil and hence a major source of CO_2 emission in biochar-amended soils (Sagrilo *et al*., 2014).

Toxins present in the biochar may also affect the decomposition rate of native SOC. In **Chapter 4**, we observed minimal emissions of CO_2 in the early stage in the *Jatropha* biochar treatment. This effect was most likely caused by toxins present in the *Jatropha* biochar, rather than by C interaction mechanisms. *Jatropha* biomass is well known to contain compounds that are toxic for animals and microorganisms, and which could also inhibit microbial activity in soils (Devappa *et al*., 2010a, 2010b). It is possible that these compounds were not degraded during pyrolysis at 380ºC. These compounds could have inhibited the activity of soil microorganisms and the subsequent decomposition of native SOC in the early stage of the experiment. Therefore, some types of biochar may add toxins to the soil, decreasing CO_2 emissions in the short term. The hazard of toxins in the biochar may limit the use of some types of residues and solid waste to produce biochar, such as animal manures (Bicudo & Goyal, 2003), or sewage sludge (Westrell *et al*., 2003).

BPCA method for biochar quantification

In **Chapter 5** the available and commonly applied benzene polycarboxylic acids (BPCA) method was optimized, and implemented in a Brazilian research institute. The BPCA method is a robust approach for quantifying and characterizing biochar. The BPCA yields indicate the amount of biochar, while the chemical composition of biochar is reflected by ratios of individual BPCA yields (Glaser *et al*., 1998). Benzene rings with 3 to 4 carboxylic acid groups (B3CA and B4CA) are derived from side chains, while benzene rings with 5 to 6 carboxylic acid groups (B5CA and B6CA) are derived from aromatic rings.

The protocol of the BPCA method was improved and a better and faster way to quantify and characterize the BPCAs derived from biochar was developed compared to the previous one. Compared with the established gas chromatography (GC) method, the improved method results in higher BPCA quantification reproducibility by exhibiting a smaller coefficient of variation (7.5%). Compared with the others high-performance-liquid-chromatography (HPLC), our optimized method (**Chapter 5**) showed to be at least 7.5 times faster than the HPLC method proposed by Dittmar (2008) and twice faster than the HPLC method proposed by Wiedemeier et al.(2013).

To compare the performance of the novel BPCA method with the solid state ^{13}C nuclear magnetic resonance (NMR), we characterized the same biochar with these two methods. In **Chapter 5**, we found that both methods quantify the aromatic structures in biochar and that the high polycondensed structures characterized and quantified by

^{13}C-NMR assisted by multivariate curve resolution correlated well with the less polycondensed BPCA rings (B3CA; B4CA). Due to the lower proportion of hydrogen in the more polycondensed BPCA (B5CA; B6CA) derived from the biochar, the ^{13}C-NMR did not detected well these structures. Therefore, there is a limitation in the use of cross-polarization ^{13}C-NMR spectroscopy to detect polycondensed structures poor in hydrogen (Freitas *et al*., 1999, 2001).Thus, I recommend the further use of BPCA method for the assessment of biochar stocks in Brazil.

6.3 Biochar has a low potential for C sequestration in savannah sandy soils

A study of the recent literature, and together with the results obtained in my thesis suggest that there is very little evidence that biochar is a reliable way for substantial C sequestration in savannah soils. If biochar is as stable as has been claimed (Cheng *et al*., 2008; Laird, 2008; Liang *et al*., 2008; Kuzyakov *et al*., 2009; Major *et al*., 2010; Novak *et al*., 2010) on average 75% of the total SOC in soil should be present as biochar-like-materials (Masiello & Druffel, 2003). However, the charcoal stocks in savannah soils comprise less than 20% of total SOC (Table 6.2). The fact that charcoal undergoes decomposition in soil may explain the divergence between charcoal production and charcoal stocks in soil (Zimmermann *et al*., 2012). This suggests that if the same mechanism applies for biochar, biochar will not be as stable in the environment as has been claimed.

Warm-dry conditions in sandy savannah soils may explain the high decomposition rates of biochar in such environments. In these environments, biochar can decompose

Table 6.2 Charcoal contents in savannah soil

Charcoal content, as % of SOC	Location, soil	Reference
4 – 18	North America, 18 Savannah soils	Glaser & Amelung (2003)
5 – 13	Northern Texas, Savannah soil	Dai *et al.* (2005)
13 - 17	Northern Texas, Savannah soil	Ansley *et al.* (2006)

faster than ordinary soil organic matter. High temperatures can enhance decomposition even of relatively recalcitrant C (Hammes *et al*., 2008). Under tropical and sub-tropical conditions polycyclic aromatic compounds may be degraded faster than any minor labile component (Zimmermann *et al*., 2012). Knorr *et al*. (2005) provided evidence that degradation of chemically recalcitrant SOC is more temperature sensitive than labile SOC. When temperature was increased from 4 to 30ºC, biochar decomposition increased from 4.6% to 14.6% after one year (Nguyen & Lehmann, 2009). Cheng *et al*. (2008) found a Q_{10} (increase in the decomposition rate with 10ºC increase in the temperature) of 3.4 for biochar when the temperature increased from 5ºC to 15ºC. This Q_{10} of biochar is higher than the Q_{10} found for fresh plant material (2.1 for leaves and 2.6 for roots) in these temperatures (Cheng *et al*., 2008). Furthermore, moisture content of soils also has an influence on biochar decomposition. Nguyen & Lehmann (2009) observed a faster decomposition of biochar under dry conditions than wet conditions. At dry and warm conditions, the chemisorption of oxygen at unsaturated carbon rings of biochar is high (Cheng *et al*., 2006), leading to the breakdown of the polycondensed structures present in the biochar. Glaser & Amelung (2003) showed a close relationship between biochar accumulation, temperature and moisture. According to the authors, cooler and moister soil environments have a higher capacity to accumulate biochar than warmer and drier environments. Thus, the stability and suitability of biochar for C sequestration also depends of the environmental conditions. Therefore, the potential of biochar to mitigate climate change has to be re-evaluated for different geographical areas.

