Endbericht
Final Report

BIOCHAR

Biochar for Carbon Sequestration in Soils: Analysis of Production, Biological Effects in the Soil and Economics

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"Neue Energien 2020, 3rd call"

A cooperation project of

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Projektdaten

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Synopsis:
Das Projekt BIOCHAR hat einen Überblick über das Anwendungspotential von Biokohle in der österreichischen Landwirtschaft ermöglicht. Zur Bodenverbesserung ist Biokohle insbesondere auf sauren, sandigen und humusarmen Böden sinnvoll. Im Trockengebiet Ostösterreichs kann Biokohle die Wasserspeicherfähigkeit des Bodens erhöhen und dadurch die Ertragssicherheit erhöhen. Der Nährstoffgehalt von Biokohle wird nur sehr langsam an Pflanzen abgegeben. Hingegen ist mit zusätzlichem Stickstoffbedarf durch Immobilisierung und Adsorption zu rechnen. Eben diese Eigenschaften sind allerdings auch für die Verringerung der Nitratverluste im Sickerwasser und verminderte Lachgas-Emissionen aus dem Boden verantwortlich. Die derzeitigen Marktbedingungen und Produktionskosten von Biokohle erlauben auf Basis der Wirtschaftlichkeit keine Anwendungsempfehlung. Dies wird sich erst ändern, wenn bisher nicht monetär bewertbare Vorteile von Biokohle sowie die dauerhafte C-Bindung im Boden finanziell anrechenbar werden.

Summary

BIOCHAR was a 3-years project (2010-2013) aimed at investigating the effects, the potential benefits and risks of adding biochar to agricultural soils. To this end, lab analyses, pot and field experiments have been performed to study the effects of different biochar feedstocks, different application rates, the interaction with different soils, the effects on soil microorganisms, plant growth, crop yield, seepage water characteristics, and soil greenhouse gas emission, and finally to investigate the economic situation of biochar production and application. The most important results may be summarized as follows:

Comparing different biochar feedstocks, the highest salt and ash contents were found in straw-derived biochars. Surface areas were low but increased (1.8–56 m^2 g^{-1}) with increasing HTT, whereas CEC decreased (162–52 $mmol_c$ kg^{-1}) with increasing HTT. The results of DSC and FTIR suggested a loss of labile, aliphatic compounds during pyrolysis and the formation of more recalcitrant, aromatic constituents. X-ray diffractometry patterns indicated a mineralogical restructuring of biochars with increasing HTT. Water-extractable major and trace elements varied considerably with feedstock composition, with trace elements also affected by HTT. Total PAH contents (sum of EPA 16 PAHs) were highly variable with values up to 33.7 mg kg^{-1}; irrespective of feedstock type, the composition of PAHs showed increasing dominance of naphthalene with increasing HTT.

We investigated the effects of biochar (BC) on soil nutrient dynamics, crop yield and quality in a greenhouse pot experiment. Three agricultural soils (Planosol, Cambisol, Chernozem), and BCs of three different feedstocks (wheat straw (WS), mixed woodchips (WC), vineyard pruning (VP)) slowly pyrolyzed at 525°C, of which the latter was also pyrolyzed at 400°C. The BCs were applied at 2 rates (1 and 3 w.- %, which would correspond to 30 and 90 t f.m. ha^{-1} in the field). Three crops (mustard (*Sinapis alba*), barley (*Hordeum vulgare*), and red clover (*Trifolium pratense*)) were grown successively within one year. The investigated soil properties included pH, electrical conductivity (EC), cation exchange capacity (CEC), calcium-acetate-lactate (CAL) extractable P (P_{CAL}) and K (K_{CAL}), C, N and nitrogen supplying potential (NSP). The results show increase in pH in all soils. The CEC increased only on the Planosol. Despite the partly improvement of soil nutrient status, yield of the first crop (mustard) and to a lesser extent of the second crop (barley) were significantly depressed through BC application (by up to 68 %); the yield of clover as third crop was not affected anymore. Only the BC from WS maintained yields in the range of the control and even increased barley yield by 6 %. The initial yield reduction was accompanied by notable decreases (Cu, Fe, Mn, Zn) and increases (Mo) in micronutrient concentrations of plant tissues while nitrogen concentrations were hardly affected. The results of the pot experiment show that despite additional mineral fertilization, short-term growth inhibition may occur when applying BC without further treatment to temperate soils.

This project also investigated the effect of biochar amendments (i) on the soil microbial communities in temperate agricultural soils, (ii) involvement of microorganisms (MOs) in degradation and (iii) means to quantify degradation of biochar in short term experiments. To

this end, an incubation experiment and a pot experiment with two arable soils (a sandy acidic Planosol and a calcareous loamy Chernozem) amended with ^{13}C-depleted biochar from wheat husk and willow plants were set up. Phospholipid fatty acids (PLFAs), ^{13}C-PLFA, CO_2, $^{13}C\text{-}CO_2$, soil organic carbon (C_{org}), and $^{13}C\text{-}C_{org}$ were monitored for 100 days. Effects of biochar application on the soil microorganisms (MOs) were generally minor. In the incubation experiment microbial biomass was elevated by wheat husk biochar, especially in the Planosol. PLFAs increase was attributed to Gram negative bacteria and actinomycetes. Fungi and Gram positive bacteria were less affected. The effects of biochar were mainly attributed to an increase in the pH of the Planosol. In the incubation, only the actinomycetal PLFA 10Me18:0 incorporated biochar C, while in the pot experiment, Gram negative bacterial PLFAs (16:1ω7c, 16:1ω5c, 18:1ω7c) and Me16:0&i17:1ω8 and i17:0 indicated degradation of biochar. Uptake of around 20 % biochar C in these PLFAs was monitored, which accounts for 2 % biochar C in the total microbial biomass. Based on PLFA data the mean residence time of biochar carbon was estimated in time scales of centuries.

The results of a microlysimeter experiment showed that fresh BC strongly retained certain nutrients, although BC soon supplied high amounts of K^+ after application to soils. Highest decreases in leaching from BC-amended treatments were recorded for nitrate (by up to 81 %), DOC (by up to 43 %), and P_{DISS} (by up to 20 %). In our experiment, the most important factor to influence leachate characteristics was the BC feedstock, with wheat straw supplying the highest amounts of soluble nutrients (notably P and K) and woodchips causing the strongest reductions in nitrate leaching.

The aim of this project was also to investigate the effects of BC on soil characteristics, nutrient uptake and crop yield in field experiments on two temperate soils (Cambisol and Chernozem) in Austria. Maize and wheat (Cambisol), and barley and sunflower (Chernozem) were grown in successive vegetation periods following different BC application rates (0, 24 and 72 t ha^{-1} at the start of the experiment), supplemented with identical mineral N supply in 33 m^2 plots. BC treatments showed varying impacts on nutrient uptake of the investigated crops. The first growing season in the Chernozem region was affected by a prolonged drought period, which resulted in positive effects of BC on soil water-holding capacity (WHC) and barley crop yield (+ 10%) for the 72 t ha^{-1} BC + N treatment compared to a control with identical nutrient supply but without BC. However, maize and wheat grain yield decreased by 46 and 70%, respectively, after the highest BC application rate (72 t ha^{-1}) in an additional treatment without supplementary N-fertilisation. Still, even with high BC application rates we did not observe any adverse effects on crop yield and nutrient uptake, as long as the soil was supplied with sufficient N according to local agricultural practice.

The economic assessment of biochar production and application did not allow for an unconfined recommendation for a wide-spread biochar use under current conditions. Although ecological benefits of biochar exist, these either cannot be monetized or they are too small to justify the current price of biochar for useful application rates in the field. Many research questions are still open and wait for answers as a basis for a reliable legal frame of biochar application.

Zusammenfassung

BIOCHAR war ein 3-jähriges Projekt (2010-2013) mit dem Ziel, WIrkungen, mögliche Vor- und Nachteile von Biokohle-Anwendungen auf landwirtschaftliche Böden zu untersuchen. Zu diesem Zweck wurden umfangreiche Laboranalysen, Gefäß- und Feldversuche durchgeführt. Diese untersuchten die Wirkungen unterschiedlicher Ausgangsmaterialien für Biokohle, verschiedene Anwendungsmengen, die Wechselwirkung mit verschiedenen Böden, die Wirkungen auf Boden-Mikroorganismen, Pflanzenwachstum, Ertrag von Kulturpflanzen, Sickerwassereigenschaften, sowie Treibhausgas-Emissionen aus dem Boden. Die wirtschaftliche Bewertung schloss die Biokohle-Produktion und Anwendungsformen ein. Die wichtigsten Ergebnisse lassen sich wie folgt zusammenfassen:

Beim Vergleich der Wirkungen verschiedener Ausgangsmaterialien für Biokohle wurden die höchsten Salz- und Aschegehalte in Biokohle aus Stroh gefunden. DIe spezifischen Oberflächen waren zwar niedrig, stiegen aber mit der Pyrolysetemperatur an (1.8–56 m^2 g^{-1}), während die Kationenaustauschkapazität (KAK) parallel dazu abnahm (162–52 $mmol_c$ kg^{-1}). Die Ergebnisse von DSC und FTIR legten den Verlust labiler aliphatischer Verbindungen und die Bildung von widerstandsfähigeren aromatischen Bestandteilen während der Pyrolyse nahe. Untersuchungen mit Röntgen-Diffraktometrie zeigte eine mineralogische Restrukturierung der Biokohlen bei höherer Pyrolysetemperatur. Wasser-extrahierbare Makro- und Mikroelemente wurden deutlich vom Ausgangsmaterial beeinflusst, Spurenelemente auch von der Pyrolyse-Temperatur. Gesamt-PAH-Gehalte (Summe 16 EPA-PAH) waren sehr variabel und erreichten Werte von bis zu 33.7 mg kg^{-1}, unabhängig vom Ausgangsmaterial. In der Zusammensetzung der PAH dominierte bei höherer Pyrolyse-Temperature zunehmend Naphthalin.

Weitere Untersuchungen erstreckten sich auf die Nährstoffdynamik, den Pflanzenertrag und Qualität in einem Glashaus-Gefäßversuch. Drei landwirtschaftliche Böden (Planosol, Kambisol, Tschernosem) wurden mit 0, 1 oder 3 % Biokohlen aus 3 verschiedenen Ausgangsmaterialien (Weizenstroh, Holz-Hackschnitzel, Rebschnitt vermischt. Dies würde einer Freiland-Ausbringungsmenge von 30 bzw. 90 t FM pro ha entsprechen. Drei Kulturen (Senf (*Sinapis alba*), Gerste (*Hordeum vulgare*) und Rotklee (*Trifolium pratense*) wurden als Fruchtfolge innerhalb eines Jahre kultiviert. Zu den untersuchten Bodeneigenschaften zählten pH, elektrische Leitfähigkeit, KAK, CAL-extrahierbarer P und K, C, N und Stickstoff-Nachlieferungspotential. Die Ergebnisse zeigten in allen Böden pH-Erhöhungen. Die KAK stieg nur im Planosol an. Trotz der teilweisen Verbesserung des Nährstoffzustandes des Bodens waren die Erträge der ersten Kultur (Senf) und in geringerem Ausmaß auch die der zweiten Kultur (Gerste) durch Biokohle signifikant erniedrigt (um bis zu 68 %); der Ertrag von Rotklee als dritter Kultur was nicht mehr beeinträchtigt. Nur die Biokohle aus Stroh hielt die

Erträge im Bereich der Kontrolle und steigerte den Gerstenertrag sogar um 6 %. Die anfängliche Ertragsreduktion war von merkbaren Reduktionen der Konzentrationen von Cu, Fe, Mn und Zn sowie Erhöhung bei Mo begleitet. Die Stickstoffkonzentrationen in den Pflanzengeweben waren kaum beeinträchtigt. Die Ergebnisse des Gefäßversuches zeigten, dass trotz zusätzlicher Mineraldüngung kurzfristige Wachstumshemmungen auftreten können wenn Biokohle ohne weitere Behandlung im Boden ausgebracht wird.

Das Projekt untersuchte auch die Wirkung von Biokohle-Anwendungen auf (i) die Boden-Mikrobengemeinschaften in landwirtschaftlichen Böden gemäßigter Breiten, (ii) die Rolle der Mikroorganismen beim Abbau und (iii) die Möglichkeiten, einen Biokohle in einem Kurzzeit-Experiment zu quantifizieren. Zu diesem Zweck wurde ein Inkubations- und ein Gefäßversuch mit zwei Ackerböden (sandiger, saurer Planosol und kalkhaltifer lehmiger Tschernosem) und mit ^{13}C-abgereicherter Biokohle aus Weizenspreu und Weidenpflanzen angelegt. Phospholipid-Fettsäuren (PLFAs), ^{13}C-PLFA, CO_2, $^{13}C\text{-}CO_2$, organischer Kohlenstoff im Boden (C_{org}), und $^{13}C\text{-}C_{org}$ wurden über 100 Tage verfolgt. Die Wirkungen der Biokohle-Anwendung auf die Boden-Mikroorganismen waren allgemein gering. Beim Inkubations-Versuch war die mikrobielle Biomasse bei Weizenspreu-Biokohle erhöht, insbesondere im Plansol. Die Zunahme von PLFA kam durch Gram-negative Bakterien und Aktinomyceten zustande. Pilze und Gran-positive Bakterien waren weniger beeinflusst. Die Wirkungen der Biokohle wurde hauptsächlich auf den pH-Anstieg im Planosol zurückgeführt. Bei der Inkubation inkorporierte nur Aktinomyceten- PLFA Biokohlen-C. während im Gefäßversuch Gram-negative Bakterien-PLFA auf einen Biokohlen-Abbau hinwies. In der mikrobiellen Biomasse wurden bis zu 2 % Biokohlen-C gefunden. Basierend auf den PLFA-Daten wurde die mittlere Aufenthaltszeit des Biokohlen-C mit mehreren Jahrhunderten geschätzt.

