Properties of thermochemically altered biomass and its effects in soil

From archaeological periods to present times

Dissertation
zur Erlangung des akademischen Grades
doctor rerum naturalium (Dr. rer. nat.)

vorgelegt an der

Naturwissenschaftlichen Fakultät III
Agrar- und Ernährungswissenschaften,
Geowissenschaften und Informatik

der Martin-Luther-Universität Halle-Wittenberg

von

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geboren am 28. April 1979 in Heilbronn

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Tag der Verteidigung: 20.04.2015

We cannot change the wind,

but the sail can be set in different ways

(Aristoteles, 384 – 322 v. Chr.)

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List of Abbreviations

ADE	Anthropogenic Dark Earth
ADE	Ancient Dark Earths (Chapter 1)
B6CA	Mellitic Acid
BC	Black Carbon
BPCA	Benzenepolycarboxlic Acids
CEC	Cation Exchange Capacity
DCA	Deoxycholic Acid
EBC	European Biochar Certificate
EC	Electric Conductivity
EDS	Energy Dispersive X-ray Spectrometry
HDCA	Hyodeoxycholic Acid
HTC	Hydrothermal Carbonization
IBI	International Biochar Initiative
LCA	Lithocholic Acid
NDE	Nordic Dark Earth
NMR	Nuclear Magnet Resonance
PAHs	Polycyclic Aromatic Hydrocarbons
PCDDs	Polychlorinated Dibenzodioxins
PCDFs	Polychlorinated Dibenzofurans
PCM	Pyrogenic Carbonaceous Material
SOC	Soil Organic Carbon
SOM	Soil Organic Matter
TEQ	Toxic Equivalency (for dioxine)
TOC	Total Organic Carbon
WHC	Water Holding Capacity

Summary

In recent years, thermochemically altered or carbonized biosolids (commonly referred to as biochar) have become a major research subject as soil conditioner. Scientific interest has been triggered by investigations of ancient Anthropogenic Dark Earths (ADE) in Amazonia (Brazil), also known as *Terra Preta de Índio*, containing large amounts of biochar. Input of biochar in combination with excrements, biomass wastes, manure, ash, and bones led to nutrient-rich soils with large soil organic matter stocks. Besides *Terra Preta de Índio*, other ancient Anthrosols with similar pedogenesis worldwide, may serve as conceptual models for sustainable land use and long-term C sequestration.

This thesis combines the following interrelated and cumulative subjects: i) review knowledge on the historical use of biochar in different climatic regions and epochs (chapter 2); ii) investigations of an ADE located in Northern Germany, in order to find parallels in formation and ecological properties to *Terra Preta de Ìndio* (chapter 3); iii) characterization and evaluation of modern carbonized biomass (biochars and hydrochars) regarding its use as soil amendment and for long-term C sequestration (chapter 4 and 5) and iv) the application of complex biochar fertilizers under field conditions in order to evaluate its short-term effects on soil and plant biomass (chapter 6).

Ancient soil management has changed fundamentally the amounts and properties of soil organic matter (SOM) and nutrients. The literature study (chapter 2) revealed that ADEs were forming worldwide, from various soil types, during various epochs, under different land use practices and different climatic conditions. Carbonaceous material was surprsingly often used intentionally for soil improvement. The study provides additional insights in various ancient soil cultivation techniques developed in different cultures and epochs such as plaggen cultiviation, slash-and-burn, formigure technique or "fire flooding". Most of the abandoned ancient biochar-containing soils maintained high soil organic matter levels and fertility until today. However, in contrast to the well-investigated *Terra Preta* soils in tropical Brazil, knowledge on ancient Anthrosols in other parts of the world is still scarce and a more systematic research is needed to understand their development and the organic input materials (beside biochar) and climatic conditions. A better understanding of individual Anthrosol development will provide well-adapted models for sustainable land use in the corresponding climatic region.

In view of important global topics such as climate change and sustainable agriculture, more attention should be paid to Anthrosols exhibiting high nutrient and

SOM stocks. Chapter 3 aimed this highly relevant field of research in order gain deeper insights in anthropogenic soil formation. For this purpose, a deep black colored ADE found during an archaeological excavation of a Slavic settlement ($10^{th}/11^{th}$ C.A.D.) in Brünkendorf (Wendland region in Northern Germany) was investigated. A central aspect of this study was to verify parallels between the famous *Terra Preta de Ìndio* and the Nordic Dark Earth (NDE) regarding main inputs, soil formation and ecological properties. For instance, potential cation exchange capacity (CEC) of NDE was 41 x higher than in adjacent soil. Black carbon content was enriched by about 400% whereas elemets such as Mg, P, Na, K, Ca, Mn, Fe were up to 554 x higher than in reference soil. The higher $\delta^{15}N$ values in NDE (up to +7.1‰), typical for manured soils, indicated input materials derrived from organic wastes and faecals. Biomarkers, such as sterols and bile acids indicated that the majority of the faecal residues derived from pigs, cows, and sheep. Amino sugar analyses showed that NDE contains high amounts of fungal-derived residues. The multi-analytical approach in this dissertation suggests strong parallels between anthropogenic soil formation of *Terra Preta de Índio* and NDE. The only obvious difference was that input of human-derived faecal material dominated in *Terra Preta de Índio*, whereas faecal residues derived from pigs, cows, and sheep played a major role in NDE. The existence of the NDE in the temperature zone of Europe demonstrates the capability of sandy-textured soils to maintain high SOM and nutrient stocks over hundreds of years. It seems highly probable that the favourable properties of the NDE are due to the large contents of highly aromatic SOM fractions (biochar), leading to a large CEC and, consequently, to large nutrient stocks when these nutrients are applied preferentially in organic forms.

Given the growing interest in biochar (and hydrochar) as soil amendment, there is a rapid development of technologies, such as pyrolysis, gasification and hydrothermal carbonization (HTC). One of the key challenges for commercial production is providing a consistent quality of the carbonized products. Standards for biochars are recommended by the “European Biochar Certificate” (EBC) or the “International Biochar Initiative” (IBI) draft guidelines. In chapter 4, biochars and hydrochars from different industrial-scale reactors were investigated according to critical criteria as recommended by the EBC or IBI, including elemental composition, black carbon, ash content, and organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs) or polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Environmental risk of investigated biochars and hydrochars was low with respect to PAH and dioxin

contents. Furthermore, the results in chapter 4 show that biochars and hydrochars have fundamentally different chemical properties. ^{13}C-NMR analysis revealed that hydrochars have a different structure (dominated by alkyl moieties) than biochars (dominated by aromatics). Black carbon analyses confirmed these observations, showing that hydrochars have lower proportions of aromatic compounds than biochars. Therefore, the residence time of hydrochars in soil will likely be shorter than that of biochars. In contrast, hydrochars are rich in functional groups, likely due to the low temperature during the thermochemical process, leading to a high nutrient retention capacity. It can be concluded that biochars and hydrochars are differently suitable for long-term C sequestration. Hydrochars are not included in the EBC and IBI standardization and need their own directive, due to different chemical properties.

In terms of a required guideline, chapter 5 focused on critical properties of hydrochars produced from different feedstocks (wheat straw, poplar wood, and olive residues) at different production temperature (180, 210, and 230 °C). The results showed that hydrochars were generally acidic, with pH values below 5, which is in contrast to the alkaline pH values of biochars (chapter 4). An increase of the process temperature led to a decrease in O-alkyl C, while alkyl C and aromatic C increased. Lignin content decreased with increasing temperature, while highly condensed black carbon moieties and PAH increased. It is recommended to use high temperatures for HTC to maintain more stable products for soil amelioration. Results in chapter 4 and 5 also strongly suggest that feedstocks with low moisture content (e.g., woody biomass) should be used for pyrolysis. HTC, however, is a suitable process for feedstocks with high water contents (e.g. maize silage or leftover food), because energy-intensive drying of biomass is not needed.

A field trial was carried out (chapter 6) to investigate short-term effects of biochar fertilizers on soil properties, maize yield and nutrition. For this purpose, agronomically relevant inorganic and organic fertilizers, such as mineral fertilizer, biogas digestate, microbially inoculated biogas digestate, and compost, were applied individually (controls) and in combination with various amounts of biochar (1, 10, and 40 Mg ha^{-1}). The results showed no negative effects of biochar on soil properties but rather equal or even better results compared to conventionally applied pure mineral fertilizer with respect to yield and plant nutrition. High doses of biochar (40 Mg ha^{-1}) increased water holding capacity (WHC) significantly, and yields tending to increase. Larger (P, K, Mg, Zn), more or less equal (N, Ca, Mn, Co, Cr, Pb) and lower (Na, Cu, Ni, Cd) element uptake into maize could be observed. The diverse effects of biochar, e.g. on plant nutrition are highly complex and differ strongly when combined with mineral or organic fertilizers.

The comparison of ADEs revealed that pyrogenic carbonaceous material, such as biochar, has the potential for long-term carbon sequestration and soil fertility improvement even in sandy soils under temperate climate. However, the traditional use of biochar (intentional or not) is not comparable with modern demands on biochar production. Research focusing on biochemical interactions in soil after biochar application is equally important as the constitution of binding guidelines at EU level for commercial biochar production.

Zusammenfassung

Das Interesse an thermochemisch karbonisierten Feststoffen (z.B. Pflanzenkohle) zur Bodenverbesserung ist in den vergangenen Jahren stark gestiegen. Als Vorbild dient die anthropogen entstandene *Terra Preta de Índio* in Amazonien, mit ihrem hohen Anteil an Pflanzenkohle. Das Zusammenwirken von Pflanzenkohle mit weiteren organischen Komponenten wie Exkremente, Bioabfälle, Kompost, Asche und Knochen führte zur Entwicklung eines nährstoffreichen Bodens mit hohem Gehalt an organischer Bodensubstanz. Neben *Terra Preta de Índio* existieren weltweit weitere anthropogene Böden, die als Modell für nachhaltige Landnutzung und langfristige Speicherung von Kohlenstoff im Boden dienen können.

Die vorliegende Dissertation behandelt folgende aufeinander aufbauende Themen: i) Literaturstudie zur historischen Nutzung von Pflanzenkohle (Kapitel 2); ii) Untersuchung einer anthropogenen Schwarzerde in Norddeutschland bezüglich ökologischer Eigenschaften und Genese und möglichen Parallelen zur *Terra Preta de Índio* (Kapitel 3); iii) Charakterisierung und Bewertung von Pyrokohlen und Hydrokohlen und ihrer Eignung zur Bodenverbesserung und langfristigen Kohlenstoffspeicherung (Kapitel 4 und 5); iv) Untersuchung und Bewertung kurzfristiger Effekte komplexer Pflanzenkohle-Dünger unter Feldbedingungen (Kapitel 6).