Under conditions of high temperatures and low moisture contents, biochar is not suitable for significant (long-term) C sequestration in savannah regions. The annual precipitation in Brazilian savannahs varies from 1200 to 1600 mm. The dry season lasts from 4 to 7 months and the mean annual temperature varies from 22ºC in the South to 27ºC in the North (Roscoe, 2002). Under these conditions, biochar suitability to sequester C in soil is low (Table 6.1). Table 6.1 shows a collection of results from field experiments with charcoal produced *in situ* or biochar applied to savannah soils. With the exception of the study of Schneider *et al*. (2011b), all of them show a high biochar/charcoal loss within years or decades. Only Schneider *et al*. (2011b) reported no loss of charcoal over a century at savannah conditions. Their conclusions seem inconsistent with the literature, requiring a further reflection on their conclusions.

Nguyen *et al*. (2008) and Schneider *et al*. (2011b) used the same soil samples to quantify charcoal loss over a century in a tropical agro-ecosystem; however, they obtained very different results. Nguyen *et al*. (2008) analysed the samples by two different methods: they found charcoal loss of 70% over a century when they analysed the samples by ^{13}C-NMR and a charcoal loss of 84% when they analysed the samples by hand-picking. Schneider *et al*., (2011b) used the BPCA method, and claimed not to find any charcoal loss. They concluded that the total charcoal stock did not decrease over a century of weathering. The question arises where this discrepancy between the two results comes from, and which one gives the likely correct fraction of biochar loss. According to Schneider *et al*. (2011b), the two methods ^{13}C-NMR molecular mixing model and BPCA correlated well ($r^2 = 0.80$), but with BPCA values being only 15-20% of those measured by ^{13}C-NMR (Nguyen *et al*., 2008). This systematic offset between the methods reflects what is determined as charcoal by the analytical window of each method (Figure 6.1).

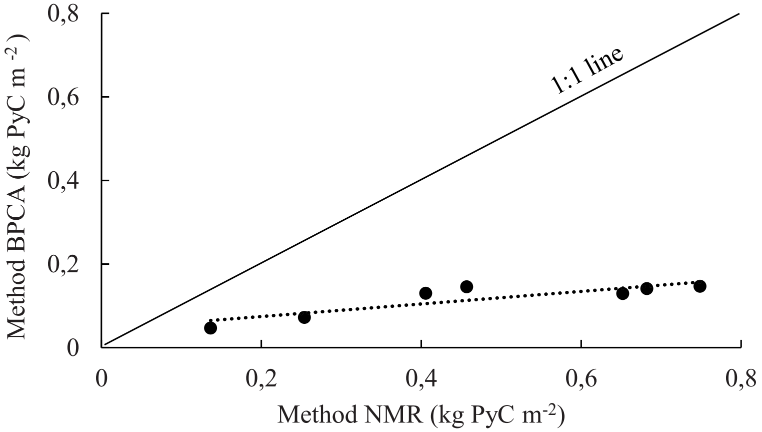


Figure 6.1 Comparison of pyrogenic carbon stocks measured by nuclear magnetic resonance spectroscopy with molecular mixing model (Nguyen *et al.*, 2008) and BPCA molecular markers (Schneider *et al.*, 2011b). Figure redrawn from Schneider *et al.* 2011b.

Each analytical method captures only a part of the combusted continuum of organic materials that comprise charcoal. The BPCA method applied by Schneider et al. (2011) assesses the molecular markers as a representative of charcoal, while the ^{13}C-NMR molecular mixing model measures the proportion of aryl C to the ^{13}C-NMR spectra (Nguyen *et al*., 2008) and from that calculates the content of charcoal. Thus, the quantity of charcoal measured by Schneider *et al*. (2011b) reflects only a small fraction of the quantity of charcoal measured by Nguyen *et al*. (2008). This small fraction (15-20%) remains almost constant over one century, showing a very low decomposition rate. This fraction thus corresponds to the chemically recalcitrant and/or protected fraction of charcoal. Based on these studies, I propose a first-order kinetic decomposition model for biochar in savannah soils.

The first-order kinetic model describes decomposition rate of biochar over 100 years. The model contains two fractions of biochar: the protected and / or recalcitrant and the unprotected and labile fractions. For model simplicity we took chemically recalcitrant and protected biochar together as both have a very low decomposition rate. The protected fraction refers to the biochar within aggregates or bound to minerals or clay in the soil. The unprotected fraction refers to the biochar that is not protected chemically and physically. The size of these fractions was determined based on a literature review (Table 6.2). According to the data, a maximum percentage of 18% of biochar is found in savannah soils. I assumed that this fraction corresponds to the protected and / or recalcitrant fraction. I adopted a conservative estimate of 20% residual (undecomposable) fraction of biochar and 80% unprotected labile fraction of biochar. Based on these assumptions and data presented by Nguyen *et al*. (2008)[1], I propose the following first-order kinetic model for biochar decomposition in these

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[1] Note that the three-parameter model previously proposed by Nguyen et al. (2008) contains an error. The problem with their model ($f = Y_0 + ae^{-kt}$) is that Y_0 is not the charcoal content at time zero, but effectively the undecomposable fraction, and a is not a constant but the decomposable fraction. Under their definition of Y_0 (total amount of charcoal at time zero), the initial amount of charcoal has this residual fraction counted twice.

soils : $f = Y_L e^{-kt} + Y_R$, where f is the fraction of biochar left, Y_L is the labile-unprotected fraction of biochar, k is the decomposition constant for that fraction and Y_R is the residual (undecomposed) part of the biochar (with a decomposition constant of effectively zero in a century).