Die Ergebnisse eines Mirkolysimeter-Versuchs zeigten, dass frische Biokohle bestimmte Nährstoffe stark zurückhielt, obwohl Biokohle bald nach der Anwendung hohe Mengen an Kalium zur Verfügung stellte. Die stärksten Reduktionen der Auswaschung aus Biokohle-behandeltem Boden waren bei Nitrat (um bis zu 81 %), DOC (um bis zu 43 %) und löslichem Phosphor (um bis zu 20 %) festzustellen. In unserem Versuch war der wichtigste Einflussfaktor auf die Sickerwasserzusammensetzung das Ausgangsmaterial der Biokohle, wobei Weizenstroh die höchsten Mengen löslicher Nährstoffe zur Verfügung stellte (insbesondere P und K) und Holz-Hackschnitzel die deutlichsten Reduktionen beim der Auswaschung von Nitrat zeigten.

Ein Ziel dieses Projekt war auch die Untersuchung der Wirkungen von Biokohle auf Bodeneigenschaften, Nährstoffaufnahme und Pflanzenertrag in Feldversuchen auf zwei österreichischen Böden (Kambisol und Tschernosem). Mais und Weizen (Kambisol) sowie Gerste und Sonnenblume (Tschernosem) wurden in aufeinander folgenden Vegetationsperioden nach einer einmaligen Anwendung (am Beginn des Versuchs) von 0, 24 und 72 t TM Biokohle pro ha kultiviert. Auf den 33 m^2-Parzellen wurde bei drei der viere Varianten mineralischer Stickstoff-Dünger ergänzt. Biokohle-Gaben zeigten auf die Nährstoffaufnahme der Kulturen unterschiedliche Auswirkungen. In der ersten Wachstumsperiode war das Gebiet des Tschernosem von einer langen Trockenperiode betroffen, was positive Effekte der Biokohle auf die Wasserhaltefähigkeit des Bodens und den Gerstenertrag (+ 10%) bei der Variante mit 72 t Biokohle/ha und Stickstoff-Ergänzung zur Folge hatte. Als Vergleichsbehandlung diente eine Variante mit gleicher Nährstoffversorgung aber ohne Biokohle. Jedoch sanken die Erträge von Mais und Weizen um 46 und 70 % bei der höchsten Biokohle-Anwendungsmenge, wenn eine ausreichende Stickstoff-Ergänzung fehlte. Dennoch war auch bei den hohen Ausbringungsmengen der Biokohle keine nachteilige Wirkung auf Ertrag und Nährstoffaufnahme festzustellen, sofern der Boden ausreichend mit Stickstoff entsprechend der guten landwirtschaftlichen Praxis versorgt wurde.

Die wirtschaftliche Bewertung der Biokohle-Produktion und –Anwendung erlaubte keine uneingeschränkte Empfehlung für einen weit verbreitete Biokohle-Einsatz unter derzeitigen Bedingungen. Obwohl ökologische Vorteile von Biokohle existieren, können diese entweder nicht monetarisiert werden oder sind zu klein, um den derzeitigen Preis von Biokohle bei nutzbringenden Anwendungsmengen rechtzufertigen. Viele Forschungsfragen sind noch offen und warten auf Antworten, um als Basis für einen verlässlichen gesetzlichen Rahmen einer Biokohle-Anwendung zu dienen.

1. Einleitung / Introduction

The project BIOCHAR (Biochar for carbon sequestration in soils: Analysis of production, biological effects in the soil and economics) is a cooperation project of AIT Austrian Institute of Technology Tulln, University for Natural Resources and Life Sciences Vienna, Joanneum Research GmbH Graz and BFW Federal Research and Training Centre for Forests Vienna. It is based on the 3rd call of the programme "Neue Energien 2020", supported by the KLI.EN-funds, and has been submitted as project proposal at October 8, 2009. After a positive decision upon financing of the project, it received the FFG-identifier 825438 and the financial conditions have been detailed in a sponsorship contract between FFG and AIT from May 18, 2010. The project duration of 3 years has started in April 1, 2010 and was finished in June 30, 2013. This report is the final report, covering an overview about the studies initiated in the 3 years of the project and results achieved in this period. Results of the first and second year usually will not be reported again but occasionally referred to and mentioned if necessary.

The project has the main objective to provide more evidence for the advantages (and possible disadvantages) of biochar applications, on biochar production under advanced technological conditions, on the real long-term carbon sequestration potential and on the economics of biochar. In Europe only very few long-term experiments exist that will be able to answer the questions about the permanence of biochar effects. Answers provided within this project will serve as a starting point for decisions upon scaling up biochar management as a regional, national or global strategy.

This study focuses on the questions:

- How can biochar be produced in the most efficient way to sequester carbon, improve soil quality and enhance crop growth effectively?
- Which of the claimed advantages of biochar application can be confirmed by experimental results and what is the extent of confirmed beneficial effects?
- Under which production conditions a biochar strategy is also economically justifiable?

In the frame of this study also field experiments have been started that will be the base for future analyses of biochar behaviour in the soil on a time range that would exceed the duration of the project. Because of a deficit of long-term biochar studies in temperate climate, establishing such experiments is a must to assess the real long-term carbon sequestration potential of biochar reliably. In different project workpackages the subsequent main objectives of the study are pursued:

- Determinations of the effects of biomass source on biochar output and quality
- Optimization of pyrolysis conditions to increase biochar yield
- Establishing the basis for long-term analyses of the carbon sequestration potential in agricultural soils
- Analysis of nutrient bioavailability after biochar application and sorption characteristics in soil
- Study of biochar effects on soil microorganisms, CO_2 and non-CO_2 greenhouse gas emissions from soils
- Definition of conditions for enhancement of plant growth and yield by biochar

- Economic evaluation of biochar production and application

The project design and the relations between the individual workpackages (WP) are displayed in Figure 1. It can be seen that WP 1 provides the biochar materials that are screened and tested in the other workpackages. WP 2 cares for the experimental setup of the pot and field experiments. WP 3–6 study different aspects of biochar applications that need further confirmation (WP 3: carbon sequestration; WP 4: effects on soil microorganisms; WP 5: effects of biochar-amended soils on plants; WP 6: soil greenhouse gas emissions). WP 7 is a cross-sectional workpackage dealing with the economics of biochar production and application at different levels. WP 8 is also cross-sectional matter and contains coordination and project management.

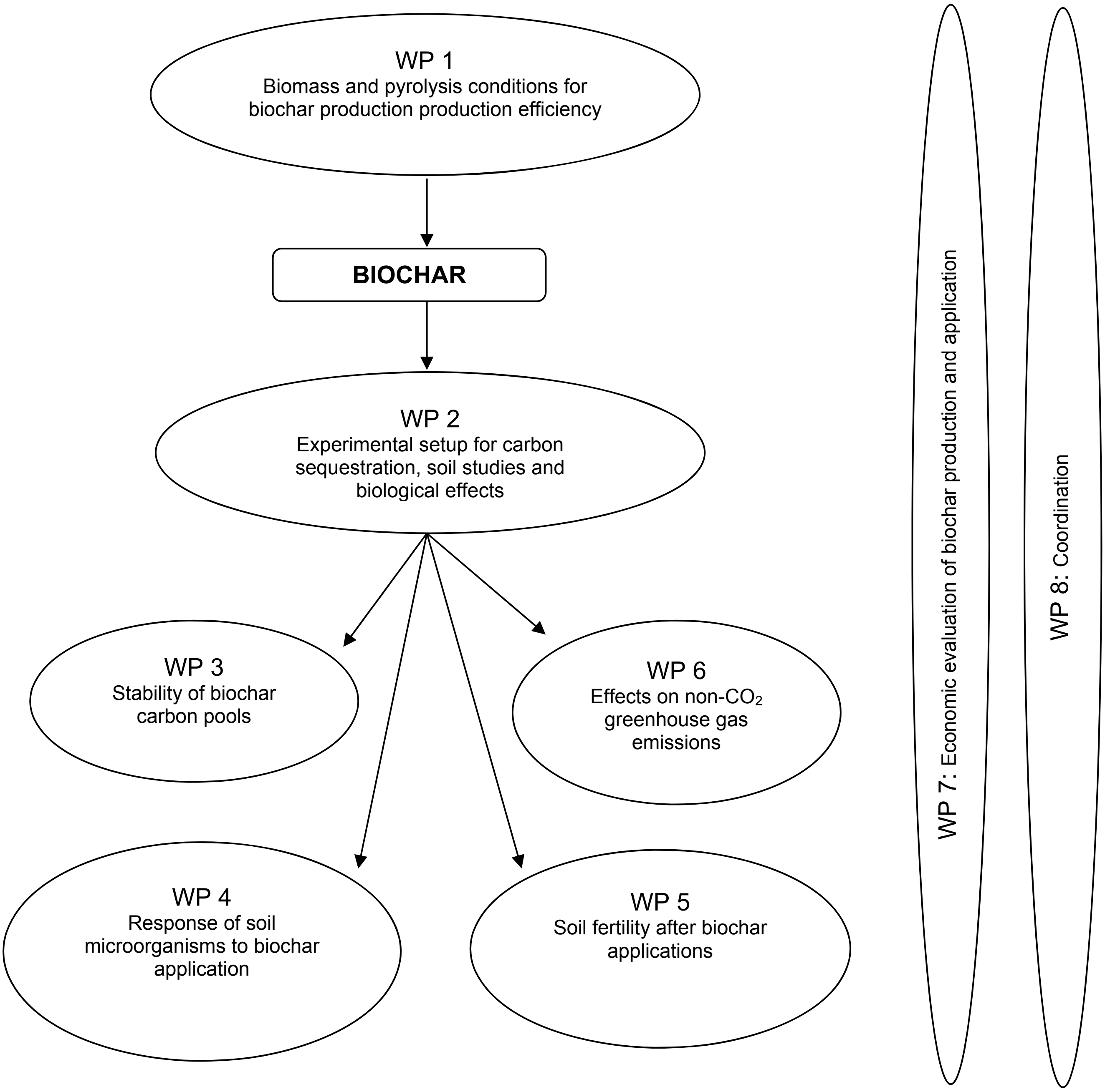

Figure 1: Workpackages and their relationships within the project BIOCHAR.

2. Inhaltliche Darstellung und Ergebnisse / Study Description and Results

2.1 Workpackage 1: Biomass and pyrolysis conditions for biochar production production efficiency

WP leader: Volker Liedtke, AAC-Research, Seibersdorf

Work package content:

Procurement of different biomass materials for biochar production. Production of biochar with different pyrolysis-conditions at the experimental scale.

After first pyrolysis trials in a standard laboratory tube furnace and based on previous experience with construction and operation of furnace systems, a tube furnace has been designed to cope with the following requirements:

- Usable volume at least 20 liters
- Operation under inert gas atmosphere
- Temperature range up to 450 °C
- Corrosion resistant
- Low manufacturing costs

Thus resulted in the following boundary conditions for the design:

- Material: Stainless steel 1.4301
- Diameter 300 mm
- Lentgh 1600 mm
- Flanges without water cooling
- O-ring based gasket seal
- Heating with standard high temperature heating tape
- Radiation shields for reducing heat loss to the flanges
- Temperature control by Eurotherm 2400 series PID controller
- Temperature measurement at the heater tapes using Type K thermocouple

Exhaust fumes and liquid or condensable pyrolysis products were cooled and then trapped inside disposable PE containers, in order to dispose of the corrosive and malodorous condensables. Residual exhaust fumes were discharged into the laboratory exhaust system without further treatment.