Bodenbearbeitungsmaßnahmen in der historischen Vergangenheit führten zu grundlegenden Veränderungen des Humus- und Nährstoffhaushalts. Die Literaturstudie (Kapitel 2) zeigt, dass anthropogen beeinflusste Böden (ADEs) aus historischer Vergangenheit weltweit erhalten sind. Diese Böden entwickelten sich unter verschiedenen Umweltbedingungen innerhalb zahlreicher Epochen. Verkohlte Biomasse wurde erstaunlicherweise recht häufig bewusst zur Bodenverbesserung eingesetzt. Hierfür wurden unterschiedlichste Techniken und Bodenbearbeitungsmaßnahmen (z.B. Plaggen, Brandrodung etc.) angewendet. Einige historische Böden weisen bis zum heutigen Tag eine hohe Fruchtbarkeit auf (Kapitel 2). Im Vergleich zu den gut untersuchten *Terra Preta*-Böden im tropischen Brasilien ist der Forschungsstand zu anderen anthropogenen Schwarzerden sehr lückenhaft. Um ihre Entstehung in Abhängigkeit des organischen Eintrags (neben Pflanzenkohle) und der klimatischen Situation besser zu verstehen, bedarf es weiterer Forschung. Die systematische Erhebung von Daten zur Genese anthropogener Schwarzerden dient dem Verständnis der nachhaltigen Landnutzung in der jeweiligen Klimaregion. Die in Kapitel 3 durchgeführte Studie leistet hierzu einen wichtigen Beitrag um die anthropogene Bodenentwicklung

besser verstehen zu können. Der tiefschwarze Boden wurde im Rahmen einer archäologischen Grabung in einer slawischen Siedlung (Brünkendorf) aus dem 10./11. Jh. n. Chr. in Norddeutschland (Wendland) gefunden (Kapitel 3). Eine zentrale Fragestellung der Studie ist, ob Parallelen zur gut untersuchten *Terra Preta de Índio* hinsichtlich der organischen Einträge, Genese und ökologischen Eigenschaften bestehen. Die Ergebnisse zeigen beispielsweise, dass die Kationenaustauschkapazität des sandigen Bodens 41 x höher ist als die des angrenzenden Bodens. Der Anteil des aromatischen Kohlenstoffs (black carbon) ist um 400% höher als im Referenzboden. Elemente wie Mg, P, Na, K, Ca, Mn, Fe sind im Vergleich bis um das 554-fache anreichert. Die deutlich angereicherten δ^{15}N-Werte (bis +7.1‰) legen organische Einträge tierischen und menschlichen Ursprungs nahe. Fäkalbiomarker wie Sterole und Gallensäuren deuten auf einen hohen Eintrag von Schweine-, Rinder- und Schaffäkalien hin. Analysen der Aminozucker zeigen eine deutliche Dominanz mikrobieller Residualmasse pilzlichem Ursprung an. Der multianalytische Ansatz in Kapitel 3 zeigt deutliche Parallelen in der Bodengenese zwischen den *Terra Preta*-Böden und dem slawischen Siedlungsboden in Norddeutschland. Ein wesentlicher Unterschied ist der hohe Anteil menschlicher Fäkalien in der *Terra Preta de Índio*, während in dem slawischen Siedlungsboden vorwiegend tierische Fäkalien eingebracht wurden. Das Vorkommen einer anthropogenen Schwarzerde in Sand dominierten Böden des gemäßigten Klima Europas ist äußerst ungewöhnlich. Das Beispiel zeigt jedoch, dass es möglich ist, die Humus- und Nährstoffvorräte in Sandböden über viele Jahrhunderte hinweg aufrecht zu halten. Ein wesentlicher Grund für die günstigen Bodeneigenschaften der nordischen Schwarzerde ist vermutlich der hohe Anteil an hocharomatischer, organischer Bodensubstanz (Black Carbon aus Pflanzenkohle), die zu einer hohen Kationenaustauschkapazität führt und folglich Nährstoffverluste verringert.

Aufgrund des steigenden Interesses an Pflanzenkohle (und Hydrokohle) als Bodenzuschlagsstoff haben sich in den vergangenen Jahren diverse Technologien zu deren Herstellung rasant entwickelt. Unerlässlich für die kommerzielle Produktion von Pflanzenkohle im Pyrolyse-, Holzvergaser- oder hydrothermalen Verfahren ist es, eine stetig gleichbleibende Qualität sicher zu stellen. Anhaltspunkte für Qualitätsstandards für Biokohle bieten das "Europäische Biokohle Zertifikat" (EBC) und die "Internationale Biokohle Initiative" (IBI). In Kapitel 4 wurden Pyrokohlen und Hydrokohlen hinsichtlich wesentlicher Kriterien nach Vorgaben der EBC oder IBI untersucht. Dabei wurden elementare Zusammensetzung, Black Carbon-Gehalt, Aschegehalt und organische

Schadstoffe, wie polyzyklische aromatische Kohlenwasserstoffe (PAKs) oder polychlorierte Dibenzodioxine (PCDDs) und Dibenzofurane (PCDFs), betrachtet. Die in dieser Studie untersuchten Kohlen wiesen nur geringe bis keine PAK- und Dioxin-Konzentrationen auf und bergen damit kein Umweltrisiko. Die weiteren Ergebnisse in Kapitel 4 zeigen, dass sich Pyrokohlen und Hydrokohlen grundlegend in ihren chemischen Eigenschaften unterscheiden. Mit Hilfe der ^{13}C-NMR-Analyse konnte gezeigt werden, dass Hydrokohlen primär aus Alkylverbindungen zusammengesetzt sind (geringe Rekalzitranz) während Pyrokohlen hocharomatische Eigenschaften besitzen. Die Ergebnisse der Black Carbon-Untersuchung bestätigen den wenig aromatischen Charakter der Hydrokohlen. Es kann folglich davon ausgegangen werden, dass die Hydrokohlen im Vergleich zur Pyrokohle eine geringere Verweildauer im Boden haben. Allerdings besitzen Hydrokohlen im Vergleich zu den untersuchten Pyrokohlen einen hohen Anteil funktioneller Gruppen, die sich aufgrund der geringen Temperatur des thermochemischen Prozesses erhalten haben. Die Nährstoffhaltekapazität der Hydrokohlen ist somit höher als die der (zunächst) inerten Pflanzenkohle. Hydrokohlen haben daher grundlegend andere chemische Eigenschaften als Pyrokohlen und sind nicht zur langfristigen Kohlenstoffspeicherung im Boden geeignet. Eine weitere Erhöhung der Prozesstemperatur könnte in Zukunft Pyrokohle-ähnliche Hydrokohlen erzeugen. Zudem sind (bindende) Richtlinien zu Qualitätsmerkmalen von Hydrokohlen, wie sie bereits von der EBC und IBI für Biokohlen vorgegeben sind, dringend erforderlich.

Für die Erstellung von Richtlinien für Hydrokohlen ist eine entsprechende Datengrundlage nötig. Kapitel 5 fokussiert daher auf grundlegende Materialeigenschaften von Hydrokohlen, die aus verschiedenen Biomassen (Stroh, Pappelholz und Olivenreste) bei unterschiedlichen Produktionstemperaturen (180, 210 und 230°C) hergestellt wurden. Der pH-Wert von Hydrokohlen liegt generell im sauren Bereich (< 5), was im Gegensatz zu den alkalischen Pyrokohlen steht (Kapitel 4). Mit zunehmender Temperatur verringerte sich der Anteil von O-Alkyl-C während Alkyl-C und der Anteil an aromatischem Kohlenstoff stieg. Während sich mit ansteigender Prozesstemperatur der Ligninanteil der Kohlen verringert, konnte eine Zunahme an Black Carbon und PAKs beobachtet werden. Hydrokohlen, die als Bodenzuschlagsstoffe eingesetzt werden, sollten bei hohen Temperaturen (mindestens 230 °C) produziert werden, um eine höhere Rekalzitranz zu erreichen. Aufgrund der Ergebnisse in Kapitel 4 und 5 ist zu empfehlen, dass Biomasse mit einem geringen Wassergehalt (z.B. Holz) für die Pyrolyse eingesetzt wird. Die hydrothermale Carbonisierung ist ein geeigneter Prozess, um Biomasse mit hohem Wasseranteil (z.B. Biogasgülle oder Lebensmittelreste) ohne vorherige energieintensive Trocknung umzusetzen.

In Kapitel 6 wurde im Rahmen eines Feldversuchs kurzfristige Effekte von Pflanzenkohledünger auf Bodeneigenschaften, Ertrag und Pflanzenernährung untersucht. Hierzu wurden landwirtschaftlich relevante anorganische und organische Dünger (Mineraldünger, Biogasgülle, mit Mikroorganismen inokulierte Biogasgülle, Kompost) verwendet. Die Dünger wurden jeweils ohne (Kontrolle) und mit Pflanzenkohlezugabe von 1, 10 und 40 Mg ha^{-1} appliziert. Die Ergebnisse des ersten Versuchsjahres zeigten keine negativen Pflanzenkohleeffekte auf die Bodeneigenschaften. Vielmehr konnten vergleichbare Ergebnisse zu mineralischen Düngern hinsichtlich Ertrag und Nährstoffaufnahme gezeigt werden. Hohe Applikationsraten an Pflanzenkohle (40 Mg ha^{-1}) führten zu einem signifikanten Anstieg der Wasserhaltekapazität und zu einem tendenziellen Anstieg des Biomasseertrags. Hinsichtlich Nährstoff- und Schwermetallaufnahme ist zu beobachten, dass P, K, Mg und Zn anstiegen, N, Ca, Mn, Co, Cr und Pb unverändert blieben, während die Aufnahme von Na, Cu, Ni und Cd von Maispflanzen reduziert wurde. Die Unterschiede in der Nährstoffaufnahme unterliegen komplexen Wechselwirkungen mit der Pflanzenkohle und zeigen eine starke Variabilität in Kombination mit den verschiedenen Düngern.

Die anthropogenen Böden verdeutlichen, dass karbonisierte Biomasse geeignet ist, um Kohlenstoff langfristig im Boden zu speichern und in Kombination mit organischen Düngern die Fruchtbarkeit zu steigern. Allerdings ist die historische Anwendung von Pflanzenkohle (gewollt oder ungewollt) nicht vergleichbar mit den Ansprüchen an die moderne Pflanzenkohleproduktion. Weitere gezielte Erforschung biochemischer Interaktionen im Boden nach Pflanzenkohleapplikation ist ebenso wichtig wie die Erstellung verbindlicher Richtlinien auf EU-Ebene für die kommerzielle Pflanzenkohleproduktion.