My proposed model showed to be very consist with the assumption that only the residual (protected plus recalcitrant) fraction of biochar will persist in the savannah environment longer than 100 years (Figure 6.2). The best fit of this model indicated a k value of 0.05 year^{-1} (somewhat lower than the Nguyen *et al*. (2008) estimate for bulk soil) implying that a large fraction of charcoal (95% of the labile-unprotected fraction) decomposes within 50 years. These results are in accordance with those by Nguyen *et al*. (2008), which predicted a loss 70-84% of charcoal over 100 years. However, their model has a conceptual error[1] in which the residual fraction of biochar is counted twice.

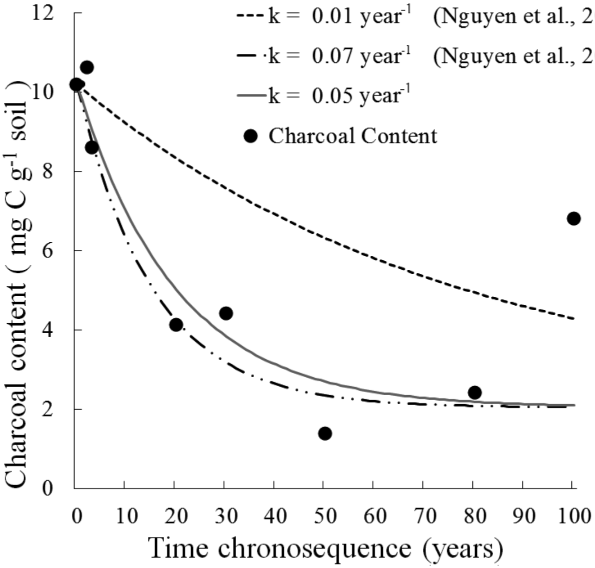

Figure 6.2 Charcoal decomposition over 100 years. The dots are the charcoal content of soil (Nguyen *et al.*, 2008). The first-order kinetic models were fitted based on the charcoal contents and k (years^{-1}) values presented (Nguyen *et al.*, 2008) and estimated. The charcoal content in 100 years is difficult to explain if one assumes there has been no fire in the last 100 years (Nguyen *et al.*, 2008).

My model suggests that only 5% of the decomposable fraction of the charcoal is left after 50 years, and that the soil charcoal content is determined by the residual (protected plus recalcitrant) fraction. These data, however, do not allow an assessment of the relative importance of protection versus recalcitrance, in determining the size of the residual fraction. However, a comparison of charcoal contents (as fraction of total soil organic matter) in 18 different soils of North America (Glaser & Amelung, 2003) allows a first approach to that question (Figure 6.3).

I found a significant relation between the charcoal contents (as fraction of total soil organic matter) and sand contents. This contrast with the conclusion of Glaser & Amelung (2003) who argued that soil texture have a minor influence on the pyrogenic carbon accumulation in the soil. Glaser & Amelung (2003) regressed pyrogenic carbon contents for silt and for clay contents separately and did not find any relation. However, they did not regress for sand (or clay + silt) content. When I regressed the

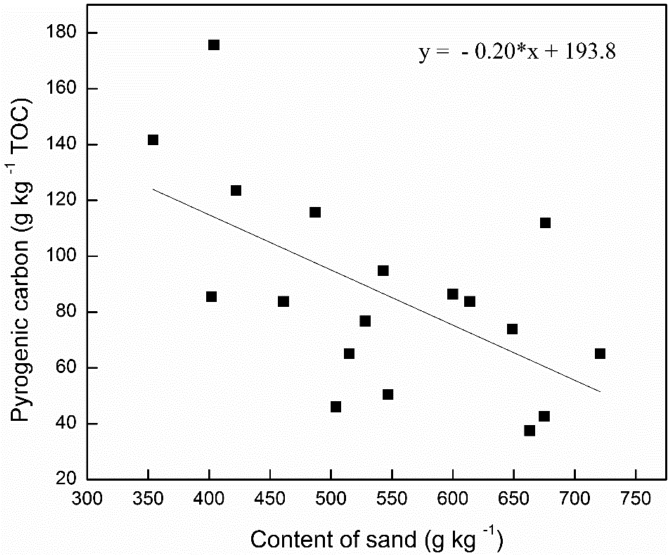

Figure 6.3 Relation between pyrogenic carbon content on the total of soil organic carbon and total sand content (0 – 10 cm) in North American prairie soils. The relation is statistically significant (P = 0.009). Based on data from Glaser & Amelung (2003).

pyrogenic carbon quantity to the sand content, I found a significant relation. Figure 6.3 shows that soils that are richer in sand content accumulate less pyrogenic carbon than soils that contain more clay plus silt. For each given percent (%) of sand the fraction of pyrogenic carbon in the soil decreases 0.2%. Thus, in a hypothetical pure sandy soil pyrogenic carbon will not accumulate, while in a soil that contains 100% of clay + silt, 20% of C would be pyrogenic carbon. Again, these data suggest that C accumulation after biochar addition is less than 20% of the biochar added, a number substantially lower than used in the literature. Therefore, the content of clay + silt have a major influence on the pyrogenic carbon accumulation in soil through mechanisms of physico-chemical and biological protection.