A schematic view of the pyrolysis furnace is depicted in the following drawing (*Figure 2*):

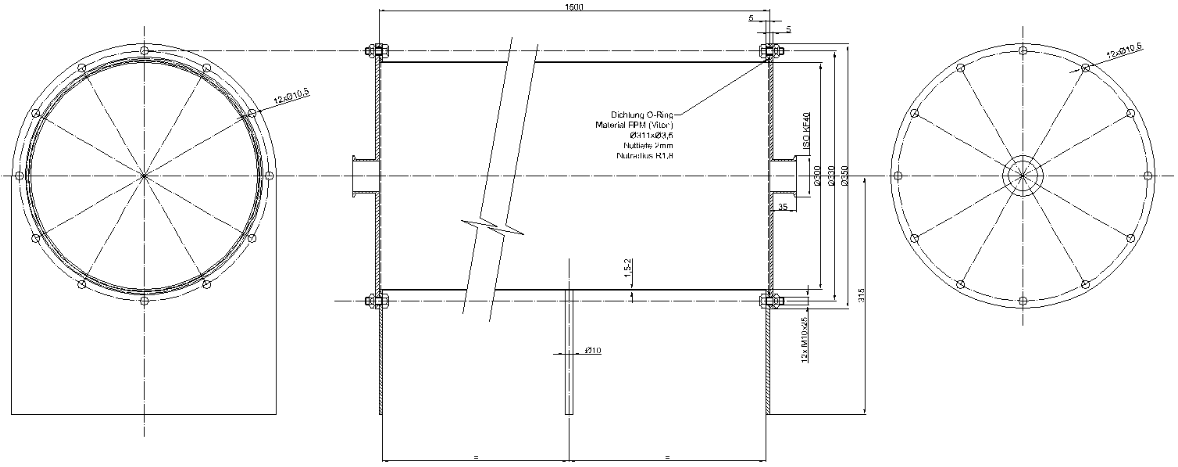

Figure 2: AutoCAD drawing of the pyrolyis furnace

With this furnace, several kinds of agricultural and forest residue materials were pyrolysed (Figure 3). For some of the materials that were expected to show distinct differences, extensive chemical characterisations have been performed. Details of the results are given in the publication shown in the appendix, published in Journal of Environmental Quality (Kloss et al., 2012).

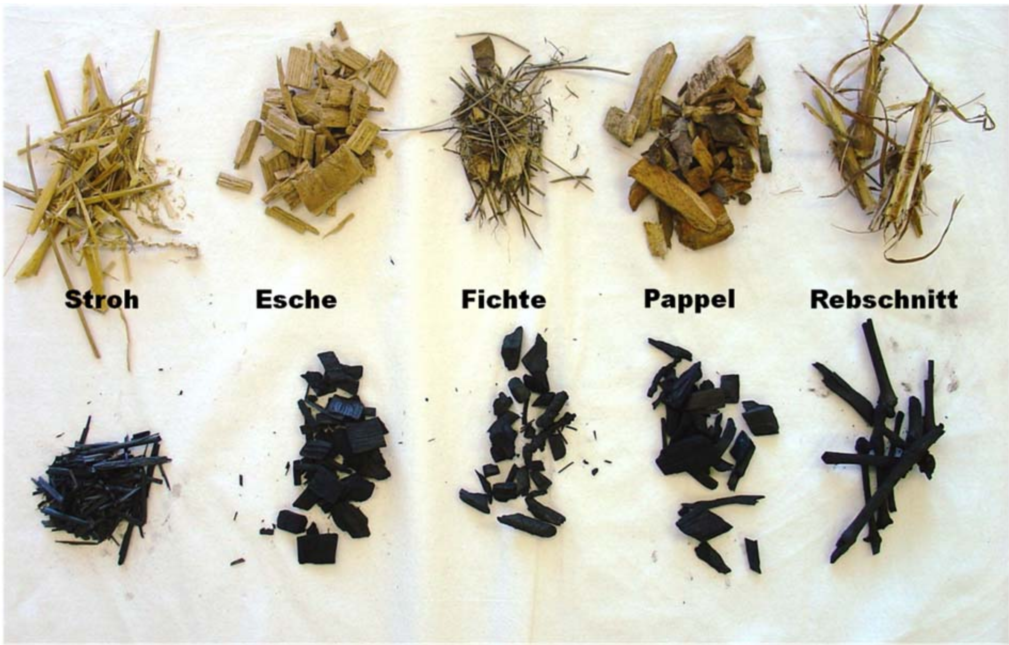

Figure 3: Biomass materials (from left to right: cereal straw, ash wood chips, Norway spruce branches, poplar wood chips, vineyard pruning) that were pyrolysed to produce biochars which were analysed chemically and deployed for the microlysimeter experiment described in WP 2

The pyrolysis reactor used for the biochar production (drawing in Figure 2) is shown in Figure 4, presenting the side with the entrance of the flush gas (Ar) that was used to create an oxygen-deficient atmosphere.

Figure 4: Pyrolysis reactor used for the biochar production of materials used later on in the microlysimeter experiment.

First pyrolysis runs

A first pyrolysis run with straw revealed that the feedstock cannot simply be packed into the pyrolysis furnace. The removal was time-consuming and by no means complete, and the product was contaminated with liquid pyrolysis by-products. Furthermore, the total volume of liquid or condensable pyrolysis products had been underestimated from the initial pre-trials. With the much larger new furnace, these condensables amount to about one third of the initial feedstock mass. This resulted in the following changes in design and operation:

- Manufacturing of a sample container made of perforated stainless steel plate
    - complanated at the lower side for separating biochar and liquid by-products
    - to be loaded and unloaded with the feedstock or biochar produce
    - lids fixed with steel wire for easy loading and unloading
- Change of off-gas system with improved cooling efficiency and 2 stage catchment tanks for more efficient trapping of condensables

A new test run revealed that the temperature at the external heaters must be set approximately 45 degrees higher for achieving the same core temperature. This is due to the thermal shielding of the sample container itself and the inevitable gap between sample container and tube furnace inner wall. The thermal models that were base of the design were found to be correct, as this deviation in operation temperature was almost correctly predicted: In both runs (*Figure 5*, *Figure 6*), the effective inner temperature was found to be 450 °C.

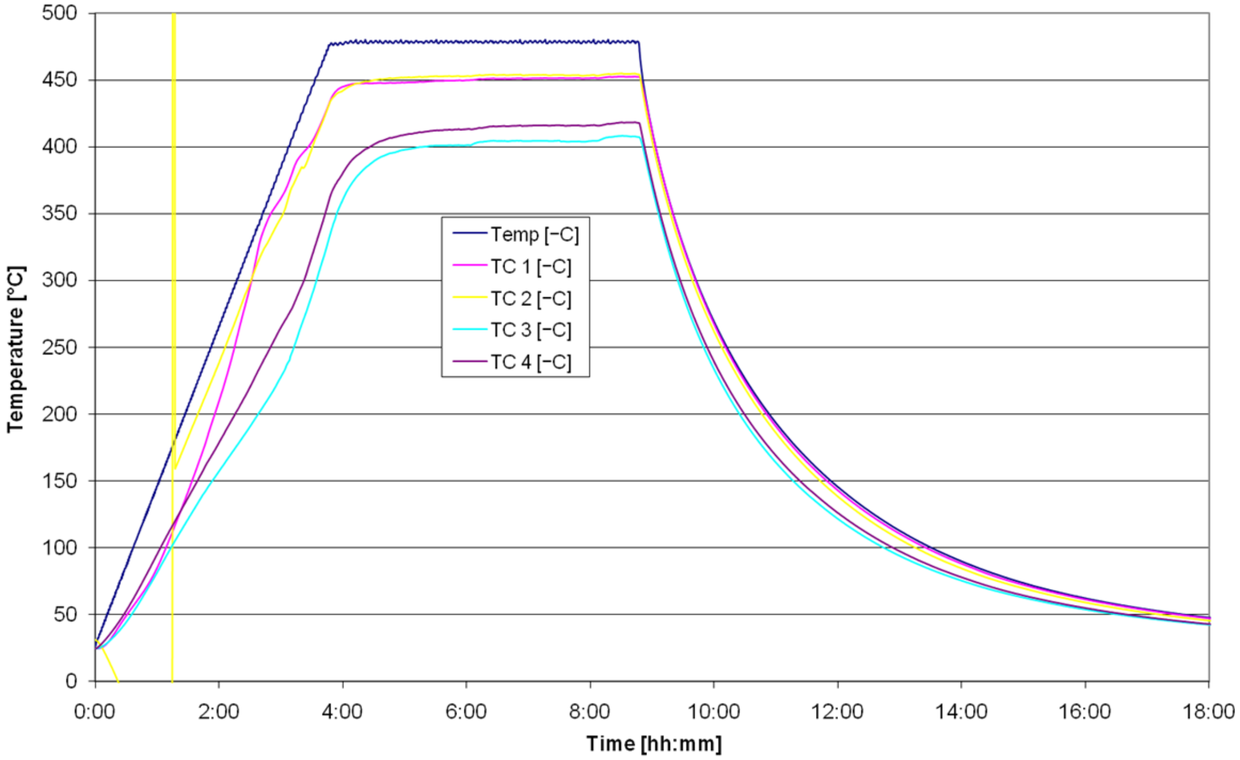

Figure 5: First test run without sample container, straw as feedstock. Heater temp 30 °C above sample temperature inside

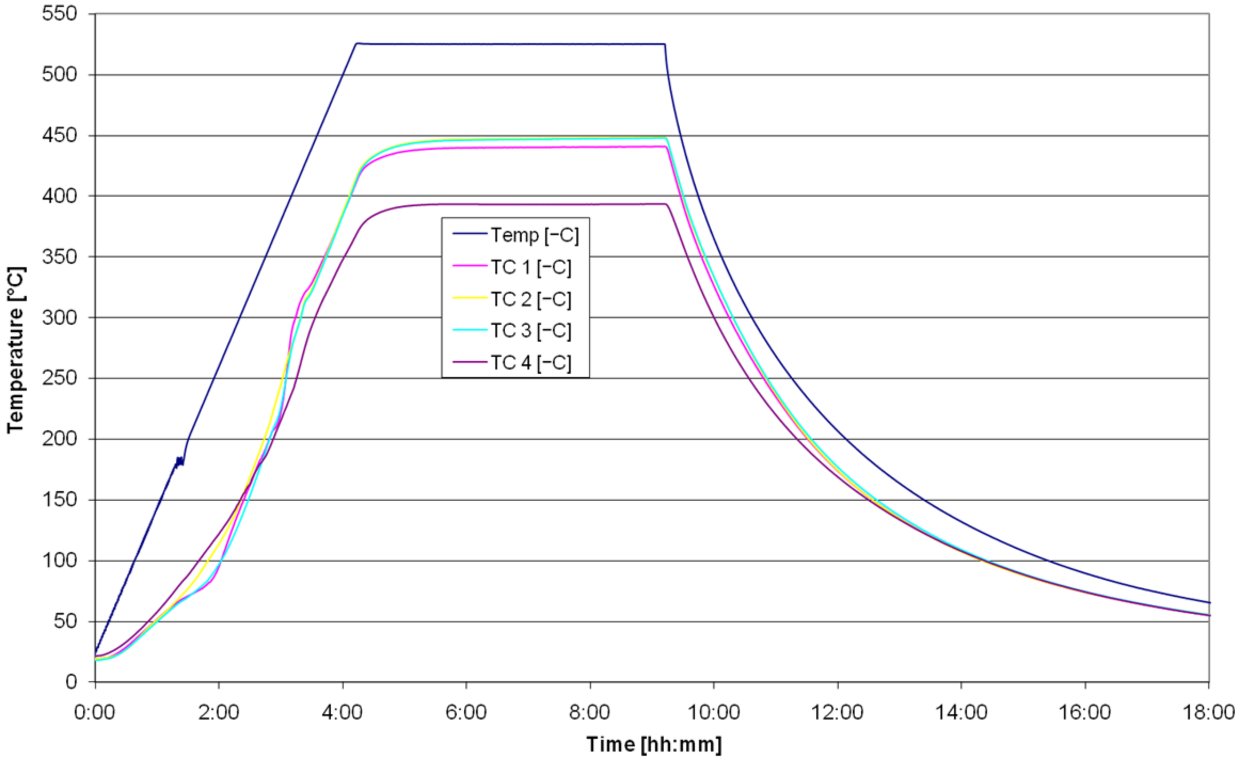

Figure 6: Second test run with sample container, straw as feedstock. Heater temp 75 °C above sample temperature inside

Based on these initial runs, and together with our initial thermal model, the following correlation between heater temperature and samples temperature had been established, notwithstanding axial thermal gradients inside the sample container:

Heater temperature [°C]	Sample temperature [°C]
400	343
425	364
450	386
475	407
500	429
525	450
550	471

Following the requirements definition from the beginning of the project, the pyrolysis furnace should have sufficient power reserve, even considering the additional need of heater power demanded by the sample container and the thus significantly increased temperature difference between sample temperature and heater temperature.

A verification of the furnace temperature profile when using vine wood revealed a different performance of the furnace, as shown in Figure 7. Apparently, the more loosely packing of the vine wood compared to straw resulted in better heat transfer into the core of the feedstock; furthermore, a steeper radial temperature gradient had been detected. The latter may however be questioned, as the precise positioning of temperature sensors was found to be more difficult in vine wood compared to straw.