Chapter 1

General Introduction

1.1 Rationale

The Kyoto Protocol (UNFCCC, 1998) is the first international agreement attempting to mitigate global climate change by focusing on sources, reservoirs and sinks of greenhouse gas emissions (GHGs, Dumanski, 2004). Under Article 3.4 of the Kyoto Protocol, carbon sequestration in agricultural soils is scheduled (Freibauer et al. 2004), pointing out the central relevance of this crucial issue. It is estimated that most agriculturally used soils already lost 50 to 70% of their original soil organic carbon (SOC) and the depletion is exacerbated by further soil degradation and desertification (Lal, 2003). Concerning atmospheric CO_2 capturing, the estimated global potential of SOC sequestration is “only” 0.6 to 1.2 Pg C y^{-1}, which may offset one-fourth to one-third of the annual increase in atmospheric CO_2 estimated with 3.3 Pg C $year^{-1}$ (Lal, 2003; Oliver et al. 2013). Nonetheless, the increase of OC supports restoration of degraded soils, enhances biomass production, contributes to the purification of surface and ground waters, reduces the rate of enrichment of atmospheric CO_2 by offsetting emissions due to fossil fuel and is therefore a win-win strategy (Tiessen et al. 2001; Lal, 2004). For soil conservation including maintaining or restoring SOC pools, various technologies such as conservation tillage, no till or mulch farming (e.g., Shaver et al. 2002; Smith 2004; McCalla and Army 1961), cover crops (e.g., Singh et al. 1998; Fullen and Auerswald, 1998), crop rotation (e.g., Uhlen and Tveitnes, 1995), nutrient management with compost, biosolids or precision farming (e.g., Gregorich et al. 2001, Woodburry et al. 1992; Epstein et al. 1976) are recommended.

Initiated by investigations of ancient ADE in Amazonia (Brazil), also known as *Terra Preta de Índio*, thermochecmically carbonized biosolids (biochar) have increasingly become subject of scientific research on long-term C sequestration in soils (e.g., Glaser et al. 2000, Glaser and Birk 2012).

1.2 Ancient Dark Earths as conceptual model for sustainable land use

The ADE *Terra Preta de Índio* in the Amazon Basin (Brazil) is one of the most prominent examples for a highly fertile soil over a long period of time (~ 2000 years and more; Sombroek et al. 2002). Its occurrence in Central Amazonia, where highly weathered Ferralsols, Arenosols, and Acrisols predominate, is unusual and its potential for long-term C sequestration may act as model for sustainable land use (Glaser et al.

2001). It is assumed that biochar is the key factor for the long-term stability of SOM in *Terra Preta* (Glaser et al. 2001; Glaser 2007). Additional input materials such as excrements, biomass wastes, manure, ash, and bones lead to a nutrient-rich soil with large SOM stocks (Glaser and Birk, 2012).

Among *Terra Preta de Índio*, ancient manuring practices resulting in dark coloured Anthrosols are documented worldwide. Examples are the ancient agricultural soils of the Andes (Sandor et al. 1995) or the Plaggen-Esch soils in Northern Europe (Davidson et al. 2006). They developed in different climatic regions, under different land management practices, and maintained high levels of SOM over long periods of time. Highly fertile soils caused by historic land-use practices may help to address some of the most urgent global change issues: The loss of SOC and nutrients from soil. Therefore, ancient Anthrosols need to be systematically investigated, to 1) better understand the anthropogenically affected cycling of SOM under different climatic conditions and land-use practices and 2) develop strategies for sustainable agricultural soil management from these examples. However, to achieve the favorable properties of e.g. *Terra Preta de Índio*, huge amounts of biochar produced in industrial scale reactors are neccessary.

1.3 Carbonization technologies – past and present

Charcoal and biochar, carbonaceous materials dominated by aromatics, formed under limited oxygen conditions at temperatures ranging between 350 and 1200 °C. Charcoal is produced in pits or kilns, e.g., for cooking, heating or metallurgy processes, whereas biochar is produced from biomass residues specifically for soil application as part of agronomic or environmental management (Brown, 2009; Lehmann and Joseph, 2009, Joseph et al. 2009).

So far it is still unknown, where and when charcoal production actually began, however, it is certain that charcoal-making in Europe had become an important industry for the recovery of iron and other metals around 1100 BC (Emrich 1985). Numerous traditional kilns and pits, differing in structure and size, have been developed for charcoal production (Figure 1; Emrich 1985). The mass yield and quality of charcoal strongly depends on the used technique and is influenced by several factors such as temperature, time, moisture, wood size, wood species and weather conditions (Schenkel et al. 1998). For instance, a mound kiln (Figure 1) yields charcoal between 20-30% on dry basis with 70% C concentration (Schenkel et al. 1998). In accordance with today's environmental requirements, traditional carbonization techniques are no longer appropriate, e.g. because of the large green house gas emissions. It is estimated that on average 0.77-1.63 kg CO_2-C (carbon as carbon dioxiede equivalents) are emitted for every kilogram of charcoal produced in the traditional way (Pennise et al. 2001). Traditional charcoal pits and kilns have almost been discontinued in industrial countries whereas developing countries still use charcoal as fuel for households and institutional cooking and heating (Pennise et al. 2001).

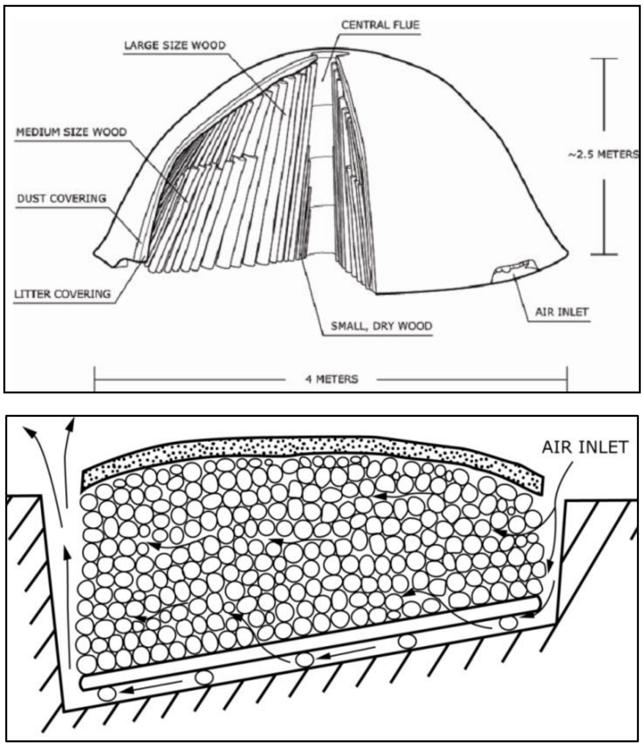

Figure 1 Examples for traditional charcoal production: mound kiln (left) and a large pit kiln (right) (Source: FAO 1983).

Currently, a variety of different commercial technologies for biochar production or other carbonaceous by-products exist. In contrast to traditional charcoal production, modern technologies offer the opportunity to produce carbonaceous materials under defined conditions (e.g. time and temperature) and from biomasses different from wood. Three main categories of thermochemical conversion of biomass can be distinguished: pyrolysis, gasification, and hydrothermal carbonization.

The pyrolysis process is characterized by temperatures between 400 and 800 °C (depending on the reactor) with limited oxygen supply. On average, pyrolysis yields (depending on feedstock) about 40-75% gas, 0-15% liquids, and 20-50% biochar (Bridgewater 2007). Figure 2 shows an example of a pyrolysis reactor (PYREG^{TM}

technology), which was used for thr production of biochar on commercial scale (chapter 4 and 6). The pre-dried biomass is heated up to 800 °C in the twin screw reactor and the syngas produced during the carbonization process is burned in the combustion chamber at 1250 °C. As a result, exhaust emissions are reduced to a minimum (for more information see www.PYREG.de).

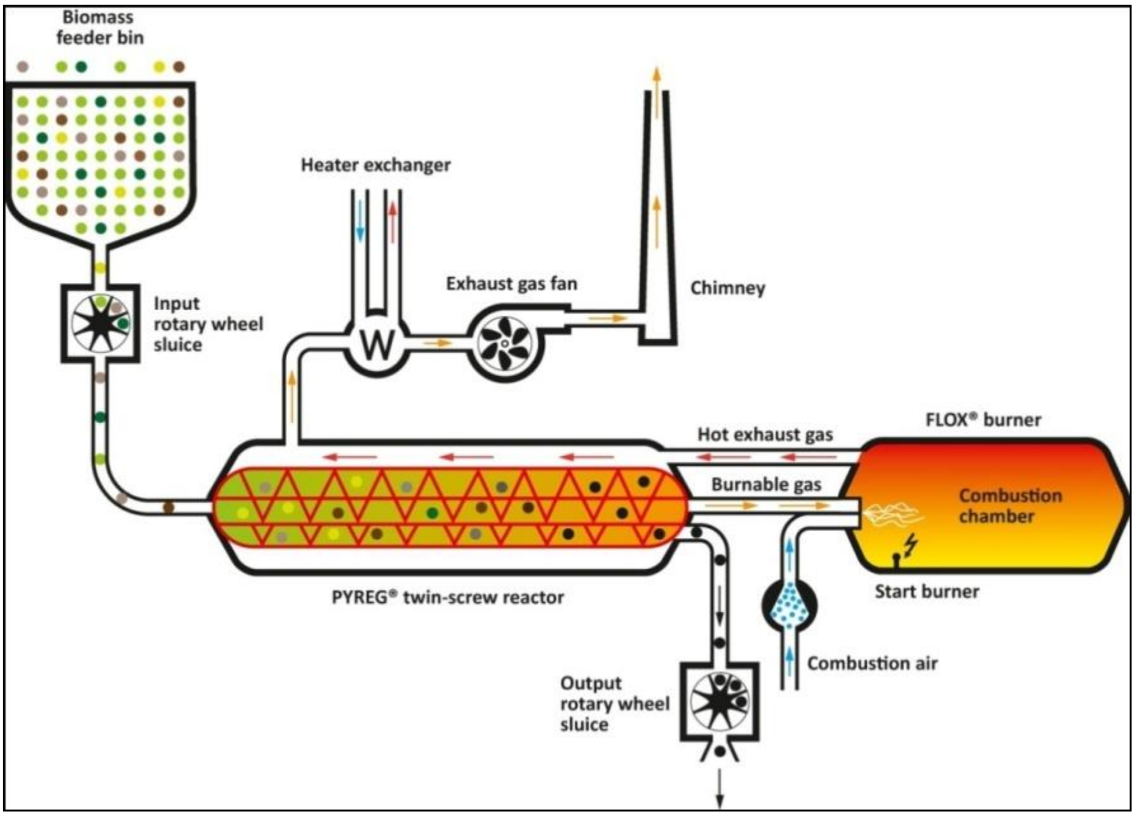

Figure 2 Main principle of pyrolysis process of PYREG (Source: www.PYREG.de; with kind permission of PYREG GmbH).

The gasification technology is an extension to pyrolysis technique – temperature typically exceeds 850 °C and biomass is partially oxidized (Overend 2004; Shackely et al. 2012). The process aims at high gas yields (up to 95%), liquids and biochar are only formed at small amounts of 1-5% and ~1%, respectively (Bridgwater 2007).

HTC for production of hydrochars includes the heating of biomass together with water and a catalyst (e.g., citric acid) in a pressure vessel at temperatures between 180 and 250 °C for several hours (Libra et al. 2011). However, the chemical properties of hydrochars are not comparable to charcoals or biochars (less aromatic and less condensed), because of different carbonization processes and thermochemical reactions (Cao et al. 2010). The advantage of the HTC is the potential use of wet feedstocks, e.g.

sewage sludge, animal manures, or municipal solid waste without energy-intensive drying before or during the process (Libra et al. 2011).