The decomposition rate of (unprotected and labile) biochar predicted by my model is much higher than the decomposition rate proposed by the conceptual model (Figure 6.4) of Lehmann *et al*. (2006), which suggests biochar loss of 10-20% within 5-10 years, and very little loss thereafter (hence a recalcitrant and / or protected fraction of 80-90%). Based on the idea of biochar inertness, the conceptual model assumes that a

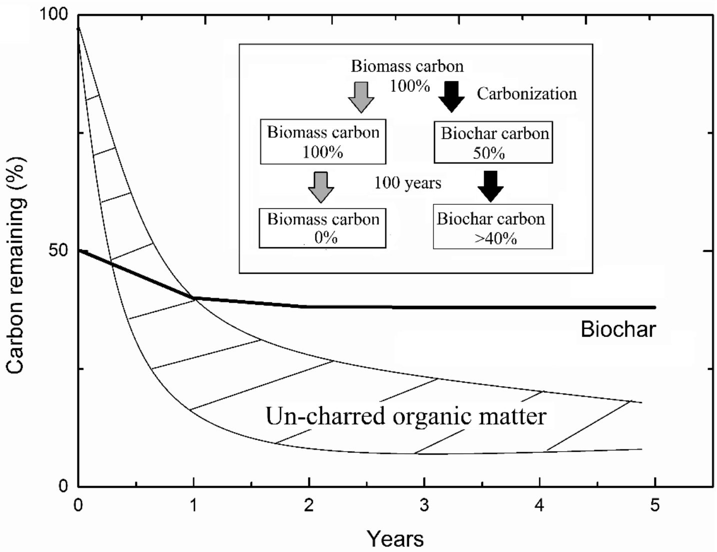

Figure 6.4 Conceptual diagram. Range of biomass carbon remaining after decomposition of crop residues; biochar carbon remaining after decomposition. Insert: biomass and biochar remaining after charring and decomposition in soil after 100 years. Figure redrawn from Lehmann *et al.* (2006).

large fraction of biochar will persist in soil for hundreds to thousands of years. The contrasting conclusions between these different models suggest that claims on the persistence of biochar need to be based on the chemical nature (recalcitrance) of the biochar produced and on the importance of protection provided by the environment. Certainly, we cannot assume that all biochars can persist in soils for centuries to millennia under all climate conditions in all types of soil.

6.4 Contesting the potential of biochar to mitigate climate change

The significance of biochar as a technology to mitigate global climate change has therefore been overstated. Claims suggest that a large part of biochar (50-70%) will stay at least for 100 years in soil, thus making it a suitable candidate for C sequestration. Eleven African nations and the UNCCD have submitted documents proposing to UNFCCC to include biochar as a high-potential climate mitigation and adaption tool in the post-Kyoto climate change agreement (IBI, 2014). However, despite their optimistic actions, biochar is not (yet) accepted in both the Clean Development Mechanism (CDM) and EU Emissions Trading Scheme. Among the reasons to exclude biochar from the carbon trading mechanism are the uncertainty about the stability of biochar in soil ; and the absence of a reliable cheap and widely available method to quantify biochar in the environment.

Data of Table 6.3 shows that the mean residence time (MRT) of the decomposable

Table 6.3 Decay constants, half-life and mean residence time (MRT) estimated for biochar under savannah environments

k (year^{-1})	**Half-life (years)**	**MRT (years)**	**Reference**
0.32-1.00	0.7-2.2	1.0 - 3.1	This thesis (**Chapter 3**)
0.11-0.38	1.8-6.2	2.6 - 9.0	Major *et al.* (2010)
0.07	10.0	14.5	Nguyen *et al.* (2008) (bulk soil)
0.05	20	13.8	This thesis (**Chapter 6**: model)
0.01	53.7	77.5	Nguyen *et al.* (2008) (surface soil)
0.01	51.0	73.6	Bird *et al.* (1999)
0.01	46.4	67.0	Zimmermann *et al.* (2012)

fraction of biochar and charcoal in savannahs is lower than 100 years. The MRT of these compounds ranged from 1.0 to 77.5 years, depending on the period of the studies. These values are lower than 100 years, implying that a large fraction of biochar will decompose over a century in savannah environments. Therefore, the predictions on biochar stability and suitability for C sequestration in all environments were too optimistic.

Our data corroborate the concerns of the CDM and EU Emissions Trading Scheme that biochar is not suitable to mitigate climate change to a large extent. The claims that biochar can mitigate climate change are based on the assumption that (all) biochars remain stable in (all) soils over thousands of years. My data from the biochar produced in traditional kilns (**Chapter 3**) might be too optimistic for the available traditional methods in other regions. The resilience of biochar produced in the traditional cook stoves in African countries might be even lower due to the lower temperatures and efficiency of these systems (Ballard-Tremeer, 1997). In some places, these may be the only available charring system to produce biochar. Therefore, the assessment of the potential of traditional biochars under African savannah sequester C also needs to be re-evaluated in order to have a better estimate of the global impact of biochar on climate change mitigation.

6.5 Policy implications

The claims that biochar might be a universal solution to mitigate climate change were disproven. Internationally, the potential of biochar to mitigate climate change is attracting actors from different sectors of society, including private companies, research institutes, NGO's, policy makers and venture capitalists (Leach *et al*., 2012). These actors are confident that biochar will deliver its promise of significantly sequestering C in soil, and are working to have biochar accepted in the climate change negotiations. Contrary to this promise, I have shown that biochar has only little potential for C sequestration under savannah conditions. The data presented in this thesis (**Chapters 3** and **6**) show that (locally produced) biochar makes a much smaller contribution to C sequestration than earlier suggested. I showed that biochar decomposes quickly in the savannah environment and that the decomposition of biochar is driven rather by environmental conditions than by its intrinsic chemical recalcitrance. These findings contest the claim that all biochars are intrinsically recalcitrant, and that they can retain carbon under all climate conditions in all types of soil over periods significant for carbon sequestration programs. This conclusion has a direct consequence for the development of policies on biochar, because we cannot ensure that biochar will sequester the same quantity of C for the same period at different geographical regions. For example, in Brazil under savannah soils biochar may have a limited potential to increase the soil C stocks and significantly contribute to the National Climate Change program.