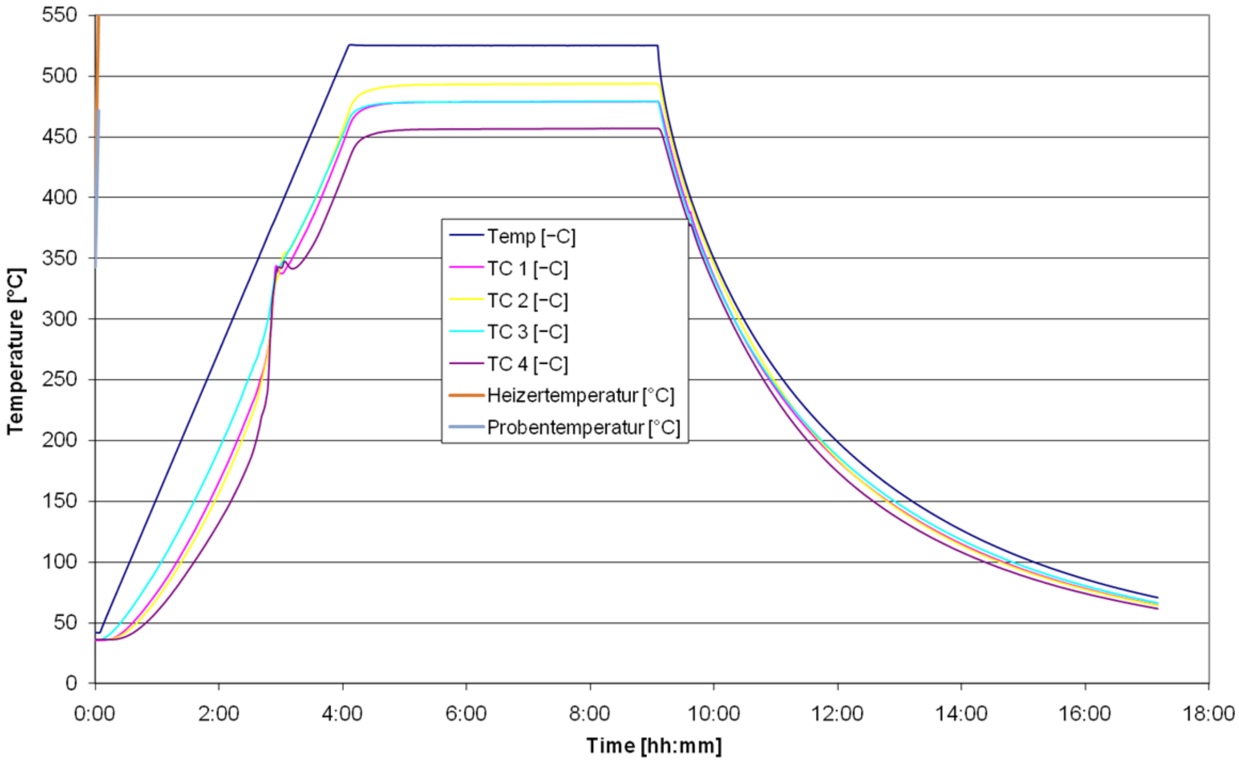

Figure 7: Third test run with sample container, vine wood as feedstock. Heater temp 45 °C above sample temperature inside

A systematic evaluation of the correlations between type and amount of feedstock, effective sample temperatures, and both axial and radial thermal gradients could however not be performed due to the following reasons:

- A well-defined positioning of the thermocouples inside the feedstock was not possible because
    - Thermocouples can only be mounted before installation of radiation shields and lid
    - The densely packed feedstock, owed to the requested high amount of biochar per pyrolysis run, made poking of 1.5 mm thermocouples inside the feedstock almost impossible
    - Thicker thermocouples could not match into the narrow gap between radiation shields and tube wall
    - Mounting of the radiation shields additionally changed the position of the sensors in an unpredictable way
- The sample container does not allow a fixed positioning of thermocouples from the „back side“
    - This was the initial planning, as the positioning of thermocouples upon loading the feedstock into the tube was very well feasible
    - The densely packed feedstock inside the sample container did however not permit any defined positioning of sensors, as they were simply pushed away from the container
- Significant changes in furnace design were no more feasible due to schedule and budget restraints

Following all the aforesaid, all temperatures as discussed in the following sections are prone to error, and the effective temperature at different locations of a feedstock loading – center of furnace or ends near thermal shields, close to furnace wall or in the axial centre – may differ up to 50 K, based on predictions of our thermal models. These gradients are expected to increase with more densely packing of the feedstock and the total mass of the loading. Thus, the gradients should be rather small when using vine wood, while spruce is expected to result in the largest gradients of all feedstock investigated. In the latter case, the overall temperature may furthermore be lower than anticipated.

Further Pyrolysis Runs

The next series of pyrolysis runs had been conducted using straw and vine wood as feedstocks. The correlation between temperature and yield was under investigation, and the effect of a feedstock pre-drying was also analyzed.

Correlation between pyrolysis temperature and biochar yield:

The correlation between pyrolysis temperature and biochar yield as of primary interest. The dwell times for straw and vine wood was 5 hrs at maximum temperature. For spruce, poplar, and ash tree, the dwell time was 10 hrs due to the significantly higher loading mass and the thus required longer period of time until reaching thermal equilibrium.

It shall be noted that the scattering of biochar yields is in the range of 1%, when considering replications under identical conditions.

Controller-Temp. [°C]	400	460	525
Effective sample temp [°C]	343	397	450
Straw	40	34-36	31
Vine wood	39-42	34-34,5	31-36
Spruce	48	33	26
Ash tree	35	29	24
Poplar	38	33	24

In one single run, the yield of vine wood was unexpectedly high.

Influence of pre-drying on the biochar yield

The various feedstocks contained substantial amounts of water:

Straw	7.5 - 8.9% (dried during storage in test hall; initial value after delivery was 8.9%)
Vine wood	11.4%
Spruce	33.3%
Ash tree	30.8%
Poplar	27.6%

Despite the partly very high amounts of water, pre-drying of feedstocks did not result in higher biochar yields when normalising the yield to dry matter. The actual water content was however interesting for assessing the effective biochar yield from the various feedstocks. A yield table referring to dry feedstock reveals the following biochar yields for different feedstocks at various temperatures:

Controller-Temp. [°C]	400	460	525
Effective sample temp [°C]	343	397	450
Straw (biochar yield in %)	43.5	37	34
Vine wood (biochar yield in %)	43-47	38	35-40 (?)
Spruce (biochar yield in %)	64 (?)	44	35
Ash tree (biochar yield in %)	46	38	31
Poplar (biochar yield in %)	48.5	42	31

Process specific problems and potential dangers

The most relevant challenges for the technical implementation of the biochar production by such a pyrolysis process originate from the properties of the by-products. While the gaseous by-products are characterized by their offensive smell, the liquid pyrolysis by-products were found to be very corrosive; this may be due to the presence of substantial amounts of various organic acids and water.

Therefore, pyrolysis equipment must fulfill the following minimum requirements:

- Fully corrosion resistant make of high alloyed steel
- Gastight to reduce odour nuisance to the environment to the absolute minimum
- Heated off gas lines for avoiding condensation of by-products (about one third of initial mass) and subsequent blocking of gas stream
- Off gas combustion, both for providing an energy-efficient process and eliminating malodorous and potentially harmful by-products

Based on these considerations, the installation costs of a biochar production plant are expected to be rather high; the operating costs are mainly determined by utilization of by-products for process heat generation and optimized heat management.

Another potential risk originated from the potentially pyrophorous biochar. Namely produces from ash tree and poplar were self-igniting after removal of produce from the pyrolysis furnace. This may be caused by the very large (internal) surface that appears to be very reactive with air oxygen.

Technically, this threat may be reduced by cooling the complete biochar loads to temperatures lower than 30 °C and avoiding local hot-spots that may be present in the core of the batch. Furthermore, inert gas dousing during cooling after removal was found to be effective for preventing self-ignition. This may reduce the oxygen partial pressure to such an extent that the – apparently inevitable – oxidation of the most reactive sites of the fresh biochar is delayed to such an extent that local hot-spot formation due to the reaction enthalpy is suppressed. Thus, a self-accelerating reaction that may get out of control is prevented.

Conclusions

Temperature:

A controller temperature of 400 °C, equivalent to an effective pyrolysis temperature of 340-350 °C, seems to be too low for producing a sufficiently good quality biochar. Namely when pyrolysing woods, i.e. spruce, poplar, and ash tree, the feedstock at the ends of the sample container facing the radiation shields is visibly under-pyrolysed due to the axial thermal gradients in the batch.

Therefore, a pyrolysis at 460 °C controller temperature or 400 °C effective inside temperature my be favourable from the viewpoints of yield and energy efficiency. This is at least true for straw and vine wood as feedstocks.

Increasing the pyrolysis temperature to 525 °c at the controller or 450 °C inside the feedstock results in lower biochar yields, but may be favourable for long term stability of the produce in the soil, despite a substantially higher energy demand for the process.

Dwell time:

For the „light“ feedstocks like straw and vine wood, a dwell time of 5 hrs at a given temperature seems sufficient for a complete pyrolysis. Due to the substantially higher bulk density of spruce, ash tree, and poplar, together with their substantially higher water contents, a dwell time of 10 hrs seems appropriate. In a first step, the water from these feedstocks needs to be evaporated, and only then the actual pyrolysis process can take place.

Yield:

The yields for the different feedstocks were strongly temperature dependent, with increasing temperature meaning decreasing yields. The optimum temperature can only be given after assessing the laboratory and field test results of the biochar characterization to be performed in subsequent work packages of the project.

Compared to the initial mass, the yields for straw and vine wood seem to be higher than for spruce, ash tree, and poplar. This is however only true when ignoring their substantially higher water contents.

2.2 WP 2: Experimental setup for carbon sequestration and soil studies

WP leader: Bernhard Wimmer, AIT Austrian Institute of Technology, Tulln

Work package content:

Installation and maintenance of pot, lysimeter and field experiments to provide sample material for soil, microbiological and plant analyses

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Objective of the workpackage

The objective of this workpackage is the establishment of different experiments to study the effect of biochar application on soil, soil microorganisms and plant performance. The goal is the experimental setup and conduction of pot experiments and field studies to provide soil and plant materials for the planned investigations in WP 3 to 6.

Pot Experiment and Micro-Lysimeter Experiments

Pot experiment and micro-lysimeter experiments

The pot experiment and the micro-lysimeter experiment were realized in a common experimental set-up at the AIT Austrian Institute of Technology. Each vessel of the pot-experiment is equipped with an outlet at the bottom to enable a collection of the seepage water from each pot so that it can be used as a micro-lysimeter. Hereinafter these two experiments are referred to as “pot-experiment”.

During summer 2010 we collected soil material (about 1 to 2 Mg per site) at 3 different locations in Austria (2 in Lower Austria, 1 in Styria). :

Kaindorf (Styria): gleyic Cambisol, loamy; N47 13 47.9 E15 50 39.1; 376 m.a.s.l.

Traismauer (Lower Austria): Calcaric Cambisol ,silty soil on loess, N48° 19.891’ E15° 44.316’; 261 m.a.s.l.

Eschenau (Lower Austria): sandy Planosol; low pH ; N 48°46’32.9’’ E 15°14’28.6’’; 535 m.a.s.l.;

Informations about the exact location and a description of the soil properties are described in WP2, chapter 2.3 and WP3. After transport to the greenhouse at the AIT in Seibersdorf the soil materials were air dried as far as possible. Large aggregates were broken to < 2-3 cm.

Figure 8: soil profiles at the soil sampling sites in Traismauer, Kaindorf and Eschenau (from left to right)

The different biochars used for the pot experiment were produced from three feedstocks at two temperatures.

- Vineyard Pruning (400°C and 525°C),
- Wheat straw (525°C), and a
- Woodchip-Mixture (525°C).

The vineyard pruning biochar was pyrolysed at a heating rate of 2°C/min with a dwell time of six hours at 525°C and eight hours at 400°C at the laboratory of AIT (technical details see WP1). The wheat straw and woodchip-mixture biochars were produced at the facility in Dürnrohr (EVN) each at a pyrolysis temperature of 525°C, dwell times of approx. one hour, and heating rates of 10-20°C/min. Argon (Ar) was constantly added during the cooling process to maintain the oxygen free environment inside the pyrolsis-furnace.

Prior to mixing with the soil the biochars were carefully ground and sieved to particles <2mm to be applicable for the pot experiments.

For the set-up of the pot-experiment sewer pipes were used. The physical dimensions of the pots are:

- 40 cm height,
- 23,5 cm diameter, and a
- Volume of 17,3 litres

A sketch of the vessels is shown in Figure 9.

For collection of the seepage water a flexible tube was connected to the bottom of each pot. The tubes have a siphon-like shape to prevent the diffusion of air into the pots from the bottom.