The principle of the commercial-scale HTC reactor used to produce the hydrochars for the study in chapter 4 is shown in Figure 3. The mixed and pre-heated biomass enters the carbonization reactor, passing a counter current flow reactor. The conversion of biomass to hydrochar takes 90 minutes under elevated pressure of 10 to 90 bar. Liquid (slurry) and solids (hydrochar) are separated by a filter press (for more information see www.cs-carbonsolutions.de).

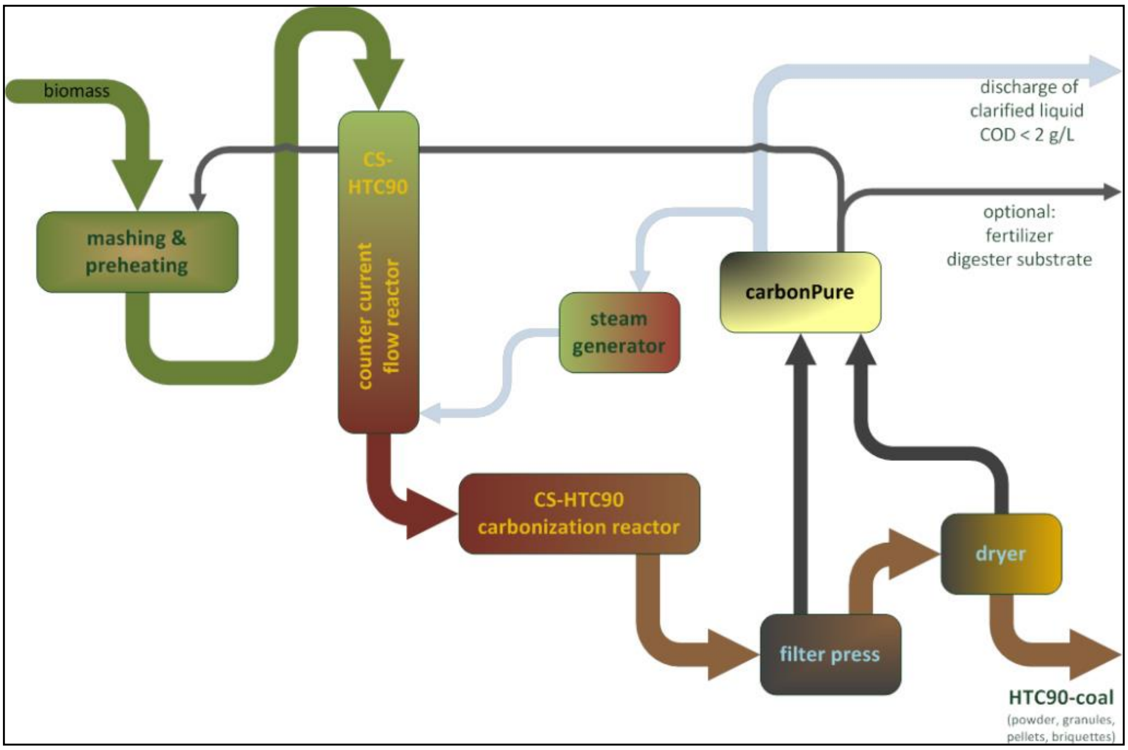

Figure 3 Main principle of hydrothermal carbonization process of carbonSolutions (Source: www.cs-carbonsolutions.de; with kind permission of CS carbonSolutions Deutschland GmbH).

HTC resembles a torrefaction process, which involves heating at 200-300 °C with slow heating rates (<50 °C/min) under an anoxic atmosphere (Amonette and Joseph 2009).

Pyrolysis, gasification and HTC technologies provide end products which differ fundamentally in their chemical and physical properties. This makes them suitable for various purposes and applications such as soil amendment, fuel or basis for carbon nano materials (Kang et al. 2012; Qian et al. 2006). A fundamental understanding of these properties and their consequences for application to soils is crucial for assessing future strategies in carbonization. In this dissertation, biochars and hydrochars are investigated in order to establish their suitability as soil amendment for long-term C sequestration and increase of soil fertility.

1.4 Objectives

The present dissertation has been part of two research projects: a) EuroChar Project (FP7-ENV-2010ID-265179) supported by the European Community and b) ClimaCarbo (01LY1110B) project supported by the German Ministry of Education and Research.
This thesis combines the following interrelated and cumulative objectives:

- Review knowledge on the historical use of biochar in different climatic regions and epochs (chapter 2)
- Identification and evaluation of parallels in soil formation of an anthropogenic dark earth located in Northern Germany (containing biochar) with *Terra Preta de Índio* in Brazil (chapter 3):
    a) to understand anthropogenic soil genesis under temperate climate conditions
    b) to reconstruct historical land-use
- Chemical characterisation and evaluation of biochars from different feedstocks and different carbonization technologies such as HTC, pyrolysis and gasification (chapter 4 and 5):
    a) to assess correlations between production technologies and biochar properties
    b) to assess the suitability of differently carbonized materials for soil conditioning or C sequestration
    c) to evaluate environmental risks caused by biochars produced in large-scale reactors
- Evaluation of the effects of complex biochar fertilizers on soil properties, biomass production and plant nutrition under field conditions in a sandy soil in Northern Germany (chapter 6):
    a) To differentiate and quantify biochar and fertilizer effects on soil properties, plant yield and nutrition

Chapter 2

Traditional use of biochar

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Published in

Biochar for Environmental Management Science and Technology

Earthscan, London, 2nd Edition

2015

Edited by

Johannes Lehmann and Stephen Joseph

2.1 Introduction

In recent years, soils rich in pyrogenic carbonaceous material (PCM) have become increasingly the subject of scientific and public interest as biochar application to soil as a possible way to improve soil properties and sustainable management of natural resources (Glaser et al. 2000; Glaser et al. 2002; Lehmann et al. 2003). The use of biochar as a PCM added to soil has been commonplace in many parts of the world for centuries and even millennia. The aim of this chapter is to synthesize available knowledge and data on the historical use of biochar. Biochar plays a prominent role leaving behind sustainable fertile black earth-like soils such as the famous Amazonian Darks Earths or *Terra Preta de Indio* (Glaser et al. 2001).

The chapter focuses mainly on the historic use of biochar and identifies its specific role in sustainable agriculture. The term “biochar” is a modern creation often used along with charcoal, pyrogenic C or black C, but not fully interchangeably or synonymous. In general, charcoal and biochar are carbonaceous materials (dominated by polycondensed aromatic moieties) produced by heating of organic material at high temperature (350-1200 °C) under low oxygen supply. While charcoal is producedas an energy carrier, e.g. for cooking, heating or metallurgy processes, biochar is produced specifically for application to soil as part of agronomic or environmental management. Table 1 gives an overview of literature reviewed in this chapter on historical use of PCM. Surprisingly, in most of the studies, it seems that PCM was used intentionally as biochar for soil improvement. For *Terra Preta*, it is not clarified whether biochar application to soil was intentional or not, however, soil improvement upon biochar application might have been noticed later on followed by intensification of land use and settlement (Glaser 2007). Biochar in soils persists against biological and chemical degradation over much longer periods of time than uncharred organic matter. We discuss historical use of biochar separated according to individual continents and countries or according to different historical epochs.

Chapter 3

Anthropogenic Dark Earth in Northern Germany — The Nordic Analogue to *Terra Preta de Índio* in Amazonia

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In press

Catena (Special Issue)

Man versus Nature: natural and anthropogenic footprints recorded in soils

(DOI: 10.1016/j.catena.2014.10.024)

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3.1 Abstract

During an archaeological excavation of a Slavic settlement (10th/11th C.A.D.) in Brünkendorf (Wendland region in Northern Germany), a thick black soil (Nordic Dark Earth) was discovered that resembled the famous *Terra Preta* phenomenon. For the humid tropics, *Terra Preta* could act as model for sustainable agricultural practices and for long-term CO_2-sequestration into terrestrial ecosystems. The question was whether this Nordic Dark Earth had similar properties and genesis as the famous Amazonian Dark Earth in order to find a model for sustainable agricultural practices and long term CO_2-sequestration in temperate zones. For this purpose, a multi-analytical approach was used to characterise the sandy-textured Nordic Dark Earth in comparison to less anthropogenically influenced soils in the adjacent area in respect of ecological conditions (pH, electric conductivity, cation exchange capacity and amino sugar) and input materials. Total element contents (C, N, P, Ca, Mg, K, Na, Fe, Cu, K, Zn, Mn and Ba) were highly enriched in the Nordic Dark Earth compared to the reference soil. Faecal biomarkers such as stanols and bile acids indicated animal manure from omnivores and herbivores but also human excrements. Amino sugar analyses showed that Nordic Dark Earth contained higher amounts of microbial residues being dominated by soil fungi. Black carbon content of about 30 Mg ha^{-1} in the Nordic Dark Earth was about four times higher compared to the adjacent soil and in the same order of magnitude compared to *Terra Preta*.

The input materials and resulting soil chemical characteristics of the Nordic Dark Earth were comparable to those of Amazonian Dark Earth suggesting that their genesis was also comparable. Amazonian Dark Earth and Nordic Dark Earth were created by surface deposition and/or shallow soil incorporation of waste materials including human and animal excrements together with charred organic matter. Over time, soil organisms degraded and metabolized these materials leaving behind deep black stable soil organic matter. The existence of the Nordic Dark Earth in the temperature zone of Europe demonstrates the capability of sandy-textured soils to maintain high soil organic matter contents and nutrient retention over hundreds of years. Deeper insights are needed urgently to understand soil organic matter stabilization mechanisms in this sandy soil to promote conceptual models for sustainable land use and long-term C sequestration.

It is argued that the knowledge of Nordic Dark Earth probably was an important part of the Viking–Slavic subsistence agriculture system, which could have had a great impact on the development of the Viking age emporia in the 9th/10th C.A.D.

Chapter 4

Chemical evaluation of chars produced by thermochemical conversion (gasification, pyrolysis and hydrothermal carbonization) of agro-industrial biomass on a commercial scale

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Puplished in

Biomass & Bioenergy 54, 91-100.

2013

(DOI: 10.1016/j.biombioe.2013.08.026)

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4.1 Abstract

Technologies for agro-industrial feedstock utilization such as pyrolysis, gasification and hydrothermal carbonization at industrial scale develop rapidly. The thermochemically converted biomasses of these production technologies have fundamentally different properties controlled by the production technology. This is reflected by general properties such as pH or elemental composition. The ^{13}C NMR spectroscopy, scanning electron microscopy and energy-dispersive X-ray spectroscopy and black carbon results confirmed these observations showing that hydrochars have lower proportions of aromatic compounds than biochars (less stable) but are rich in functional groups (higher cation exchange capacity) than biochars. Analyses of pollutants indicate that polycyclic aromatic hydrocarbons as well as dioxin contents of most samples were under the threshold values recommended by International Biochar Initiative and European Biochar Certificate. In conclusion, biochars and hydrochars are entirely different from each other and these materials will probably have a complementary reaction in a soil environment.