6.6 Reflections on interdisciplinary research

The combination of social and natural sciences enable to identify the discourses related to biochar and tested the main claims on the potential of biochar to mitigate climate change. On one hand, I could analyze the policy discourses around the biochar. On the other hand, I could also test the main claims that sustain the discourse on the potential of biochar to mitigate climate change. Using this approach, I was able to conclude that the policy claims about biochar and its potential to sequester C are not confirmed by the scientific findings.

Personal view of interdisciplinary research

Based on my own experience, I would like to recommend two things to improve the efficiency of interdisciplinary research between multiple institutions. First, an interdisciplinary PhD is more time demanding than a traditional PhD project. An interdisciplinary PhD requires a consensual proposal among different areas, which takes extra time for learning new scientific methods and languages. Furthermore, an interdisciplinary PhD across multiple international institutions also requires additional travelling, that costs extra money and time that normally are not foreseen in the budget and time planning of the project. In this respect, I would recommend that granting agencies were more flexible to extend the subsidies if needed or to accommodate goals that are more conservative. Second, a sandwich-interdisciplinary project may not be the best model for interdisciplinary research. Interdisciplinary research already is complex by itself, adding more complexity by combining different international institutions in one PhD project makes it unnecessarily more difficult. The management structure and responsibilities within the project need to be defined very clearly. Otherwise, it will require substantial adaptation of the PhD project.

6.7 Main conclusions and future research

My thesis substantially weakens the claims on the potential of biochar to mitigate climate change. Based on my data and available literature, I found no evidence that (all) biochars in (all) soils will persist for thousands of years. I showed that when biochar is applied in savannah sandy soils, it decomposed at the same rate or even faster than native SOC. Warm and dry conditions seem to stimulate the decomposition of unprotected biochar in soils.

The decomposition of biochar may be caused by abiotic or biotic processes and interactions between them. One possible abiotic mechanism is the chemisorption of oxygen at unsaturated carbon rings, which leads to the formation of carboxylic groups. This mechanism was found to be enhanced at higher temperatures (Cheng *et al*., 2006) and drier conditions (Bird *et al*., 1999). Some organisms may also play an important role in biochar decomposition. There are reports in the literature about fungal populations establishing on the surface of biochar, however it is not clear if they use biochar as their major C and energy source (Wiedner & Glaser, 2013). Some microbes also were capable of readily decomposing polyaromatic structures of biochar (Zimmermann *et al*., 2012).

Here, I suggest that the chemical-physical protection of biochar plays an important role in its permanence in soil. While ^{14}C dating indicates that charcoal in ADE is very old (Pessenda *et al*., 2001), the size of the fraction of biochar that accumulates in soil must be limited by the properties of soil (e.g. minerals and clay content). There is evidence that biochar can be very stable when stabilized within microagregates (< 250 µm), and/or bound in organic-mineral complexes and clay minerals in soils, where it is protected from degradation. These mechanisms may substantially reduce biochar availability to decomposers, increasing the biochar fraction that is sequestered in soils. Results from laboratory experiments showed a relationship between biochar and calcium and phosphorus contents, suggesting that the presence of calcium and phosphorus in soils protects biochar from decomposition (Clough & Skjemstad, 2000). In the ADE, biochar was partly embedded within plaques of oxides on mineral surfaces, indicating organo-mineral interactions with the soil matrix (Glaser *et al*., 2000). Therefore, soils with low C contents and protection mechanism are not suitable for soil C sequestration. In this regard, C sequestration by adding biochar into savannah sandy soils does not seem feasible to mitigate climate change. Furthermore, ADE cannot be simply recreated by the addition of biochar. Although the mechanisms behind the stabilization of charcoal and native SOC in ADE are still poorly understood, we can conclude that the intrinsic chemical recalcitrance of charcoal is not the major mechanism responsible for its accumulation in the ADE soils.

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Summary

In this PhD thesis I studied the influence of biochar discourses on the political practices in Brazil and the impact of biochar on soil organic carbon (SOC) stocks, thus contributing to the current debate on the potential of biochar to mitigate climate change. Biochar is the solid material obtained from the carbonization of biomass. The deliberate production and application to soil distinguishes biochar from other carbonized products, e.g. charcoal. Inspired by the aged charcoal found in the fertile Amazonian Dark Earth (ADE; also known as *Terra Preta de Índio*), the current application of biochar in soil is claimed to simultaneously address four global challenges: food production, climate change, energy supply and waste reduction (**Chapter 1**). Biochar is supposed to be an absorbent and stable material, which can be used to retain nutrients in the soil, increasing agricultural productivity, while sequestering carbon over extended periods of time. Therefore, biochar is claimed to be a means to mitigate global climate change. Furthermore, if biochar is produced in a modern pyrolysis plant, it also can co-produce bio-oil and syngas that could be used as energy. And if biochar is produced by carbonization of agricultural residue, biochar may reduce the quantity of solid waste that needs to be disposed of.

In **Chapter 2**, I analysed the policy arrangement related to biochar along the four dimensions of the policy arrangement approach, which are actors, discourse, power and rules. I focused on Brazil, which is an important player in the international biochar debate. My analysis shows that scientists in research institutions are the dominant players in the network, while policymakers, businessmen and farmers are marginally positioned. Experts from Embrapa occupy central positions and thus exercise most power in the network. Moreover, experts linked to ADE have lost prominence in the network. The cause for this reduction was the shift from the ADE/biochar to the biochar/technology discourse. The latter discourse includes different coalitions, such as: ‘climate change mitigation’, ‘improvement of soil fertility’ and ‘improving crop residue management’. Although the biochar/climate coalition is dominant at international level, it is far less prominent in Brazil. Nationally the discourses of

‘improvement of soil fertility’ and ‘improving crop residue management’ have particularly prompted actors’ relationships and practices. However, the biochar/technology discourse is not (yet) institutionalized into formal rules in Brazil. As a consequence, the country lacks an established biochar policy field.