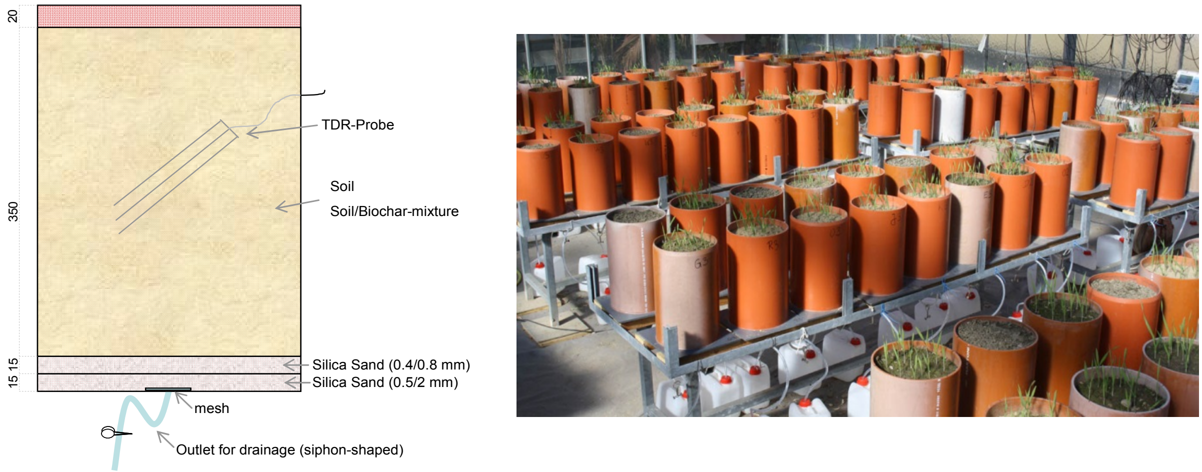

Figure 9: Sketch of one vessel for the pot experiment; lengths in mm (left); set-up of pot experiment in the greenhouse (Photo: J. Bücker)

During November 2010 we set up a total of 125 pots, positioned in 4 double rows, using a randomized block design. The total number is made up of 25 treatments with 5 replicates each.

The different treatments, bulk density of the 3 soils and the biochar-soil mixtures are described in Table 1.

Table 1: Overview of soils, biochars, different treatments and bulk density used during the set-up of the pot experiment (BC = Biochar)

Soil	Biochar-Feedstock	Temp of BC pyrolysis	Amount of biochar	Nitrogen fertilizer	Water content during filling	Dry bulk density
		°C	%-M of total mixture	Equivalent to kg/ha	%-M	Mg/m^3
Planted treatments						
Eschenau	Woodchips	525	1	100	5.63	1.32
Eschenau	Woodchips	525	3	100	6.94	1.29
Eschenau	Wheat-straw	525	3	100	5.4	1.28
Eschenau	Vine-prunings	400	3	100	5.35	1.31
Eschenau	Vine-prunings	525	3	100	4.77	1.32
Eschenau	Woodchips	525	3	0	6.94	1.29
Eschenau	Woodchips	525	3	50	6.94	1.29
Eschenau	Woodchips	525	3	200	6.94	1.29
Eschenau	Control without BC		0	0	3.76	1.35
Eschenau	Control without BC		0	50	3.76	1.35
Eschenau	Control without BC		0	200	3.76	1.35
Kaindorf	Woodchips	525	3	100	10.33	1.11
Traismauer	Woodchips	525	3	100	6.08	1.23
Kaindorf	Woodchips	525	1	100	9.82	1.12

Traismauer	Woodchips		1	100	4.62	1.25
Eschenau	Control without BC		0	100	3.76	1.35
Kaindorf	Control without BC		0	100	5.94	1.17
Traismauer	Control without BC		0	100	3.31	1.28
Unplanted treatments						
Eschenau	Woodchips	525	3	100	6.94	1.29
Eschenau	Wheat-straw	525	3	100	5.4	1.28
Eschenau	Vine-prunings	400	3	100	5.35	1.31
Eschenau	Vine-prunings	525	3	100	4.77	1.32
Kaindorf	Woodchips	525	3	100	10.33	1.11
Eschenau	Control without BC		0	100	3.76	1.35
Kaindorf	Control without BC		0	100	5.94	1.17

Directly after filling the soil columns were carefully irrigated with artificial rain water using a concentration of 3 mg Ca l^{-1} (50 % of Ca was added as $CaCl_2*2H_2O$, the other 50 % as $CaSO_4*2H_2O$). The amount of irrigation water was calculated according to the soil specific water holding capacity. If necessary the amount of irrigation water was increased until at least 200 ml of seepage water drained out of each pot. During each leachate sampling campaign, 200 ml of leachate was collected and immediately conserved by gamma-radiation using a ^{60}Co source (MediCare, Seibersorf, Austria).

Directly after moistening the soil we planted mustard (Sinapis Alba, variety Servil, obtained from Saatbau Linz GmbH, Austria) at the pots intended for vegetation (see Table 1). For the temperature conditions in the greenhouse a defined day-night cycle was applied : 12°C (18h-6h), 16°C (6h-8h), 20°C (8h-16h), and 16°C (16h-18h).

The standard fertilizer rate of the pot experiment was an amount equivalent to 100 kg N $ha^{-1}*a^{-1}$ (N100), which was predefined for the second crop (barley, Hordeum vulgare). Mustard (Sinapis alba) is commonly used as green manure or preceding crop in agricultural crop rotations, hence we reduced the additional (standard) N-fertilizer rate from 100 kg N ha^{-1} to 40 kg N ha^{-1}. Consequently, the amount of N-fertilizer applied to each pot ranged from 0,578g to 2,312g.

We used a regular compound fertiliser, Linzer Star (NPK(S)-Fertiliser 15/15/15 (+3)) from Linzer Agro Trade GmbH. Prior to application, the fertiliser was ground to particles < 2 mm to ensure solubility, infiltration with the irrigation water and a more regular distribution on the soil surface to avoid concentration in a few spots. For the treatments with varying N-rates the fertilizer application ranged between equivalent amounts between 0 to 200 kg N $ha^{-1}*a^{-1}$. Besides, nitrogen (N) also phosphorus (P), potassium (K) and sulphur (S) was added by fertilization due to the utilisation of a compound fertiliser.

For each control and each treatment one pot was equipped with sensors for monitoring the water content in the central part of the pot.

Directly at filling the pots and at defined time steps during the growth of the mustard soil and leachate samples were taken and provided for analysis in the WPs 3 to 6. The growth of the mustard was monitored by measuring its height at several time steps. The mustard was harvested on 17th of February 2011. The biomass of each replicate was dried, weighed and prepared for further plant analysis.

A few days after harvesting the mustard we planted barley sprouts (Hordeum vulgare) into the pots. A first fertilization rate with an equivalent amount of 50 kg N ha^{-1} was given to the plants on 14th of March 2011. In contrary to the nitrogen fertilization the amount of phosphorus and potassium was kept constant for fertilizing the barley (equivalent amounts of 48 kg ha^{-1} P_2O_5, 80 kg ha^{-1} K_2O).

Furthermore caps of different size were constructed to cover the soil surface of the pots during collection of gas samples (see WP 6).

After finalizing the first crop (mustard) at the micro-lysimeter experiment spring barley (Hordeum vulgare) was planted on 18th of February 2011. On the surface of the micro-lysimeters 11 barley seeds were sown (5+3+3 seeds) in a depth of 10 mm. The seeds were covered and slightly compressed with the removed soil from the rows. To produce adequate moisture conditions for the development of the plants 500 mL of synthetic rainwater was added. At sowing, pre-germinated seeds (24 h at 20 °C) have been used.

The number of risen barley plants per pot was controlled and adjusted 10 days after sowing. If a pot contained less than 10 plants, the number of plants was supplemented to eleven. If a pot contained ten plants, no additional barley seed was set in.

Fertilizer was added at two times. A first fertilization rate with an equivalent amount of 50 kg N ha^{-1} was given to the plants on 14th of March 2011 (standard treatment). In contrary to the nitrogen fertilization the amount of phosphorus and potassium was kept constant for fertilizing the barley (equivalent amounts of 48 kg ha^{-1} P_2O_5, 80 kg ha^{-1} K_2O) for all treatments. For the second fertilization of barley only nitrogen was applied at the micro-lysimeters (Nitramoncal 27 % N; equivalent amounts of 50 kg ha^{-1} for the standard treatment). A description of the different treatments can be found in the first interim report (May 2011). Further details about the fertilization can be found in the Diploma Thesis of Jannis Bücker (Bücker 2012).

Leachates were collected two times during the cultivation of barley (4th and 5th leachate sampling of the micro-lysimeter experiment) and analyzed for their volume, pH-value, EC, ammonium (NH_4^+), nitrate (NO_3^-), dissolved phosphorus (PDISS), (secondary) plant nutrients (Ca^{2+}, Mg^{2+}, K^+) and DOC-concentrations (Bücker 2012).

The harvest of barley took place on 21st of June 2011. Biomass of grains, straw, number of ears, grains per ear and thousand-seed weight was determined.

Further details about the cultivation of barley on the micro-lysimeter can be found in

Study sites

To study the behaviour and carbon sequestration of biochar under natural conditions we established field experiments at two sites. The two study sites are located in Lower Austria and Styria, Austria, adjacent to the places where we collected the soil samples for the pot experiment.. The soil in Traismauer, Lower Austria (48°19'52.6''N, 15°44'20.5''E; parent material loess; 547 mm mean annual precipitation), was classified as a Chernozem with silt loam texture (pH (CaCl2): 7.4, CEC: 208.6 mmolc kg-1, C/N ratio: 11.9, carbonate: 15.8 w.-%). The soil in Kaindorf, Styria (47°13'46.0''N, 15°50'40.6''E; parent material tertiary sediments; 883 mm mean annual precipitation), was classified as Cambisol with clay loam texture (pH (CaCl2): 6.6, CEC: 209.4 mmolc kg-1, C/N ratio: 13.8, carbonate: 0.0 w.-%). A detailed characterisation of the two soils was given in Kloss et al. (2013).

Maps with the location of the experimental sites are shown in Figure 10 and Figure 11.

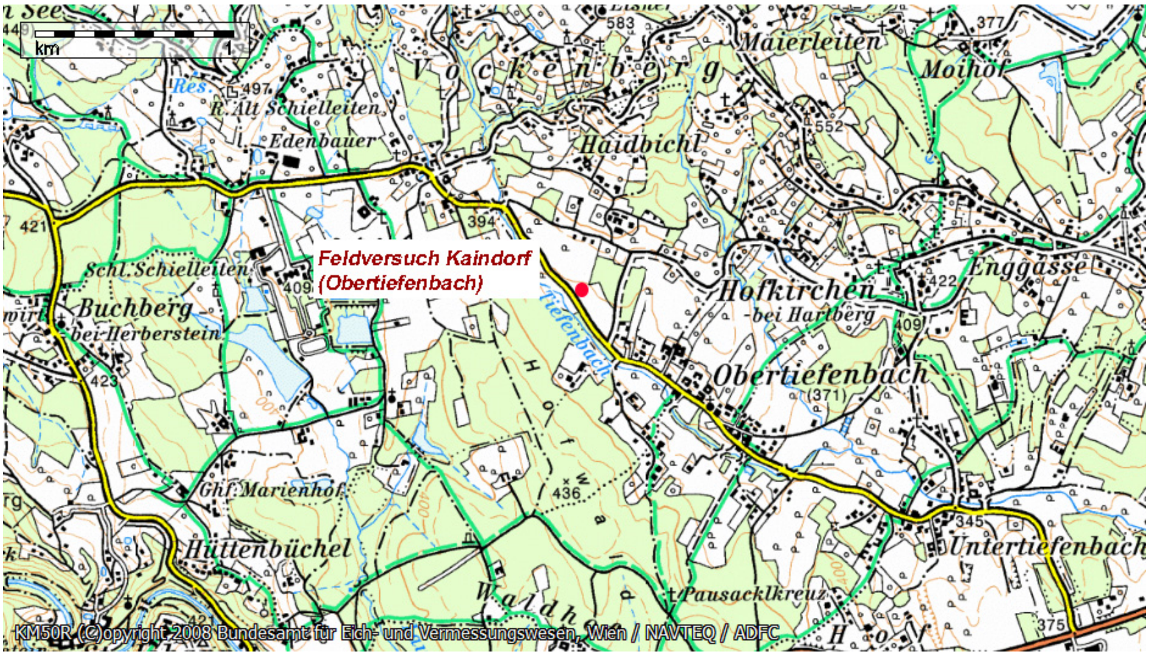

Figure 10: Location of the field experimental site in Obertiefenbach near Kaindorf