Highlights

- Production technologies influences fundamentally chemical properties of chars
- Carbonized materials have different behavior in soil environment
- Environmental risk of chars is low with respect to PAH and dioxin contents
- Certification standard for biochars is not suitable for hydrochars
- Commercial scale reactors are able to produce high quality biochars according the regulations of the EBC or IBI

Chapter 5

Chemical modification of biomass residues during hydrothermal carbonization – What makes the difference, temperature or feedstock?

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Puplished in

Organic Geochemistry 54, 91-100.

2013

(DOI: 10.1016/j.orggeochem.2012.10.006)

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5.1 Abstract

Hydrothermal carbonization (HTC) of biomass may be a suitable technique to increase its carbon sequestration potential when applied to soils. However, the properties of end products of HTC (hydrochars) could be significantly influenced by feedstock source and temperature during the carbonization process. This study focused on chemical modification of wheat straw, poplar wood and olive residues through HTC at different temperatures (180 °C, 210 °C and 230 °C). Besides general properties such as pH, electrical conductivity (EC), ash content, elemental composition and yield, we evaluated bulk chemical composition (^{13}C NMR) and contribution of specific compounds (lignin and black carbon). Moreover, the possible environmental risk of using hydrochars was assessed by determining their polycyclic aromatic hydrocarbon (PAH) and their dioxin contents. Our results showed that hydrochars were generally acidic with a pH value below 5. The highest EC (1710 µS/cm) and ash content (10.9%) were found in wheat straw derived hydrochars. Hydrochar yields and C recovery decreased with increasing temperature to about 50% and 75%, respectively for all feedstocks at 230 °C. N recovery increased with increasing temperature but N content of feedstock is more important. H/C and O/C ratios showed a linear decrease with increasing production temperature for all feedstocks. O–alkyl C decreased while alkyl C and aromatic C increased with increasing temperature and no significant feedstock dependence could be observed. Carboxyl C was not influenced by feedstock and temperature. Lignin content decreased with increasing temperature, while its oxidation degree and the content of black carbon and PAH contents increased. We conclude that transformation of biomass was most advanced at 230 °C only. Feedstock did not significantly influence the chemical composition of the hydrochars apart from N content and recovery. Instead, HTC temperature is the main driver determining the chemical composition of hydrochars. Environmental risk of investigated hydrochars is low with respect to PAH and dioxin contents. Despite the advanced biomass transformation during the HTC process at 230 °C, chemical properties indicated that the end product might have a less stable structure than pyrochar. Considering the higher hydrochar yields and C and N recoveries, its C and N sequestration potential in soil could have some advantages over hydrochars but this still remains to be evaluated.

Highlights:

- Hydrothermal carbonization temperature is the main control of hydrochar chemistry.
- Feedstock did not influence hydrochar composition except for N content and recovery.
- Environmental risk of hydrochar is low with respect to PAH and dioxin contents.
- Hydrochar may be less stable than pyrochar but show higher C and N yields.

Chapter 6

Biochar organic fertilizers from natural resources as substitute for mineral fertilizers

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Published in

Agronomy for Sustainable Development 35, 667-678.

2015

(DOI: 10.1007/s13593-014-0251-4)

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6.1 Abstract

Abstract Biochars are new, carbon-rich materials that could sequester carbon in soils improve soil properties and agronomic performance, inspired by investigations of *Terra Preta* in Amazonia. However, recent studies showed contrasting performance of biochar. In most studies, only pure biochar was used in tropical environments. Actually, there is little knowledge on the performance of biochar in combination with fertilizers under temperate climate. Therefore, we conducted an experiment under field conditions on a sandy Cambisol near Gorleben in Northern Germany. Ten different treatments were established in 72 m^2 plots and fivefold field replicates. Treatments included mineral fertilizer, biogas digestate, microbially inoculated biogas digestate and compost either alone or in combination with 1 to 40 Mg ha^{-1} of biochar. Soil samples were taken after fertilizer application and maize harvest. Our results show that the biochar addition of 1 Mg ha^{-1} to mineral fertilizer increased maize yield by 20%, and biochar addition to biogas digestate increased maize yield by 30% in comparison to the corresponding fertilizers without biochar. The addition of 10 Mg ha^{-1} biochar to compost increased maize yield by 26% compared to pure compost. The addition of 40 Mg ha^{-1} biochar to biogas digestate increased maize yield by 42% but reduced maize yield by 50% when biogas digestate was fermented together with biochar.

Biochar-fertilizer combinations increased K, Mg and Zn and reduced Na, Cu, Ni and Cd uptake into maize. Overall, our findings demonstrate that biochar-fertilizer combinations have a better performance than pure fertilizers, in terms of yield and plant nutrition. Therefore, an immediate substitution of mineral fertilizers is possible to close regional nutrient cycles.

Chapter 7

General discussion and conclusions

7.1 Overview: Main results of the studies

Table 1 Title, objectives and main conclusion of the studies included in this dissertation.

Study	Objectives	Main Conclusion
Chapter 2: **Traditional use of biochar (Review)**	**1.** Historical use of biochar (from Neolithic until present) on a global scale. **2.** Identification of biochars specific role in sustainable agriculture.	**1.** Carbonized materials (such as biochar) played a prominent role in ancient intensive agriculture worldwide. **2.** Ancient Anthrosols (beside T*erra Preta de Ìndio*) may act as model for sustainable land use.
Chapter 3: **Anthropogenic Dark Earth in Northern Germany - The Nordic Analogue to *Terra Preta de Índio* in Amazonia**	**1.** Identification of parallels between the Dark Earth and *Terra Preta de Ìndio* with respect to formation and ecological properties. 2. Verification of organic input materials in the NDE and comparison to *Terra Preta de Ìndio*	**1.** Strong parallels between the NDE and *Terra Preta* regarding the input materials such as bones, faecals and charred residues. **2.** In *Terra Preta*, input of human-derived faecal material dominated, whereas in NDE human-derived faecal material played only a minor role with the majority of the faecal residues derived from pigs, cows and sheep.
Chapter 4: **Chemical evaluation of chars produced by thermochemical conversion (gasification, pyrolysis and hydrothermal carbonization) of agro-industrial biomass on a commercial scale**	**1.** Assessing whether large-scale reactors are able to provide a consistent quality standard of end products regarding the recommendation of the EBC and IBI. **2.** Assesssing whether products differ between the different production technologies. **3.** Evaluation whether biochars and hydrochars are comparable carbonized materials and suitable for the same purpose such as soil conditioning or C sequestration. **4.** Evaluation whether the environmental risks of the field application are acceptable with respect to organic pollutants.	**1.** Commercial scale reactors are able to produce high quality biochars according the regulations of the EBC or IBI. Certification standard for biochars is not suitable for hydrochars. **2.** Production technologies affect fundamentally the chemical properties of chars. **3.** Biochars and hydrochars, are not equally suitable for C sequestration in soils. **4.** Environmental risk of chars is low with respect to PAH and dioxin contents.

Chapter 5: **Chemical modification of biomass residues during hydrothermal carbonization – What makes the difference, temperature or feedstock?**	**1.** Identification of the main influencing factors (e.g. production temperature and feedstock) on chemical properties of hydrochars. **2.** Evaluation of the stability of hydrochars and its contribution to long-term C sequestration in soils based on its elemental and chemical composition. **3.** Assessing the risk of hydrochars as a possible source of organic pollutants.	**1.** HTC temperature is the main driver determining the chemical composition of hydrochars. **2.** Feedstock did not significantly influence the chemical composition of the hydrochars apart from N content and recovery. **3.** Environmental risk of investigated hydrochars is low with respect to PAH and dioxin contents. **4.** Hydrochars have a less stable structure (dominated by alkyl moieties) than biochars (dominated by aromatics).
Chapter 6: **Biochar organic fertilizers from natural resources as substitute for mineral fertilizers**	**1.** Evaluation of biochar effects at different application rates (1, 10 and 40 Mg ha^{-1}) on soil properties, yield and plant nutrition. **2.** Assessment of fertilizer effects on soil properties, yield and plant nutrition.	**1.** High biochar application rates (40 Mg ha^{-1}) increased soil pH, CEC, nutrient stocks and yield. **2.** Nutrient uptake by maize varied widely for different nutrients, biochar application rates and fertilizers.

7.2 Benefits from knowledge on Anthropogenic Dark Earths for modern agricultural soil management

Chapter 2 aimed at assessing the specific role of carbonaceous material (biochar) in ancient agricultural practices and its potential to improve soil fertility and C sequestration over a long period of time. This study showed that ADEs were forming worldwide, from various soil types, during various epochs, under different land use practices and different climatic conditions. The reviewed literature in chapter 2 revealed that carbonaceous material was very often used intentionally for soil improvement. It is remarkable that most of the abandoned ancient biochar-containing soils maintained soil fertility even until present time. For instance, Neolithic ADEs located in the Lower Rhine Basin (NW Germany, temperate climate), maintained black carbon contents up to 46% of the TOC (Gerlach et al. 2006). In Australia, up to 1600 yr old ADEs were found along the Murray River (Mediterranean climate) with similar chemical properties (high nutrient and aromatic C contents) like *Terra Preta* (Downie et al. 2011). The study (chapter 2) provides additional insights in various ancient soil cultivation techniques developed in different cultures and epochs. Medieval plaggen soil cultivation, for instance, well known from Germany, Netherlands and Belgium, was carried out in a similar way in New Zealand, Scotland, Northern Russia or Southern Peru. Remarkably, some plaggen soils originate already from Late Neolithic and Bronze Age.

ADEs offer unique insights to long-term effects of carbonaceous-rich materials in the soil environment. This links to the idea of using biochars for amending modern agricultural soils for improved soil fertility (Glaser et al. 2001). However, biochars from lignin-rich biomass do not significantly contribute to the soil nutrient stocks, due to their poor nutrient contents (Cantrell et al. 2012). It is suggested that nutrients such as P, N, Ca, and K in *Terra Preta* soils derived from ash and organic waste, e.g. mammal and fish bones as well as faeces (Lima et al. 2002; Woods et al. 2003; Schäfer et al. 2004; Arroy-Kalin et al. 2009; Birk et al. 2011). However, due to lacking data of most studies reviewed in chapter 2 deeper insights were not possible in order to understand soil genesis. Therefore, a central aspect of chapter 3 was to gain deeper insights in soil genesis of an ADE found during an archaoelogical excavation of a Slavic settlement (10^{th}/11^{th} C. A.D.) at Brünkendorf (Wendland region, Northern Germany). The genesis of deep black soils in the Wenldand region were nutrient poor, sandy soils are predominate is very unusual. Investigation of the elemental composition, showing increased C, N, P, Ca, Mg, K, Na, Fe, Cu, K, Zn, Mn and Ba levels and input materials (human and animal excrements) provided strong evidence of an anthropogenic origin, which is underlined by numerous artefacts. In comparison to adjacent soil, element levels were enhanced up to a factor of 13 x for Mg, 25 x for Na, 15 x for K and 554 x for Ca. Phosphorus, traditional marker for human activities was 37% higher in the Dark Earth compared to the surrounding soil. Huge amounts of bone in the ADE (e.g., cattle, chicken, and pig) are the likely source of phosphorous. The $\delta^{15}N$ values of the ADE were up to +7.1‰ enriched (compared to the adjacent soil). This is typical for manured soils (Simpson et al. 1997), indicating excrement input in NDE. To verify that assumption, stanols and bile acids were analysed as manure-specific biomarkers of faecal input in the NDE. The (coprostanol + epicoprostanol) / (coprostanol + epicoprostanol + 5 α-cholestanol) ratio of < 0.6 indicated faecal input of omnivores, whereas coprostanol to 5β-stigmastanol ratio between 0.23 and 0.32 indicated faecal input by ruminants (Evershed and Bethell 1996; Bull et al. 1999). Bile acids such as hyodeoxycholic (HDCA) and deoxycholic acid (DCA), both indicative markers for porcine and ruminants, were highly enriched in the NDE. Lithocholic acid (LCA), an indicator for human faeces, was also found in small quantities. In comparison to *Terra Preta*, where mainly human-derived faecal matter was found (Birk et al. 2010), faecal input in NDE was dominated by animals such as cows, pics and sheep and only to a minor degree by humans (chapter 3).