Brazilian biochar practices focus on the carbonization of the available residues into biochar and on the application of biochar in soils to increase the SOC content and consequently the fertility of these soils. In this context, in **Chapter 3** I tested in the field the potential of biochar produced in traditional kilns to increase the C contents of sandy savannah soils. My results show that biochar produced in traditional kilns is less thermally altered than that produced by industrial kilns and therefore rapidly decomposes. The decomposition rate of traditionally produced biochar was higher (decomposition constant $k = 0.32\text{-}1.00$ year^{-1}) than generally assumed ($k = 0.0005\text{-}0.005$ year^{-1}), and higher than the decomposition of native SOC ($k = 0.22$ year^{-1}). In **Chapter 4** I demonstrated in a short-term laboratory experiment that oilseed-derived biochar had a similar or higher decomposition rate than native SOC. My results show that all three tested oilseed biochars decelerate the decomposition of SOC in the biochar-amended soils, with biochar richer in aromatics having a stronger negative effect than biochar richer in aliphatics. Therefore, oilseed biochar directly increases soil C stocks and indirectly raises soil C sequestration in the short term through decreasing the decomposition of native SOC.

In my research, the decomposition studies were performed using ^{13}C isotope analysis. However, the ^{13}C isotope analysis cannot be used when the differences of ^{13}C isotope abundance between biochar and soil are not sufficiently large. Therefore, its use can be limited. In **Chapter 5**, I aimed at improving the benzene polycarboxylic acid (BPCA) method. I re-designed the protocols of the BPCA method and found a better and faster way to quantify and characterize the BPCAs derived from biochar, compared to the previous protocols. The improved method was then successfully tested and implemented in a laboratory in Brazil.

Combining my findings with results of the literature, I conclude (**Chapter 6**) that there is no evidence that biochar is a reliable way for C sequestration in sandy soils under savannah environments. Biochar decomposition is highly variable, depending on charring conditions, soil and climate: (i) biochar produced by traditional kilns is less thermally degraded than those pyrolysed by industrial kilns; (ii) in sandy soils less biochar accumulates than in clay-silt soils; and (iii) warm-dry conditions raise the decomposition of biochar. These conclusions have a direct consequence for the development of policies on biochar, because we cannot ensure that biochar will sequester the same quantity of C for the same period at different geographical regions.

Samenvatting

In dit proefschrift heb ik de invloed van het discoursen over *biochar* op de Braziliaanse politiek, en het effect van *biochar* op organische stof (*soil organic carbon*: SOC) in de bodem bestudeerd. Daarmee heb ik willen bijdragen aan de discussie over het vermogen van *biochar* om effecten van klimaatverandering te compenseren. *Biochar* is verkoolde organische stof die ontstaat wanneer biomassa verbrand wordt bij lage zuurstofbeschikbaarheid. Het doel is toediening aan de bodem, en daarmee onderscheidt *biochar* zich van ander verkoolde organische stof, zoals bijvoorbeeld houtskool. De aanwezigheid van *biochar* in Zwarte Aarde van de Amazone (ook bekend als *Amazonian Dark Earth* (ADE) of *Terra Preta de Índio*; zeer vruchtbare bodems) heeft geleid tot beweringen dat *biochar* bijdraagt aan het oplossen van vier wereldproblemen: voedseltekort, klimaatverandering, brandstoftekort en ophoping van afval (**Hoofdstuk 1**). *Biochar* zou een stabiel, sterk adsorberend materiaal zijn, dat nutriënten in de bodem kan vasthouden, de landbouwproductie kan verhogen en koolstof gedurende lange tijd in de bodem kan vastleggen. Om deze laatste reden wordt beweerd dat *biochar* effecten van klimaatverandering kan verminderen. Als *biochar* wordt geproduceerd in een moderne pyrolyse installatie, worden naast *biochar* ook biogas en –olie geproduceerd uit biomassa, welke als biobrandstof benut kunnen worden. En als *biochar* wordt geproduceerd door verkoling van reststoffen uit de landbouw, draagt het bij aan vermindering van het volume vast afval.

In **Hoofdstuk 2** heb ik het Braziliaanse beleidsveld m.b.t. *biochar* geanalyseerd langs de vier dimensies van de beleidsarrangementen-benadering, namelijk. actoren, discours, macht en regels. Ik heb me gericht op Brazilië, omdat dit land een belangrijke speler in het internationale *biochar* debat is. Mijn analyse laat zien dat wetenschappers van onderzoeksinstituten de belangrijkste actoren zijn. Beleidsmakers, mensen uit het bedrijfsleven en uit de landbouw, daarentegen, spelen nog slechts een marginale rol. Omdat experts van Embrapa centraal in het *biochar* netwerk zijn geplaatst, zijn zij de meest machtige spelers en bepalen zij ook grotendeels inhoud en karakter van het debat.. Echter, experts op het gebied van ADE hebben de afgelopen jaren minder macht gekregen door de verschuiving van het ADE/*biochar* discours naar het *biochar*/technologie discours. In dit laatste discours zijn verschillende coalities te onderscheiden, zoals ‘beperking van klimaatverandering’, ‘verbetering van bodemvruchtbaarheid’ en ‘verbetering van afvalverwerking’. De *biochar*/klimaat coalitie is weliswaar internationaal dominant, maar dit is veel minder het geval in Brazilië. Op nationaal niveau hebben vooral de discoursen over ‘verbetering van bodemvruchtbaarheid’ en ‘verbetering van afvalverwerking’ actoren gemobiliseerd om samenwerkingsverbanden op te zetten. Ofschoon het *biochar*/technologie discours sterk in Brazilië is opgekomen, heeft het nog niet tot het opzetten van formeel overheidsbeleid aanleiding gegeven. Een gevolg hiervan is dat Brazilië geen officieel beleid kent m.b.t. *biochar*.