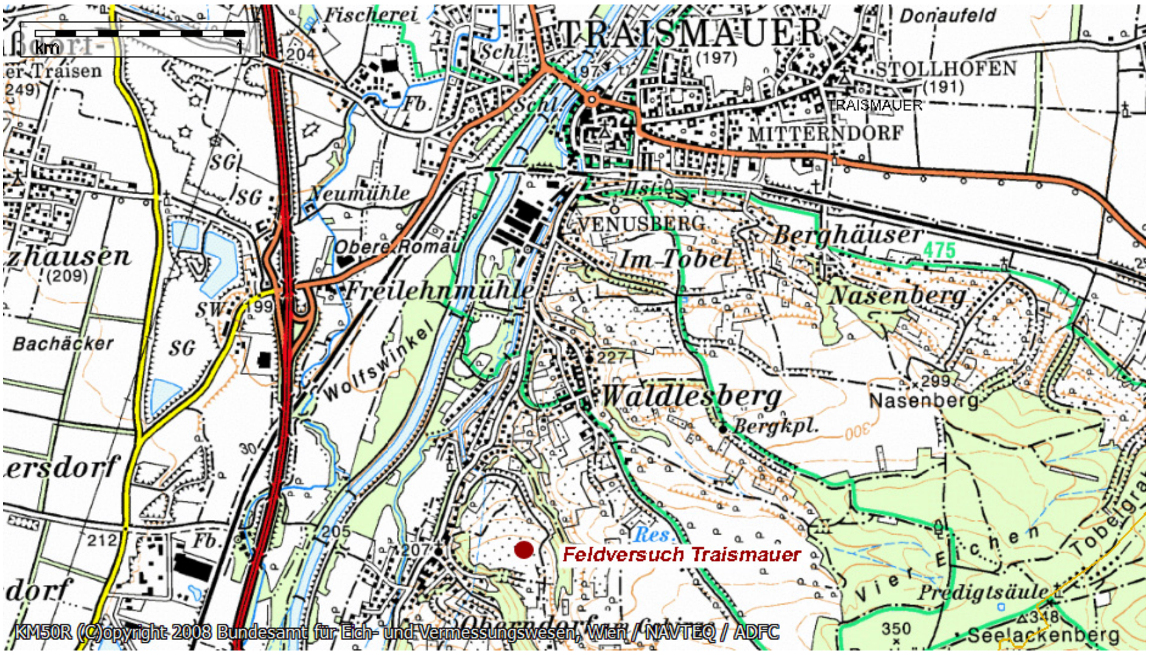

Figure 11: Location of the field experimental site in Oberndorf near Traismauer

Experimental setup in the field

Plots had a circular shape because this geometry guaranteed the best ratio of large experimental area to low circumference. This lowered the risk of soil mixing at the outer plot zones and prevented the mixing in the inner (net) plot area. Each circular net plot (used for harvest analysis, soil and plant sampling) with a diameter of 3.5 m was positioned in the centre of a gross plot with 6.5 m diameter. The minimum distance between the outer borders of net plots was 6.5 m; the minimum distance between the outer borders of gross plots was 0.5 m. There were four different treatments with four replicates (n=4), arranged as Latin Square. Nutrients (N, P, K) were supplied according to standard agricultural practices in the respective region (Table 1). The treatments consisted of three different BC application rates (0, 24 and 72 t ha-1) with identical mineral N fertilisation and one additional treatment without N supplement but with a BC application rate of 72 t ha-1. The high BC application rate of 72 t ha-1 was chosen to simulate carbon enrichments observed in historically amended, terra-preta-like soils. Among the four treatments we included one BC treatment without nitrogen addition because the - for a wood-based BC - relatively high N concentration of 0.4% would have meant an N addition of 288 kg ha-1. This treatment should show if at least a part of this N pool could be of any use for the crops. BC was applied to the soil by dividing each plot in 8 sub-plots; each of these received the amount of BC corresponding to the area of this sub-plot. BC was moistened by hand with a watering-can immediately after application to avoid wind erosion. Incorporation into soil was achieved to a depth of 10 cm with a rotary hoe at low rotation speed.

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As third crop clover (*Trifolium pratense* Reichersberger neu) was planted on the micro-lysimeters on 2011-07-26. The timeline of harvesting, fertilization and leachate collection during the cultivation of clover can be found in **Fehler! Verweisquelle konnte nicht gefunden werden.**. The standard fertilization rate of nitrogen was 50 kg N ha^{-1} and varied according to the different treatments. The fertilization rate of phosphorus and potassium was kept constant again at equivalent amounts of 48 kg ha-1 P_2O_5 and 80 kg ha^{-1} K_2O. The collected leachates were analysed for ammonium and nitrate.

Field Experiments

Study sites

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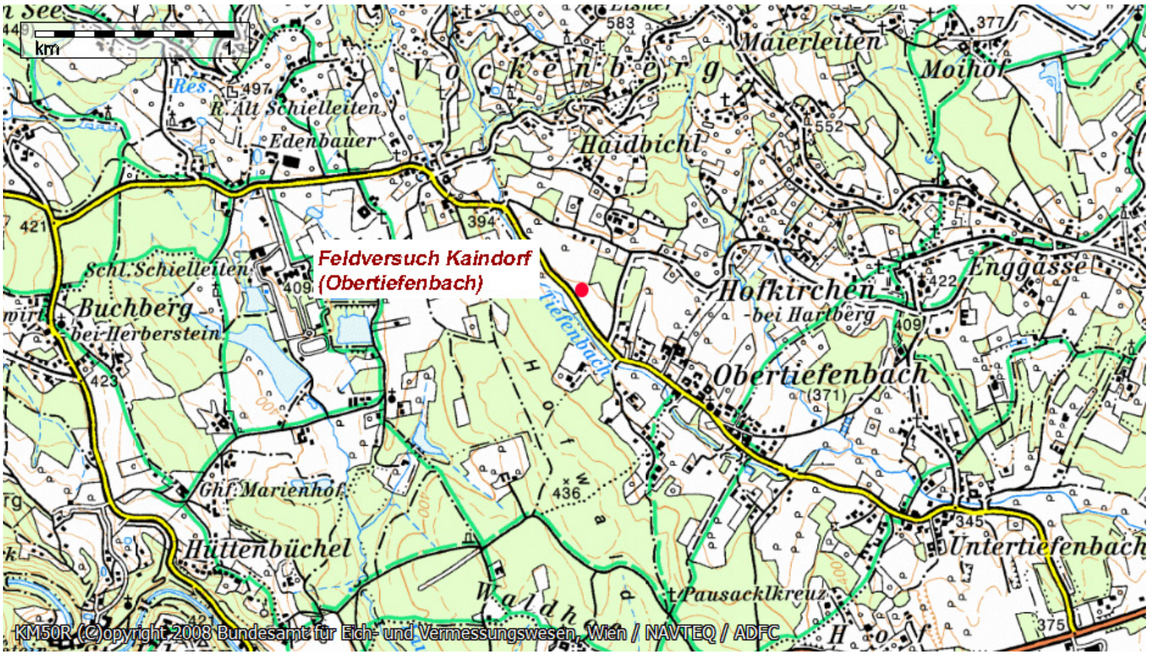

Figure 10: Location of the field experimental site in Obertiefenbach near Kaindorf

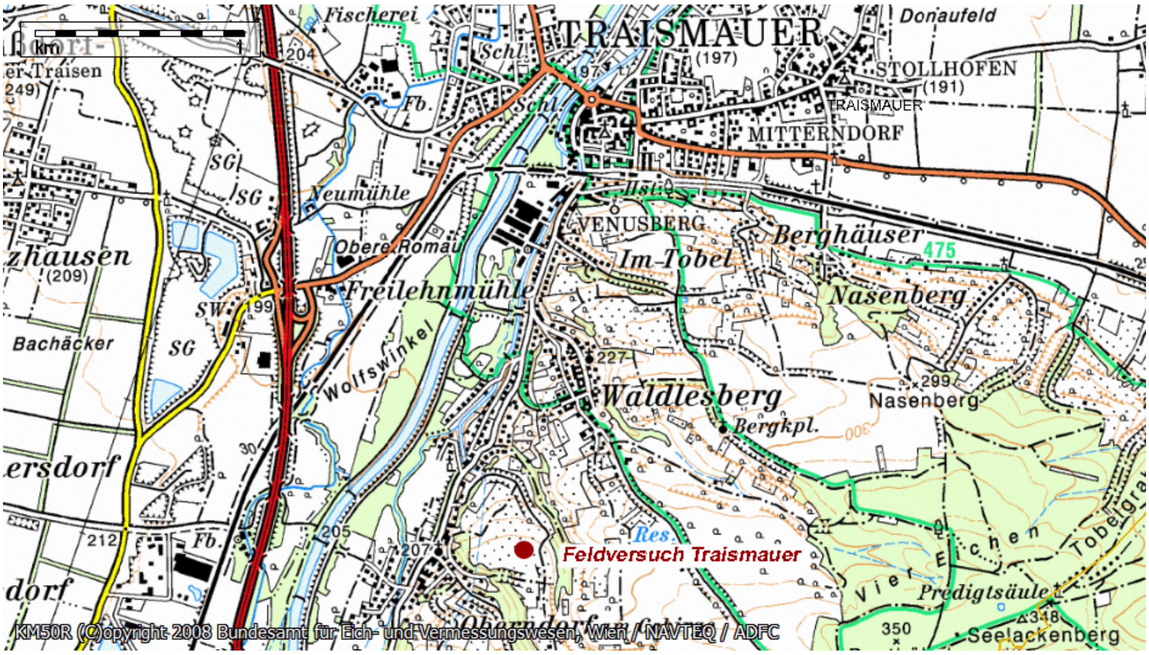

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Table 2 BC application and fertilisation rates on the Cambisol and Chernozem in 2011 and 2012. N: Nitrogen; P: Phosphorus; K: Potassium. BC or fertiliser application rates are given for 2011 / 2012.

	Treatment	**BC [t ha^{-1}]**	**N [kg ha^{-1}]**	**P [kg ha^{-1}]**	**K [kg ha^{-1}]**
Cambisol (Kaindorf)	fertiliser without BC (control)	0 / 0	150 / 120	13 / 0	46 / 0
	24 t ha^{-1} BC + fertiliser	24 / 0	150 / 120	13 / 0	46 / 0
	72 t ha^{-1} BC + fertiliser	72 / 0	150 / 120	13 / 0	46 / 0
	72 t ha^{-1} BC without N supplement	72 / 0	0 / 0	13 / 0	46 / 0
Chernozem (Traismauer)	fertiliser without BC (control)	0 / 0	120 / 75	26 / 31	50 / 100
	24 t ha^{-1} BC + fertiliser	24 / 0	120 / 75	26 / 31	50 / 100
	72 t ha^{-1} BC + fertiliser	72 / 0	120 / 75	26 / 31	50 / 100
	72 t ha^{-1} BC without N supplement	72 / 0	0 / 0	26 / 31	50 / 100

The plots were arranged according to a randomized block design (see Figure 10). For a homogenous application of the biochar the plots were subdivided into smaller parts as shown in Figure **12** (right side).

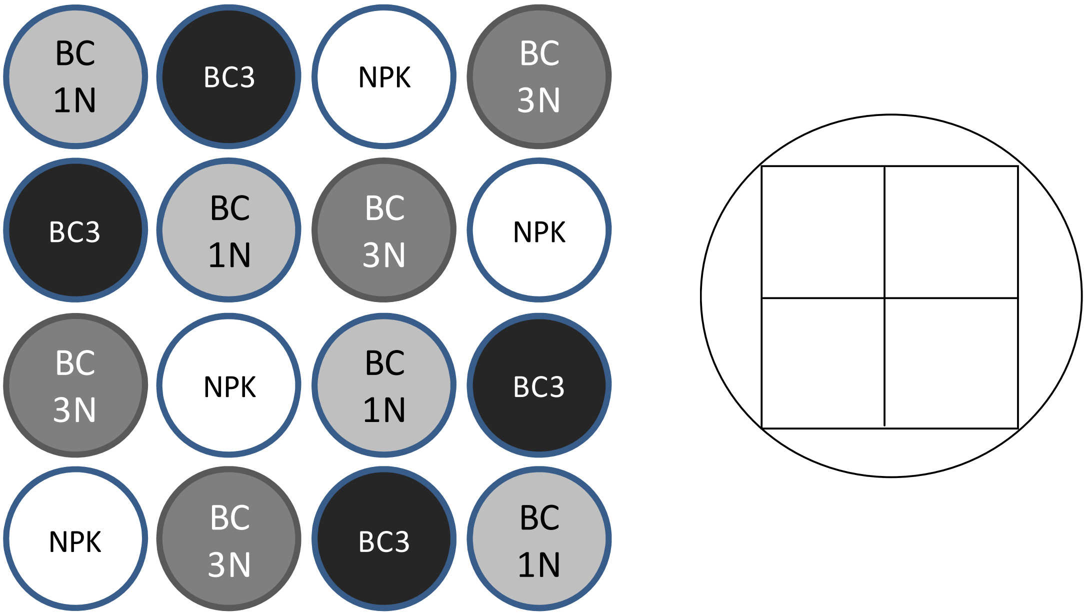

Figure 12: Randomized block design of the treatments and the control plots at both field experimental sites Traismauer and Kaindorf (left); subdivision of the plots for a homogenous application of the biochar (right)

Experimental management and sampling

Kaindorf

The addition and incorporation of BC into the Cambisol in Kaindorf took place on March 31st, 2011. The site was fertilised on April 12th, 2011 (nitrogen (N), phosphorus (P), potassium (K) = NPK; N: P2O5: K2O = 20: 6: 11, Linzer Star, Borealis Linzer Agro Trade GmbH, Austria). Subsequently, maize (Zea mays L.) was sown on April 25th 2011, followed by N fertilisation (Nitramoncal = 27% ammonium nitrate) on July 6th 2011. The maize was harvested on September 28th, 2011, followed by the sowing of winter wheat (Triticum aestivum L.) on October 10th, 2011 and fertilised with N (Nitramoncal = 27% ammonium nitrate) on March 12th, 2012. The winter wheat was harvested on July 17th, 2012. Composite soil samples were taken on the days of harvest. From each plot, approximately we attained 20 soil samples randomly from a depth of 0-17 cm and mixed.