Black carbon (BC) amounts, an indicator for carbonaceous material (biochar) in soil in NDE was 31 Mg BC per hectare in 0.8 m soil depth, whereas *Terra Preta* soil contained on average 50 Mg BC per hectare in 1.0 m soil depth (Glaser et al. 2001). Amino sugar analyses showed that NDE contained higher amounts of fungal residues, which is also similar to *Terra Preta* soils (Ruivo et al. 2009; Glaser and Birk 2012). The input materials and resulting soil properties (e.g. elevated CEC, high nutrient and SOM stocks) of the NDE are similar to those of *Terra Preta* in Brazil, suggesting a comparable genesis of both soils despite the entirely different climatic conditions.

In conclusion, ADEs offer unique insights to long-term effects of carbonaceous-rich materials in the soil environment. ADEs are interesting research subjects for various reasons because these soils contain important information about e.g. agricultural practices, animal husbandry and livestock or handicraft activities. From an archaeological point of view, studies about land use reconstruction can lead to a deeper understanding of the functioning of life and economy in the historic past. Due to important global topics such as climate change and sustainable agriculture, more attention should be paid to Anthrosols exhibiting high nutrient and SOM stocks. In order to achieve the favourable properties of ADEs in modern agricultural soils, suitable biochar production technologies are needed. Major requirements in the production of carbonaceous-rich materials (such as biochars or hydrochars) is to maintain a constantly high level of quality free from environmentally and harmful hazardous substances.

7.3 Organic pollutants in biochars and hydrochars - A risk assessment

An important demand for commercial scale production of biochars and hydrochars is the limitation of environmental risks by organic pollutants such as polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) and polycyclic aromatic hydrocarbons (PAHs).

It is well-known that (activated) charcoal is able to adsorb environmental pollutants, like heavy metals and PAHs (e.g. Walters and Luthy 1984). Beside that, biochars and hydrochars may be undesired sources of toxic substances such as PAHs, PCDDs, and PCDFs (Hilber et al. 2012). Due to their persistence and toxicity, it is of great importance to set up regulations (at political level), including threshold values for PAHs, PCDDs and

PCDFs (chapter 4). First draft regulations have been published in outlines of the “European Biochar Certificate” (EBC) and the “International Biochar Initiative” (IBI).

From the technical point of view, gasifier biochars have a higher risk of PAH contamination, due to secondary thermochemical reactions at temperatures of ≥ 700 °C, generating tar enriched in polyaromatic compounds (Pakdel and Roy 1991; Ledesma et al. 2002; Li et al. 2008). At lower temperatures (350-700 °C), PAHs mainly form through chemical alteration of vapours, resulting in deoxygenated tars (Ledesma et al. 2002; Pakdel and Roy 1991). In chapter 4, biochars from gasification (and pyrolysis) had on average negligible total PAH contents (median 0.55 mg kg^{-1}), which contrasts results on gasification-derived biochars investigated by Schimmelpfennig and Glaser (2012), having PAH concentrations up to 3000 mg kg^{-1}. Chapter 5 revealed that total PAH contents of hydrochars increased from 1.8 to 5.0 mg kg^{-1} with increasing temperature (180, 210 and 230 °C), pointing at PAH formation during the HTC process at rather low temperature.

PCDDs and PCDFs are carcinogenic by-products of combustion processes and among the most toxically environmental pollutants. Currently, 210 compounds of PCDDS and PCDFs are known, 17 compounds of these two groups are extremely carcinogenic even in small amounts. Due to their lipophilic and persistent nature, PCDD/Fs are able to bioaccumulate and bioconcentrate in organisms and thus, in the food chain. The molecular structure of this group of compounds is composed of two benzene rings either linked by one (dibenzofurane) or two oxygen bridges (dibenzo-1,4-dioxin). The basis structure can be associated with up to 8 chlorine or other halogen atoms. The presence of chlorine and organic carbon during combustion temperatures between 300 and 900 °C favors synthesis of PCDDs. At temperatures of 900 °C and higher, PCDDS will be destroyed. PCDD/Fs are ubiquitous in the environment but the highest concentrations are found in biota, soils, and sediments. In soil, loss of PCDD/Fs may occur via leaching, biodegradation, and volatilization.

PCDD/Fs contents of biochars and hydrochars investigated in chapter 4 and 5 were negligible, mainly even below detection limit (< 5.98 ng TEQ/kg). For hydrochars, production temperature of < 250 °C is too low for PCDD/Fs formation. However, feedstocks may already contain PCDD/Fs and HTC temperature is too low to destroy them. In contrast, pyrolysis temperature (< 600 °C) offers ideal conditions for dioxin formation when feedstocks (e.g., press or chip boards) contain chlorinated adhesives. If production temperature for biochar is > 1000 °C (like for most gasification systems) dioxins will be destroyed (McKay 2002).

Currently, there are no binding guidelines for maximum concentrations of PAHs or dioxins in biochars and hydrochars. For producers it is recommended to use given threshold values for organic pollutants in soil. In Germany, the German Bundes-Bodenschutz- und Altlastenverordnung (BBodSchV 1999) give maximum limits of 3 or 10 mg kg^{-1} of total PAHs depending on the humus content ≤ 8% or > 8%, respectively. For international producers, the EBC recommended limits for PAHs in biochars of <4 mg kg^{-1} (premium grade biochar) or < 12 mg kg^{-1} (basic grade biochar). For PCDD/Fs, the EBC and IBI recommend threshold values of 20 and 9 ng kg^{-1}, respectively. Knowledge on bioavailability and bioaccessability of single PAH fractions in soils is still lacking (Hale et al. 2012). However, the sorption capacity of pyrogenic material such as activated charcoal have been studied extensively in the past (e.g. Walters and Luthy 1984; Luehrs et al. 1996). It is assumed that sorption of PAHs on biochar surface could lead to a decrease of microbial bioavailablity and therewith to a localized PAH accumulation (Quilliam et al. 2013; Rhodes et al. 2008; Xia et al. 2010).

This dissertation has conclusively shown, that the selection of the approppriate carbonization technology strongly depends on feedstock qualitiy. In addtion, caution is needed when selecting feedstocks for HTC, gasification, and pyrolysis since the different thermochemical conditions can produce a variety of pollutants such as PAHs, PCDD/Fs. Also each technology needs to be certified e.g. according to existing EBC and/or IBI guidelines. In turn, gasification technology might be a possibility to remove, e.g. PCDD/Fs from contaminated feedstocks (e.g. sewage sludge), making previously contaminated feedstocks suitable as soil amendments. In addition, regulation for single PAH concentrations is of same importance as for total PAH contents. As shown in chapter 4 and 5, individual PAH concentrations in biochars and hydrochars are highly variable, even for the same production process (and also between different processes), demonstrating the heterogeneity of carbonized products. The envrionmental fate of PAH assossiated on biochars or hydrochars is still poorly understood and further research is urgently needed before commercial biochar application.

7.4 Carbonization technologies and characteristics of the products

Data of chapters 3 and 4 show that chemical properties of biochars (from pyrolysis and gasification) and hydrochars differ fundamentally and therefore, varying reactions in soil can be expected. For instance, ^{13}C-NMR revealed that hydrochars are dominated by alkyl moieties and biochars by aromatics (Figure 1). It can be expected that hydrochars are less resistant to biodegradation than biochars. However, hydrochars are rich in functional groups (hydroxyl, carboxyl and carbonyl; Figure 1) initially, which makes them highly reactive in soils (higher CEC) while fresh biochars lack of functional groups. High O/C and H/C ratios confirm the ^{13}C-NMR results, indicating low demethylation (loss of CH_3) and decarboxylation (loss of CO_2) of hydrochars. Thus, the low temperatures during the HTC process are not capable to break down lignocellulose rich in oxygen-containing functional groups. This is due to the fact that degradation of hemicellulose starts at ~180 °C and is completed at ~315 °C, whereas cellulose decomposes at ~315 °C (Yang et al. 2007; Grénman et al. 2011; Brown 2009). Lignin represents the most stable component of lignocellulosic biomass, however, its degradation starts at 160 °C in a slow but steady process and may extend to up to 900 °C (Brown 2009).

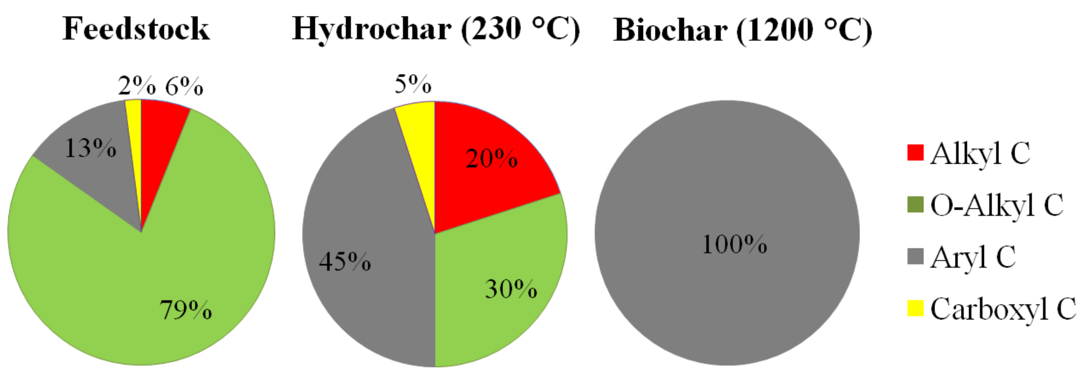

Figure 1 Changes of the chemical composition of poplar wood (feedstock) after hydrothermal carbonisation at 230 °C (chapter 5) and gasification at 1200 °C (chapter 4).

Stability of carbonaceous material is crucial due to its potential for long-term C sequestration in soils. Besides the proportion, also the quality of highly aromatic compounds, derived from charred organic matter can be estimated by using benzenepolycarboxylic acids (BPCAs) as molecular markers for black carbon (Glaser et al. 1998). The proportion of black carbon from total organic carbon (TOC) in biochars and hydrochars (chapter 4 and 5) provide information on its potential stability in soil.