In de praktijk richt de aandacht zich op verkoling van beschikbare restproducten en de toediening van *biochar* aan bodems om het SOC gehalte, en daarmee de bodemvruchtbaarheid, te verhogen. Tegen deze achtergrond heb ik in **Hoofdstuk 3** getest wat het vermogen is van *biochar*, gemaakt in traditionele houtskoolovens, om het SOC gehalte in een zandgrond uit de savanne the verhogen. Ik laat zien dat deze *biochar* in mindere mate thermisch veranderd was dan *biochar* die in industriële ovens was geproduceerd. Daardoor brak het sneller af. De afbraaksnelheid van deze traditioneel geproduceerde *biochar* was hoger dan algemeen wordt aangenomen (afbraak constante $k = 0.32\text{-}1.00\ yr^{-1}$ i.p.v. $0.0005\text{-}0.005\ yr^{-1}$) en ook hoger dan van SOC ($k = 0.22\ yr^{-1}$). In **Hoofdstuk 4** heb ik in een kortdurend laboratoriumexperiment aangetoond dat *biochar* gemaakt van oliehoudende zaden een vergelijkbare of hogere afbraakconstante heeft dan SOC. Ik heb ook laten zien dat alle drie de geteste *biochars* van oliehoudende zaden de afbraak van SOC vertraagden. Dit vertragende effect was groter naarmate de *biochar* rijker was aan aromatische, en armer in alifatische verbindingen. Daarom verhoogde *biochar* van oliehoudende zaden de koolstof (C) vastlegging in de bodem op twee manieren: op korte termijn doordat C wordt toegevoegd aan de bodem, en op de lange termijn door vertraging van de afbraak van SOC.

Voor bovenbeschreven onderzoek naar afbraak, het ik ^{13}C isotopen analyse gebruikt. Deze methode kan echter niet gebruikt worden als het verschil in ^{13}C gehalte tussen *biochar* en SOC te klein is. Voor die gevallen zijn alternatieven nodig. Daartoe heb ik in **Hoofdstuk** 5 de benzeen polycarboxyl zuur (*benzene polycarboxylic acid*: BPCA) methode verbeterd. Ik heb een nieuw protocol ontwikkeld, waarmee de BPCAs van *biochar* sneller en beter gekarakteriseerd en gekwantificeerd kunnen worden. De verbeterde methode is getest en in de praktijk gebracht in een Braziliaans laboratorium.

Tegen het licht van mijn resultaten en van wat reeds beschreven was in de literatuur, concludeer ik in **Hoofdstuk 6** dat *biochar* toediening aan zandgronden van de savanne, geen betrouwbare manier is om C vast te leggen in de bodem. De afbraak van *biochar* varieert sterk en hangt af van de procescondities tijdens de productie, van bodemeigenschappen en van het klimaat: (i) *biochar* die is geproduceerd in traditionele houtskoolovens, is minder thermisch veranderd dan wanneer het geproduceerd is in industriële ovens; (ii) in zandgrond hoopt minder *biochar* op dan in kleigrond; (iii) warme en droge omstandigheden verhogen de afbraaksnelheid van *biochar*. Deze conclusies zouden gevolgen moeten hebben voor van beleid t.a.v. *biochar*, want het kan niet gegarandeerd worden dat *biochar* in verschillende geografische regio's in dezelfde mate bijdraagt aan C vastlegging.

Acknowledgments

I had the help of many people during my PhD journey on the land of tulips, canals and stroopwafel.

I would like to thank all my supervisors, working with you individually and collectively was both exciting and challenging. Thomas Kuyper, I thank you a lot for your challenging discussions on different issues, they were included in many parts of this thesis. Ellis Hoffland for the constructive comments and criticism, your comments helped me improving my self-criticism. Bas Arts for patiently guiding me on the policy side of my thesis, I learned a lot with you. Etelvino Novotny for sharping my scientific skill in an unique way. I would also like to thank Luiz Fernando Leite for his valuable comments on the thesis proposal.

I big thank to Fabiano Balieiro for the daily helping on the steps of my work during my time in Brazil. Bruno Alves for let me feel welcome in the Embrapa Agrobiology. Annibal and Wildson to introduce me the new world of analytical chemistry. Achete to welcome me at Inmetro and Gabriela to guide me around the several laboratories at Inmetro.

I was very luck to belong to the cardume family: Marielos, Andre, Estelita, Clara, Paulo, Carlos, Edvaldo, Angela, Joana, Isabel, Simon, Camilo and Wellington. The monthly discussion with you help me to improve my work and develop my criticism. Edvaldo, a special thank for you who was not only my colleague in the research programme, but also a co-thinker during my PhD journey. Thanks to the Soil Quality staffs: Marnella, Anita, Ester, Peter and Caroline who kindly helped me in issues related to my PhD in different moments. Thanks Soil Quality friends and colleagues with who I shared great moments: Pelin, Xinxin, Angie, Walter, Mart, Supriatin, Joana, Jimeng, Wei, Valentina, Kimo, Sebastian, Ma Lin, Yunyu, Jana, Li, Thamas, Thomas, Ingrid, Inge.