Traismauer

Here, BC was incorporated on March 16th, 2011, followed by NPK (N: P2O5: K2O = 15: 15: 15, Linzer Star) fertilisation on April 11th, 2011. Spring barley (Hordeum vulgare L.) was sown on April 12th, 2011 and fertilised (Nitramoncal) on May 10th, 2011. Spring barley was harvested on July 21st, 2011. Sunflower (Helianthus annuus L.) was sown on April 20th, 2012, and NPK (Nitramoncal = 27% ammonium nitrate and DC 45 plus (12: 20)) added on May 3rd, 2012.

Sunflower was harvested on September 26th, 2012. Composite soil samples (see above) were taken on the days of harvest.

Climate and weather conditions

In 2011, Kaindorf total annual precipitation sum was below average, with only 69.2% of the long-term mean 1971 – 2000 (Fig. 1). In the first nine months of 2012, the precipitation was 83.4% of the long-term mean.

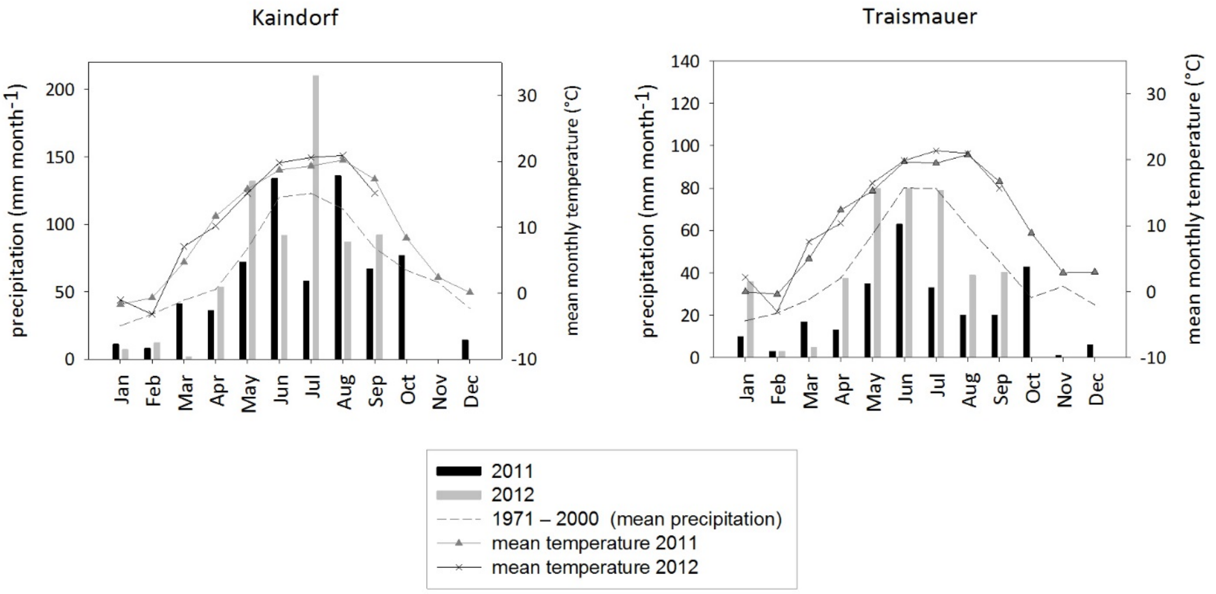

Figure 13 Monthly precipitation and temperature at the two study sites Kaindorf and Traismauer in 2011 and 2012 compared to the mean monthly precipitation (1971 – 2000). Weather data for 2012 are given until September, the month of the last harvest.

Traismauer experienced a more pronounced precipitation deficit in 2011, with only 50.4% of the long-term mean 1971 – 2000 (Figure 13). However, in the first nine months of 2012, precipitation was only slightly below average, reaching 93.1% of the 30-year mean.

2.3 WP 3: Stability of biochar carbon pools

WP leader: Franz Zehetner, University for Natural Resources and Life Sciences, Institute for Soil Science, Vienna

Work package content:

Differentiation of labile and stable carbon pools for assessment of carbon sequestration

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Objective of the WP

Biochar (BC) is considered to be a very stable compound once incorporated into the soil; therefore it can be seen as a potential strategy for carbon (C) sequestration in soils. However, as BC properties including C and ash content and aromaticity depend on pyrolysis conditions and feedstock, the stability of the individual BCs may vary. In addition, the soils treated with BC may have an influence on BC stability, e.g. through their soil pH and composition of soil microorganisms.

The objective of WP 3 was to analyze ^{13}C labeled biochar stability using a long-term incubation experiment under constant conditions at the University of Natural Resources and Life Sciences (BOKU), Vienna.

Background

Biochar (BC) is the solid residue derived from pyrolysis of biomass and is considered to be very recalcitrant in the soil due to its high aromaticity. Therefore, BC application to soil is seen as a potential measure for long-term carbon (C) sequestration in the soil (Goldberg, 1985; Kuhlbusch and Crutzen, 1995; Lehmann and Joseph, 2009). BC application to soil may result in a net withdrawal of CO_2 whilst also reducing non-CO_2 gas fluxes from the soil (Lehmann, 2007; Van Zwieten et al., 2009). The knowledge about the recalcitrance of BC in the soil is based on findings in the Amazon region, where the anthropogenic Terra Preta soils feature high amounts of highly condensed aromatic and carboxylic structures caused by burning activities. Charcoal particles in these soils may be up to 7000 years old (Glaser, 2007). The longevity of BC in the soil depends on a variety of factors such as specific soil characteristics including pH, C/N, soil temperature and microbial composition, but also on BC characteristics itself, such as pH, C/N and O/C ratio, aromaticity and ash content. Mineralization rates of soil-native soil organic matter (SOM) may change upon BC application. Depending on the type of priming agent added to the soil, those priming effects may be positive or negative. A positive priming effect occurs when a new, labile substrate is added to the soil and stimulates an accelerated mineralization of SOM. This may either be caused by the production of extracellular enzymes that cause co-metabolism or by changes in microbial activity, nutrient sources, soil aeration and moisture, respectively (Kuzyakov et al., 2000). A negative priming, on the other hand, occurs when native SOM decomposition is decelerated after any substrate addition, which may be due to microbial inhibition (Zimmerman et al., 2011). Regarding BC application to soil, BC is often expected to act as a stimulant as it provides a labile C fraction, nutrients and a pore system that offers a habitat for microorganisms (Chan and Xu, 2009; Thies and Rillig, 2009), although both positive and negative priming effects have been found after BC application (Zimmerman et al., 2011).

The objective of WP 3 was to analyze BC stability in two different soils using ^{13}C labeled BC in a long-term incubation experiment carried out at the University of Natural Resources and Life Sciences, Vienna. In detail, we focused on following aspects:

- Influence of biochar feedstock on biochar stability
- Influence of pyrolysis temperature on biochar stability
- Influence of soil properties on biochar stability
- Temperature sensitivity of biochar decomposition

Materials and Methods

Experimental setup

The long-term incubation experiment was carried out with ^{13}C labeled BC. To do so, we grew wheat (Triticum aestivum) and willow (Salix alba) in the glasshouse in Seibersdorf. For the experimental setup, spring wheat *Monsun* with a thousand- seed weight of 43.955 g was grown in boxes with the dimensions 60 × 40 × 31 cm (~ 75 dm³). The purpose of the box system was, on the one hand, to provide a seedbed for the wheat seeds; on the other hand, the boxes were used to create a self- watering system for the seeds. Four holes with a diameter of 8 mm were drilled in the bottom of each box. Glas fiber wicks with 6 mm diameter were cut to the lengths 70 cm and 100 cm, respectively. The ends of each wick were wrapped with tape to prevent the ends from frazzling. Two wicks of each size were arranged diagonally and about three fourth of the wicks were drawn through the drilled holes. The setup of an empty box can be seen in Figure 14.

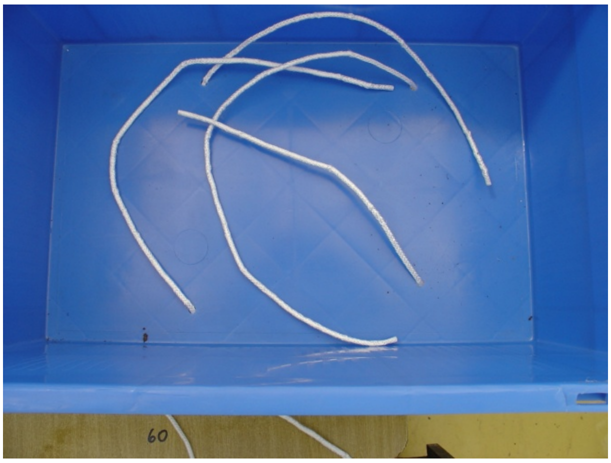

Figure 14 Empty box and glassfiber wicks used for self irrigation of the wheat plants

The boxes were filled with the culture media Frux ED 63 containing raised bog peat, natural clay and fertilizer. About 65 dm³ soil was put in each box. To provide for a consistent water distribution within the box, the wicks were arranged lengthwise at two different heights (Figure 15**).**

Figure 15 Arrangement of the wicks within the box used for growing wheat.

After filling 25 boxes with Frux ED 63, the boxes were set up in the greenhouse. The boxes were positioned on top of other boxes that were filled with water. The remaining wicks outside of each box were put in the water. After this, the soil was saturated with water to make the wicks draw. The complete setup can be seen in Figure 16.

Figure 16 Experimental setup for growing wheat in the glasshouse. The dark blue boxes below provide the water for self-irrigation.

To grow the wheat, three rills were prepared and filled with approximately 30 seeds so that one box each contained 90 *Monsoon* seeds at a depth 1- 2 cm. Finally, the top of the soil was once more slightly watered.

The willows were grown in a separate glasshouse chamber. They were grown in big pots; once they reached a certain height they needed to be repotted. Unlike the wheat, the willows were irrigated manually. The setup of the willows can be seen in Figure 17.

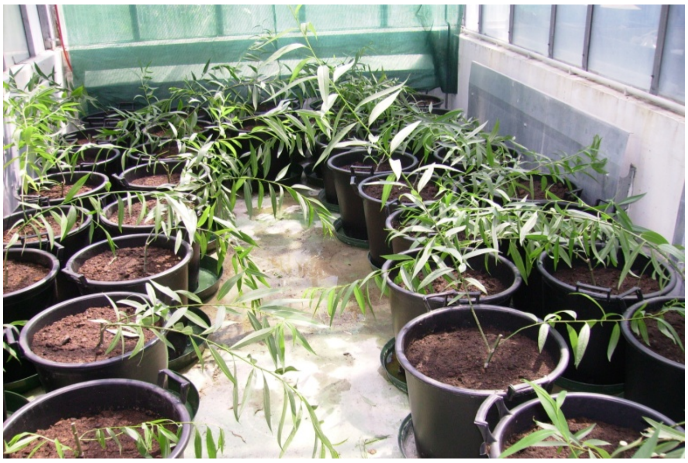

Figure 17 Experimental setup for growing willow in the glasshouse.

Both glasshouse chambers were equipped with a methane combustor. Methane combustion was chosen to effectuate sufficient ^{13}C labeling. The methane combustor is displayed in Figure 18.

Figure 18 Methane combustion unit for ^{13}C labeling of the plants used for the incubation experiment.

After harvest, wheat husks and willow wood were pyrolyzed in a stainless tube furnace under Ar atmosphere. Both feedstocks were pyrolyzed at 525°C. In addition, wheat was pyrolyzed at 400°C. The BC yield was approximately one third of the original biomass.

We chose two different soil types for our incubation experiment, which are described in more detail in WP 5. Briefly, the two soils were a Planosol (location: Eschenau; NÖ; 48°46’32.9’’N, 15°14’28.6 E; parent material granite, 667 mm mean annual precipitation) with a loamy sand texture and a pH of 5.4 as well as a Chernozem (location: Traismauer, NÖ; 48°19’52.6’’N, 15°44’20.5’’E; parent material loess; 547 mm mean annual precipitation) with a silt loam texture and a pH of 7.4.

The experimental setup was performed according to OECD guideline TG 307 (2002). The soils and BC were both sieved to < 2mm and then mixed at a 3 w.-% BC application rate. In addition, we provided controls in form of soils without BC application. After mixing BC and soil manually, they were filled into 50 mL Erlenmeyer flasks. Prior to the experiment, we originally pre-determined the sampling dates, which were 0, 0.5, 1, 3, 6, 12 and 24 months after start of the experiment. In order to avoid any disturbances during sampling, the soil-BC mixtures to be sampled at each sampling date were incubated in individual flasks. Selected Erlenmeyer flasks filled with the respective soil-BC mixture are shown in Figure 19.