Black carbon contents of hydrochars (median: 31g BC kg^{-1} TOC) are on average 10 times lower than in biochars (median = 293 g BC kg^{-1} TOC) (chapter 4). Hydrochars are poor in benzene hexacarboxylic acid (B6CA), which is released from highly condensed aromatic cores of BC structures (Glaser et al. 1998), indicating the most stable fraction of black carbon.

In summary, hydrochars resemble lignite, with low degree of aromaticity, as indicated by high H/C and O/C ratios and low black carbon contents. Biochars are dominated by highly condensed aromatic rings (e.g., high proportions of B6CA and a 100% O-aryl C signal) similar to coal. Hydrochars are rich in oxygen-containing functional groups, making them highly reactive in soils. These results are in agreement with findings by Kuzyakov et al. (2009) and Steinbeiss et al. (2009), who estimated that biochars might have a residence time of ~2000 yr, whereas hydrochars are already degraded after a few decades. Whithin this dissertation it was shown that biochar and hydrochars have fundamentally different properties. Consequently, they are not equally suitable for achieving the main ameliorations expected from the application of carbonaceous material. However, hydrochars are initially more likely to interact with his functional groups in soil and therefore i.e. to increase CEC and nutrient storage. Biochars were shown to be the more stable and therefore appropriate for C sequestration. Freshly produced biochar lacks of functional groups, as indicated by low O/C ratios (see Figure 2 in chapter 4). Formation of oxygen-containing functional groups at the edges of the aromatic backbone of biochar, which causes the increase in CEC (Glaser et al. 2002), is a slow process, especially under the conditions in the soil environment. Also, surface oxidation of biochar is strongly related to mean annual temperature (MAT) and microbial activity in soil (Cheng et al. 2008). To achieve the favourable properties of ADEs within a short period of time in modern agricultural soils (see chapter 6), development of suitable biochar production technologies (see chapter 4 and 5) and methods for accelerative biochar alteration are needed.

The relationship between hydrochar and biochar properties and its effects in agricultural soil is still poorly understood. The establishment of the appropriate process conditions in order to produce a biochar with desired characteristics (Brewer et al. 2010) can not be recommended generally. Interactions of the same biochar or hydrochar is most likely different depending on soil environment. The use of standard soils (e.g. from LUFA or OECD) for biochar studies might facilitate comparability of data, however, the relation to practice is not given. Biochar field trials under various conditions are therefore urgently needed in order to assess the long-term effects of biochar on soil properties and plant growth in "real" agricultural ecosystems.

7.5 Short-term effects of complex biochar fertilizers under field conditions

To evaluate the effect of biochar on soil properties, maize nutrition and yield in a sandy soil in Northern Germany, a field study was carried out (chapter 6). Agronomically relevant inorganic and organic fertilizers, such as mineral fertilizer, biogas digestate, microbially inoculated biogas digestate, compost were applied individually (controls) and in combination with various amounts of biochar (1, 10, and 40 Mg ha^{-1}).

High doses of biochar (40 Mg ha^{-1}) significantly increased WHC (up to 23%) in the sandy soil. Considering that agriculture in Europe consumes 30% of total water use the importance of irrigation will increase, also in Germany (Baldock et al. 2000; Lavelle et al. 2009). Furthermore, the cultivation of crops on poor (sandy) soils will increase and necessary investigations for irrigation systems are cost-intensive and water will get even more expensive. An experiment by the Chamber of Agriculture in a sandy soil in Lower Saxony showed that maize yield increased by 35% when 143 mm were irrigated during the growing season (Landwirtschaftskammer Niedersachsen, 2014). In the field experiment in chapter 6, maize yields increased up to 43% when 40 Mg biochar per ha^{-1} had been applied without additional irrigation. In how far the yield increase of maize is attributable to increased WHC and therewith related effects (e.g. increased nutrient uptake, higher microbial activity in soil etc.) need to be further examined. A detailed economic study regarding the costs and cost savings under different scenarios (e.g. different amounts of biochar, different soils and crops, etc.) would provide deeper insights in the profitability of biochar. The environmental benefits, however, are already given.

As expected, pH values increased up to 1.3 units right after biochar application, especially when high doses (40 Mg ha^{-1}) had been applied, however, this effect was leveled off after one vegetation period. Interesting are exchangeable cations (determined at soil-inherent pH) in particular of 40 Mg ha^{-1} biochar amendments right after fertilization and after harvesting. Figure 2 shows that exchangeable cations significantly increased from application date to post-harvest soil ($p < 0.05$), except when biochar was combined with mineral fertilizer. Exchangeable cations of biochar are closely related to surface oxygen-containing carboxyl, hydroxyl, and phenolic functional groups (Li et al.

2013). Under which conditions and periods the functional groups are generated on biochar surface has not been conclusively clarified yet. Cheng et al. (2006) for instance, incubated freshly produced biochar and biochar-soil mixtures at two temperatures (30 °C and 70 °C), with and without microbial inoculation, nutrient addition, or manure amendment for four months. The experiment showed that abiotic reaction mechanisms were more prominent for surface oxidation of biochar than biotic processes. The results in chapter 6 imply that microbial processes are responsible for formation of biochar surface functional groups. Previous studies already showed that microbial activity is higher in organic fertilized soils than in mineral fertilized soils (e.g. Leita et al. 1999). Exchangeable cations in soil containing biochar for one vegetation period increased in the following order NPK < digestate < digestate inoculated with indigenous microorganisms < compost. This order indicates an increasing microbial activity in soil. Ongoing investigations beyond this dissertation try to clarify this hypothesis.

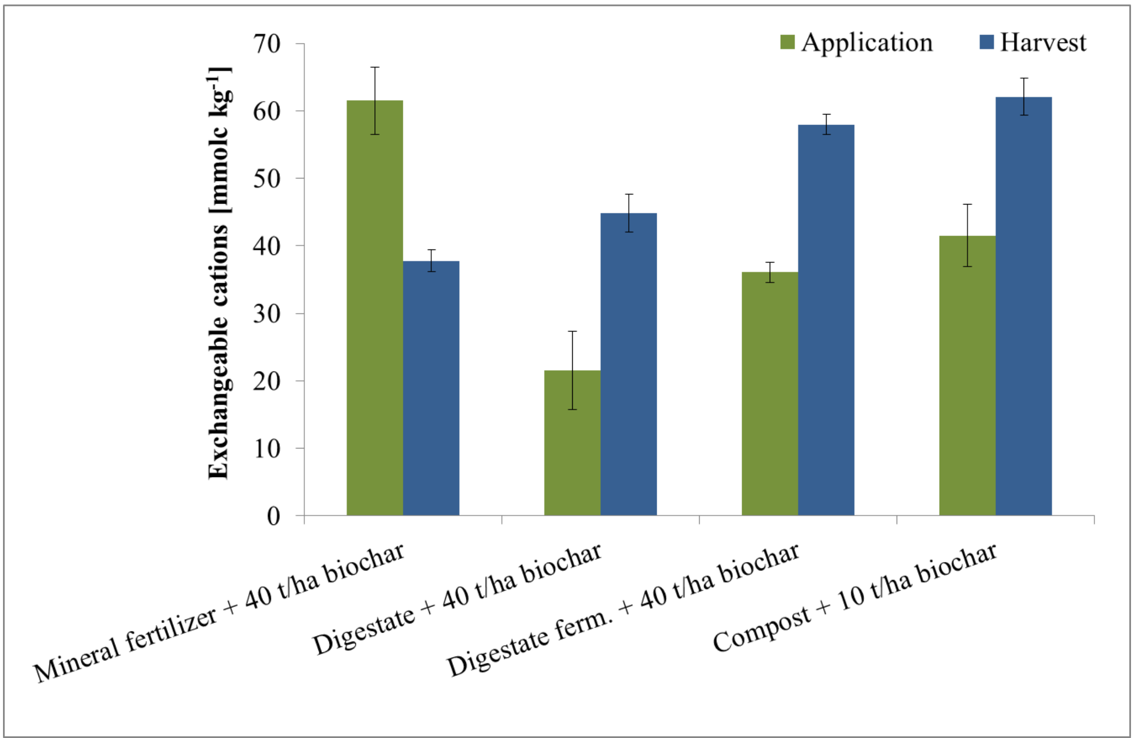

Figure 2 Exchangeable cations of directly after application of biochar fertilizer and post-harvest soil with 10 and 40 Mg ha^{-1} biochar application; data adapted from chapter 6, Table 1; ($p < 0.05$).

Plant nutrients and heavy metals uptake into maize plants showed no consistent increasing or decreasing trend when biochar has been added to fertilizers. Table 1 visualizes the increase or decrease (mean values) of nutrient and heavy metals uptake by maize plants from chapter 6 in comparison to the according fertilizer without biochar. The pattern in Table 1 clearly shows that Na, Ni, Co, Cr, Pb and Cd uptake decreased (with some exceptions) in the presence of biochar (in some cases significant) which is inherent with previous studies in the past (Namgay et al. 2010, Karami et al. 2011, Cui et al. 2012). It could be observed that microbially inoculated digestate and compost limit the uptake of most nutrients after biochar addition. Na uptake decreased for all biochar substrates. Apart from this two cases, macro- and micronutrient uptake tended to increase (and partly significant) in the presence of biochar (Table 1). There is no doubt that biochar influences physico-chemical and biological processes controlling mobility and availability of macro and micronutrients for plants such as adsorption/ desorption, complexation/dissociation, oxidation/reduction, and mobilisation/immobilization (He et al. 2005; Park et al. 2011; Uchimiya et al. 2011). The investigations in chapter 6 provide a good basis for further studies which are urgently need for a better understanding of biochar-plant-soil interactions.

Table 2 Element uptake by maize plants in the presence of biochar compared to corresponding fertilizers without biochar observed in chapter 6 (original data see chapter 6, table 2).

	N	P	Ca	K	Mg	Na	Mn	Cu	Ni	Co	Cr	Pb	Cd
BC (1) + NPK	increase	increase	increase	increase	decrease	decrease	increase	increase *	decrease *	decrease	decrease	decrease	decrease
BC (40) + NPK	increase	increase *	increase	increase *	decrease *	decrease *	increase *	increase *	decrease	decrease *	decrease	decrease *	decrease
BC (1) + Dig.	increase	increase	increase	increase	increase *	decrease	decrease	increase *	decrease *	decrease	decrease *	increase	decrease
BC (40) + Dig.	increase	increase *	increase *	increase	increase	decrease *	increase	increase *	decrease *	decrease	decrease *	increase	increase
BC (40) + Dig. + ferm.	decrease *	increase	decrease	decrease	decrease	decrease	increase	decrease	decrease *	decrease *	increase	decrease *	decrease *
BC (10) + Compost	decrease	decrease	decrease	increase *	increase	decrease *	decrease	increase	decrease	decrease	decrease	increase *	decrease *

* = significant ($p < 0.05$) increase decrease

In conclusion, favourable effects on soil properties and yield can be achieved with high doses of biochar. This was also shown by a field study of Liu et al. (2012) in a nutrient-poor sandy soil in NE Germany. The authors applied up to 20 Mg ha^{-1} before achieving marked effects on soil properties and crops. The field trial in chapter 6 aimed at improving the positive effects shown by Liu et al. (2012) and to simulate the final state. However, considering the current market value of biochar of about 500 € per ton, continuous application of low biochar doses, e.g., 1 Mg ha^{-1} $year^{-1}$ is more realistic from an economical point of view. Currently, a total area of about 400 hectares can be treated with biochar annually with one PYREG™ reactor with an annual production capacity of about 400 Mg. The purchase and maintenance of a local reactor for biochar prodcution at regional scale might lower the costs.