I want to thank my awesome officemates: Karst, Andreas, Yong and Paulo. I was very luck to share an office with such nice guys. I already miss the nice atmosphere of the office, our talking, coffees, discussions, diners, drinks and laughing.

I am also very thankful for the friendship of Roberto Oliveira, Suzanne Wagner and Sandra Vaz in all moments of my life. A big 'thank you' goes to my triple-continental friend Natalie Oram who made my days happier in Brazil, Canada and The Netherlands.

I thank the Brazilian Wageningen community: AnaBela and Wiebe, Aninha and Willian, Márcia and José, Franco and Rose, Giovanni and Josi, Fernanda and Maurício, Carol and Dennis, Dani e Paulo, Adrielli e Thiago, Mônica e Edvaldo, Catá e André, Anderson and Zany, Charles, Pancho, Laura, Vanja, Manuela, Deived, Itaynara, Giovanni, Alexandre, Sidnei, Cecilia, Murilo, Kassia, Ulisses, Naira, Gabriel, Lara (you are almost one). You turned the Dutch days towards tropical days with spontaneous parties, good music and tonnes of delicious food.

The biggest 'thank you' goes to Andre Meriac to be always there during the hard and good times of my PhD and life. You make my life happier. I specially want to thank my mother Maria Rittl for being always my example of humanity, my father Luiz Rittl for his valuable advices and my brothers Luiz Eduardo, Luiz Fernando and Luiz Gustavo Rittl for supporting me. I also want to thank my family (aunts, uncles and cousins) who encourage me to follow my dreams.

Muito obrigada !!!

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Tatiana Francischinelli Rittl was born in Itu, São Paulo, Brazil. She is an environmental manager with master degree on soil science. She obtained both degrees at University of São Paulo (Brazil). During her master studies she did an internship at University of Guelph, Canada. In this period she got involved in three research projects: (i) subsidies for territorial planning at the buffer zone of Petar State Park, São Paulo, Brazil (University of São Paulo, 2009-2011); (ii) spatial-temporal variations in hydro-physical properties soil under different management systems in settlement Luiz Macedo (University of São Paulo, 2009-2010); and (iii) quantification of the micromorphology of Brazilian soils (University of Guelph, 2010). In 2011, she started as a PhD candidate at the Soil Quality Department and Forest Nature Conservation Group in Wageningen University. Her PhD thesis was part of the Terra Preta Programme, and it focused on the potential of biochar to mitigate climate change.

List of publications

Rittl, T. F.; Novotny, E. H.; Balieiro, F. C.; Hoffland, E.; Alves, B. J. R; Kuyper, T. W. Negative priming of native soil organic carbon mineralization by oilseed biochars of contrasting quality. European Journal of Soil Science, 2015. *doi: 10.1111/ejss.12257*

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Maia, C. M. B. F.; Novotny, E. H.; **Rittl, T. F.**; Hayes, M. H. B. Soil organic matter: chemical and physical characteristics and analytical methods. A review. Current Organic Chemistry, v. 17, p. 2985-2990, 2013.

Rittl, T.; Cooper, M.; Heck, R. J.; Ballester, M. V. R. Object-based method outperforms per-pixel method for land cover classification in a protected area of the Brazilian Atlantic Rainforest region. Pedosphere, v. 23, p. 290-297, 2013.

PE&RC Training and Education Statement

With the training and education activities listed below the PhD candidate has complied with the requirements set by the C.T. de Wit Graduate School for Production Ecology and Resource Conservation (PE&RC) which comprises of a minimum total of 32 ECTS (= 22 weeks of activities)

Review of literature (6 ECTS)

- Pyrogenic carbon: chemical and physical characteristics and analytical methods (2013)

Writing of project proposal (4.5 ECTS)

- Pyrogenic carbon and its impacts on soil organic carbon and climate change

Post-graduate courses (7.4 ECTS)

- Geostatic; PE&RC (2011)
- Summer school : participatory forest management as practice and performance; FGV-FNP (2011)
- Nuclear magnetic resonance techniques for soil organic matter assessment; EMBRAPA (2012)
- Multivariate analysis; EMBRAPA (2013)
- 2nd European biochar summer school; Ithaka Institute (2013)

Laboratory training and working visits (4.5 ECTS)

- Analytical chemistry; UFF (2012)
- Analytical tools; INMETRO (2013)

Invited review of (unpublished) journal manuscript (2 ECTS)

- Journal Environmental Quality: biochar and agriculture (2011)
- Journal Environmental Quality: biochar and soil organic matter (2012)

Deficiency, refresh, brush-up courses (3 ECTS)

- The carbon dilemma (2013)

Competence strengthening / skills courses (3 ECTS)

- Competence assessment; PE&RC (2011)
- Techniques for writing and presenting a scientific paper; PE&RC (2011)
- Project and time management (P&TM); WUR (2013)

PE&RC Annual meetings, seminars and the PE&RC weekend (2.4 ECTS)

- PE&RC PhD Introduction weekend (2011)
- PE&RC Day symposium (2013)
- PE&RC Weekend (2014)
- PE&RC Day symposium (2014)

Discussion groups / local seminars / other scientific meetings (4.5 ECTS)

- Terra Preta discussion group; Wageningen (2011-2015)
- Analytical Chemistry group; UFF (2013)

International symposia, workshops and conferences (9 ECTS)

- Wageningen Conference on Applied Soil Science; poster presentation (2011)
- International Workshop of the Terra Preta; oral presentation (2012)
- International Workshop of the Terra Preta; oral presentation (2013)
- Humic Substance Society; oral presentation (2013)
- Impact of Natural and Anthropogenic Pyrogenic carbon in Mediterranean Ecosystems; poster presentation (2013)