7.6 Conclusions and directions for future work

The first two studies in this thesis demonstrate the potential of biochar for long-term C sequestration in different pedoclimatic environments over centuries and even millennia. The literature review of chapter 2, however, did not contribute to a deeper understanding in ADE genesis due to missing appropriate analytical methods (e.g. biomarker) in most studies. To gain deeper insights into soil formation in the presence of biochar a ~ 1000 yr old ADE in Northern Germany (chapter 6) was investigated. The multi-analytical approach revealed close parallels to *Terra Preta de Índio* regarding input materials and ecological properties. Due to the high variability of anthropogenic soil formation, a more systematic research of ADEs is urgently needed in order to understand the anthropogenically affected cycling of SOM under different climatic conditions and land-use practices.

To achieve the favourable properties of ADEs in agricultural soils, highly aromatic SOM fractions are certainly a key factor (Glaser et al. 2001). In recent years, technologies such as pyrolysis, gasification and hydrothermal carbonization at industrial scale developed rapidly. The results in chapter 4 and 5 clearly show the entirely different properties of biochars (from pyrolysis and gasification) and hydrochars mainly in the degree of aromaticity and the presence of functional groups and also with respect to persistant organic pollutant concentrations. Biochars are therefore more suitable for long-term C sequestration, whereas hydrochars have higher CEC potential due to the presence of oxygen containing functional groups. The two characterization studies have additionally demonstrated the potential of HTC using non-traditional wet feedstocks (e.g. leftover food, maize silage, sewage sludge etc.) which are not suitable for pyrolysis or gasification. In contrast to biochar, hydrochar research is still in its infancy and largely characterized by visions. For instance, the input of the keywords "biochar" and "hydrochar" in ISI Web of Knowledge leads to 1336 ("biochar") and 64 ("hydrochar") peer-reviewed scientific articles. A guideline as prepared by the IBI or EBC for biochars, has not yet been developed for hydrochars due to the little available data from a variety of feedstocks and HTC reactors. Chapter 4 and 5 aimed at closing the gap due to the high importance for binding guideline at EU level for commercial biochar as well as hydrochar production. Parallel, extensive research should be performed investigating the effects of biochars and hydrochars in agricultural soil environment.

The field study in Northern Germany (chapter 6) aimed at evaluating the short-term effects of biochar in combination with agronomically relevant fertilizers. The results showed no negative effects of biochar fertilizers on yield, plant nutrition and soil properties. However, biochar effects on soil properties, plant nutrition and growth are highly complex and differ strongly in combination with mineral or organic fertilizers. Future research should target the process-based biochemical interactions influencing soil-plant-water-root-nutrient interactions. Additionally, the long-term effects of the complex biochar substrates in "real" agricultural environments need to be further examined in order to optimize complex biochar fertilizers for field application. From an economical point of view, targeted strategies should be established e.g. for municipalities or agricultural holdings increasing the attractively of biochar application.

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5. Contributions to the included publications and manuscripts

In the present cumulative dissertation, 5 studies are included. Four from five manuscripts were prepared by me as first author. In the following, the approximate contributions of the co-authors and me are given:

Study 1

K. Wiedner:	70% (manuscript preparation)
B. Glaser:	30% (contribution to the manuscript – text, comments to improve the manuscript)

Study 2

K. Wiedner:	65% (laboratory work, manuscript preparation, discussion of the results)
J. Schneeweiß:	15% (contribution to the manuscript – text and map)
M. Dippold:	10% (help for laboratory work, data evaluation, contribution to the manuscript - text)
B. Glaser:	10% (comments to improve the manuscript)

Study 3

K. Wiedner:	65% (laboratory work, manuscript preparation, discussion of the results)
C. Rumpel:	10% (contribution to the manuscript – text, laboratory work)
B. Glaser:	10% (comments to improve the manuscript)
C. Steiner:	5% (provision of biochars, contribution to the manuscript – text)
A. Pozzi:	5% (provision of biochars, contribution to the manuscript – text)
R. Maas:	5% (provision of hydrochars, contribution to the manuscript – text)

Study 4

K. Wiedner:	62% (laboratory work, manuscript preparation, discussion of the results)
C. Rumpel:	15% (contribution to the manuscript – text, laboratory work)
B. Glaser:	10% (comments to improve the manuscript)
C. Naissé:	5% (laboratory work)
A. Pozzi:	5% (provision of feedstocks, contribution to the manuscript – text)
P. Wieczorek:	3% (preparation of the hydrochars)

Study 5

B. Glaser:	49% (manuscript preparation, discussion of the results)
K. Wiedner:	40% (laboratory work, comments to improve the manuscript)
H.-P. Schmidt:	5% (draft for field experiment, comments to improve the manuscript)
S. Seelig:	3% (draft for field experiment, field work)
H. Gerber	3% (provision of feedstocks)

List of publications

I) Peer reviewed journals

Wiedner K., Fischer D., Walther S., Criscuoli I., Favilli F., Nelle O., Glaser B. (2015): Acceleration of biochar surface oxidation during composting? Journal of Agricultural and Food Chemistry, 63: 3830-3837.

Wiedner K., Schneeweiß J., Dippold M., Glaser B. (2014): Anthropogenic Dark Earth in Northern Germany – The Nordic Analogue to *Terra Preta de Índio* in Amazonia. Special Issue Catena: Anthropogenic footprints recorded in soils, Catena, *in press*.

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Wiedner K., Rumpel C., Steiner C., Pozzi A., Maas R., Glaser B. (2013): Chemical evaluation of chars produced by thermochemical conversion (gasification, pyrolysis and hydrothermal carbonization) of agro-industrial biomass on a commercial scale, Biomass and Bioenergy 59: 264-278.

Naisse C., Alexis M., Plante A., **Wiedner K.**, Glaser B., Pozzi A., Carcaillet C., Criscuoli I., Rumpel C. (2013): Can biochar and hydrochar stability be assessed with chemical methods? Organic Geochemistry 60: 40-44.

Wiedner K., Naissé C., Rumpel C., Pozzi A., Wieczorek P., Glaser B. (2012): Chemical modification of biomass residues during hydrothermal carbonization - What makes the difference, temperature or feedstock? Organic Geochemistry54: 91-100.

II) Book contributions

Wiedner, K. and Glaser, B. (2015): Traditional use of biochar. Lehmann, J., Jospeh, S. (Eds.) Biochar for Environmental Management, earthscan, London.

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Glaser B., **Wiedner K.**, Dippold M. (2013): Studying the role of biochar using isotopic tracing techniques. In: Ladygina N., Rineau F. (Eds.) Biochar and Soil Biota, CRC Press, Boca Raton, FL. Link.

III) Conference proceedings

Wiedner K., Glaser B., Polifka S., Klamm M. (2014): Biomarker in begrabenen historischen Böden (Beispiele: Wendland, Memleben), 8. Deutscher Archäologiekongress, Berlin, Germany (oral presentation).

Wiedner K., Glaser B., Polifka S., Klamm M. (2014): Historic Anthrosols- An interdisziplinary source of knowledge, 20th Annual Meetıng of the European Assocıatıon of Archaeologısts, Istanbul, Turkey (oral presentation).

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Naisse C., Rumpel, C., **Wiedner K.** (2014): Biochar and hydrochar reactivity assessed by chemical, physical and biological methods. EGU 2014, Vienna, Austria (Oral presentation).

Wiedner K., Schneeweiß J., Dippold M., Birk J., Glaser B. (2013): Anthropogene Schwarzerden im Einzugsgebiet der Unteren Mittelelbe? (Anthropogenic Dark Earth in the lower Elbe basin?), Deutsche Bodenkundliche Gesellschaft, Jahrestagung 2013, Rostock, Germany (Oral presentation).

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Wiedner K., Rumpel C., Glaser B. (2013): Pyrolysis, gasification and hydrothermal carbonization a chemical evaluation of endproducts. 1st MEDITERRANEAN BIOCHAR SYMPOSIUM AGENDA, Vertemate com Minoprio, Italy (Oral presentation).

Wiedner K., Glaser B., Hilber I. (2012): Biochars and Hydrochars – A possible source of organic pollutants? EuroSoil, Bari, Italy (Oral presentation).

Acknowledgements

I would like to express my deepest appreciation and thanks to my advisor and mentor Professor Dr. Bruno Glaser. I would like to thank him for encouraging my research and for allowing me to grow as a research scientist. His advice reargding research and my career have been priceless. Thank you!!!

I also want to thank my colleagues from Soil Biogeochemistry and Soil Sciences, namely Dr. Thomas Kühn, Dr. Klaus Kaiser, and Hardy Schulz for their time and patience during my thesis, special thanks to you!

I would also like to thank the technical staff Stefanie Bösel, Heike Maennicke, Christine Krenkewitz, Gudrun von Koch, Alexandra Boritzki from Soil Biogeochemistry and Soil Sciences for their kind help in the lab and the support to collect my data.

I would especially like to thank the student assistants Katharina Winter, Steven Polifka and Tobias Bromm and all other students, for the unlimited help in the field and lab.

A very special thanks goes to remarkable persons namely Dr. Michaela Dippold, Prof. Dr. Nicole Kemper, Dr. Michael Zech, Dipl. Biol. Janine Sommer, and Dipl. Geoök. Silke Hafner and Dr. Mario Tuthorn to whom I may count on, also beyond my thesis!!!

A 'thank you' is not enough for the humor, patience and endurance of Dipl. Geogr. Marianne Benesch, a friend you can go 'through thick and thin' (true friends are just very rare)!!!

In conclusion, I recognize that this research would not have been possible without the financial assistance of the European Community for financial support within the EuroChar project (FP7-ENV-2010ID-265179) and the “Federal Ministry of Education and Research (BMBF)” for financial support within the ClimaCarbo project (FKZ: 01LY1110B). A special thanks to the initiators of the two projects and all the project partners!

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Declaration under oath / Eidesstattliche Erklärung

Ich erkläre an Eides statt, dass ich die Arbeit selbstständig und ohne fremde Hilfe verfasst, keine anderen als die von mir angegebenen Quellen und Hilfsmittel benutzt und die den benutzten Werken wörtlich oder inhaltlich entnommenen Stellen als solche kenntlich gemacht habe.

I declare under penalty of perjury that this thesis is my own work entirely and has been written without any help from other people. I used only the sources mentioned and included all the citations correctly both in word or content.

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