Figure 19 Erlenmeyer flasks filled with soil-BC mixtures. The flasks are placed inside the incubator. The flasks were plugged with cotton balls to prevent contamination.

After filling in the soil-BC mixtures, which amounted to 25 g, the flasks were plugged with a cotton ball to prevent contamination during incubation, but account for a sufficient gas exchange. In order to investigate temperature sensitivity, we incubated samples at 20°C and 30°C, respectively. Due to the high mass loss during pyrolysis, samples with wheat-husk derived BC were only incubated at 20°C. A picture of the incubators is given in Figure 20.

Figure 20 Incubators used for the long-term incubation experiment at BOKU.

The irrigation was carried out every two weeks according to the soils' water holding capacity. At this, distilled water was added gravimetrically until 50 % water holding capacity was reached.

Sampling and analyses

The incubation experiment started in January 2011 and was originally planned until January 2013. Based on the results we obtained within the course of the experiment, we reconsidered the sampling dates and prolonged the whole incubation experiment (see below). The sampling dates that have been carried out so far are summarized in Table 3.

Table 3 Sampling dates of the incubation experiment

time since start of the incubation	**sampling date**
0 days	18.01.2011
2 weeks	01.02.2011
1 month	15.02.2011
3 months	13.04.2011
6 months	13.07.2011
24 months	15.01.2013
1 sampling open	

After each sampling, the soil-BC mixtures were dried at 60°C, capped with lids and stored under ambient air in a dark and dry place. Preliminary results of the ^{13}C isotope analyses, which were performed at the Austrian Institute of Technology (AIT) showed that there was no decomposition of the BC after 6 months. Hence, the samples that were intended for the 12 months sampling were left in the incubator and taken 24 months after the start of the incubation experiment instead. Up to now, we still have one sampling date open (Table 3). We plan to prolong the incubation experiment beyond the current project until January 2016 in order to investigate the stability of biochar carbon pools over a longer period of time (5 years). Sample preparation for ^{13}C measurements are described in 1.1.1.

Biochar characterization:

In addition to ^{13}C measurements, the used BCs were characterized for basic physicochemical and molecular properties. For Fourier-transform infrared spectroscopy (FTIR) measurements of the pure BCs, KBr pellets according to Tatzber et al. (2007) were made. At this, 0.5 mg of ball-milled biochar was mixed with KBr and pressed to 200 mg pellets. FTIR was carried out with a 4 cm^{-1} resolution measuring the absorbance from 4000 to 400 cm^{-1} (64 scans per sample; Tensor 27 SN 1683; Bruker, Austria). A spectrum correction was done measuring a pure KBr pellet and the surrounding air as a background spectrum. Total C and nitrogen (N) were measured using an elemental analyzer (CHNS-O EA 1108; Carlo Erba Instruments, Milano, Italy) following the method of Tabatabai and Bremner (1991). Brunauer-Emmett-Teller N_2 surface area (SA) was measured with a surface area analyzer (Flow Sorb II 230; Micromeritics, Aachen, Germany).

1.1.1. Preparation of samples for isotopic measurements

Inorganic carbon is known to interfere with the measurements of soil organic ^{13}C. Hence, the carbonates from the Chernozem-treated samples needed to be removed prior to measuring the ^{13}C labeling. Initially, a carbonate-containing subset was treated with 10% HCl to remove the carbonates; however, this proved to be a very perpetual method, which required a week-long addition of HCl and often ended in a HCl addition beyond the amount needed for a complete removal of the carbonates. Hence, we followed the fumigation method of Harris et al. (2001), who used concentrated HCl vapor for the removal of carbonate. We put our ball-mill ground and moistened samples into a desiccator along with a beaker of concentrated

HCl. In addition, the desiccator was connected to a vacuum pump. After generating a vacuum inside the desiccator, the HCl started to boil and the HCl vapor was able to diffuse into the wetted samples. According to Harris et al. (2001), a full carbonate removal can be expected after 6 hours. However, we modified the method and left the soils in the desiccator for several days. Within this period, the vacuum pump was run several times to remove the CO_2, which evolved during carbonate dissolution. In addition, we also fumigated the Planosol-treated soils to provide a similar treatment of all samples independent of the carbonate content. After several days, the samples were removed from the desiccator and transported to the AIT, where they were dried at 60°C. Afterwards, the samples were weighed into Sn capsules. According to their C content, the weight ranged from 0.3-0.8 mg. $^{13}C/^{12}C$ ratio was measured by EA-IRMS (elemental analysis-isotopic ratio mass spectrometry; Carlo Erba EA 1108, equipped with a WLD and connected to a Finnigan MAT 251 via a Conflow II). The international IAEA Standard NBS 22 was used for calibration. The isotopic composition was then determined using the delta value (δ) in relation to the Vienna Pee Dee Belemnite (V-PDB) standard.

Results and Discussion

Biochar characterization

The results of the C and N content of wheat husk and willow wood pyrolyzed at 525°C are displayed in Figure 21.

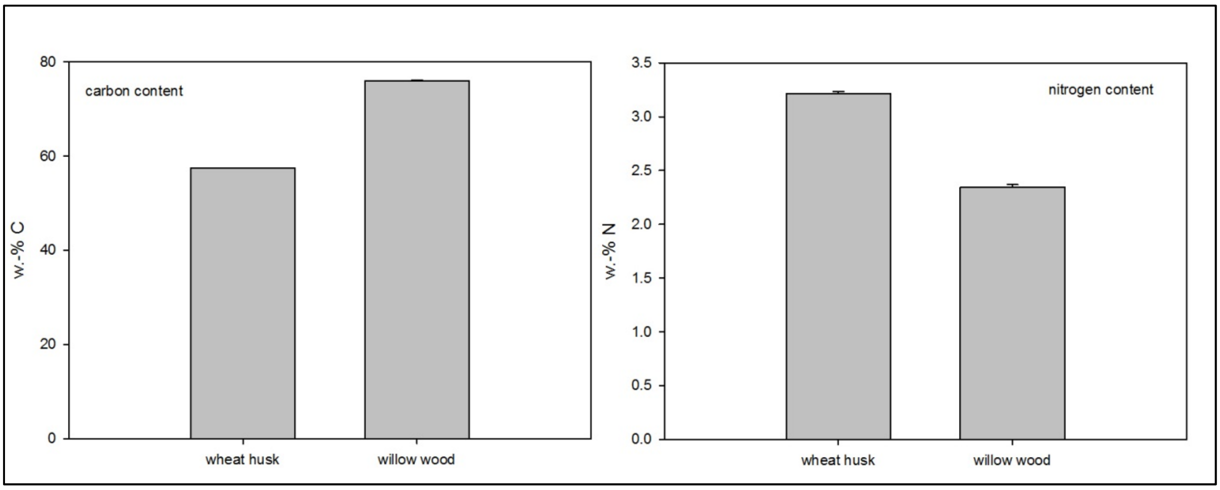

Figure 21 C and N content of wheat husk and willow wood derived biochar (525°C pyrolysis temperature; n=3).

The graph shows that the C content of willow wood is considerably higher (76 %) than the C content of wheat husks (58 %). On the other hand, the N content of wheat husk was higher than that of willow wood. Table 4 shows the ash content and specific surface area of the investigated BCs. The highest ash content was found in the wheat husk BC. Specific surface area was generally low in all BCs.

Table 4 Ash content and specific surface area of the investigated biochars (n=3).

Biochar		ash content (w.-%)	BET-N_2 SA ($m^2 g^{-1}$)
willow wood	400°C	7.1	1.68 ± 0.0
	525°C	8.7	4.49 ± 0.4
wheat husk	525°C	20.7	1.87 ± 0.1

FTIR spectra of the ^{13}C labeled BCs used in the incubation experiment are displayed in Figure 22.

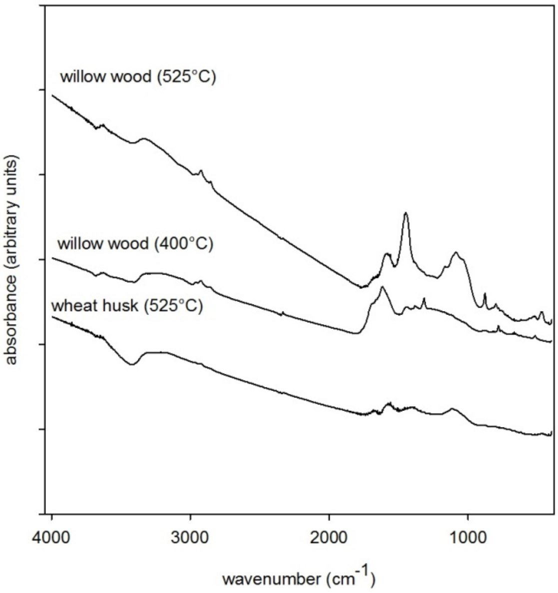

Figure 22 FTIR spectra of the 13C labeled biochar used for the incubation experiment. Respective pyrolysis temperatures are given in brackets.

FTIR spectra of the original BCs hardly showed a peak of the bands assigned to O-H stretching vibration as well as the aliphatic C-H stretch vibration, which shows a decrease in hydrogen-containing functional groups occurred during pyrolysis of the chars (Stuart et al., 2004; Tatzber et al., 2007; Schnitzer et al., 2007; Sarmah et al., 2010). Wheat husks (HTT 525°C) showed hardly any notable bands, whereas willow wood (HTT 400°C and 525°C, respectively) showed several bands within the oxygen-containing functional groups (1800-1100 cm^{-1}; Ibarra et al., 1996) at which the latter feedstock showed a more distinct formation of functional groups at higher pyrolysis temperature, especially the band assigned to aliphatic CH_2 units (1446 cm^{-1}). In addition, willow woods showed bands in the range of 875- 720 cm^{-1} that may be contributed to aromatic C-H out of plane vibrations (Ibarra 1996; Lee, 2010) or to carbonate.

Results of the ^{13}C analyses (prelim. tests after 6 months of incubation)

On the basis of the measured δ ^{13}C values, the relative amount of pyrogenic C (BC.C) of the total organic C was calculated using the following equation:

$$\left[\frac{(\delta sample) - (\delta controlsoil)}{(\delta BC) - (\delta controlsoil)}\right] * 100 = BC.C\ (\%\ of\ Corg) \qquad (1)$$

In order to determine whether a considerable BC decomposition already occurred after 6 months, BC.C of the non-incubated and 6 months incubated Planosol soil samples was calculated. The effect of different BC types within a 6 months incubation period on the relative amount of pyrogenic C is displayed in Figure 23.

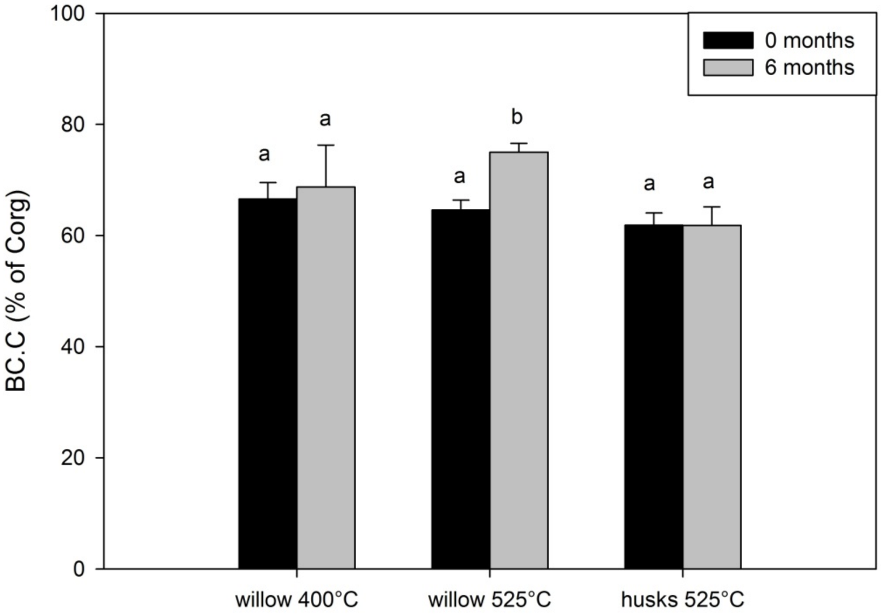

Figure 23 Effect of different biochars and pyrolysis temperatures on relative amount of pyrogenic C of the total organic C in the Planosol (n=3). Incubation temperature was 20°C, incubation time: 6 months. Different letters indicate significant differences at p < 0.05. Temperature addition next to the feedstock refer to the pyrolysis temperature.

Figure 23 suggests that BC did not decompose over the 6 months of incubation (the organic C contents of the samples did not decrease measurably; data not shown). BC.C even significantly increased for willow 525°C, which indicates a positive priming effect (Zimmerman et al., 2011). This means that an increased decomposition of soil organic matter (SOM) occurred in the soil, which then caused a relative increase of the BC.C. This effect was not found for willow 400°C, although lower pyrolysis temperatures tend to be accompanied by a higher amount of volatile compounds. Also, husks pyrolyzed at 525°C were not affected either. The effect of incubation temperature on BC.C is given in Figure 24.

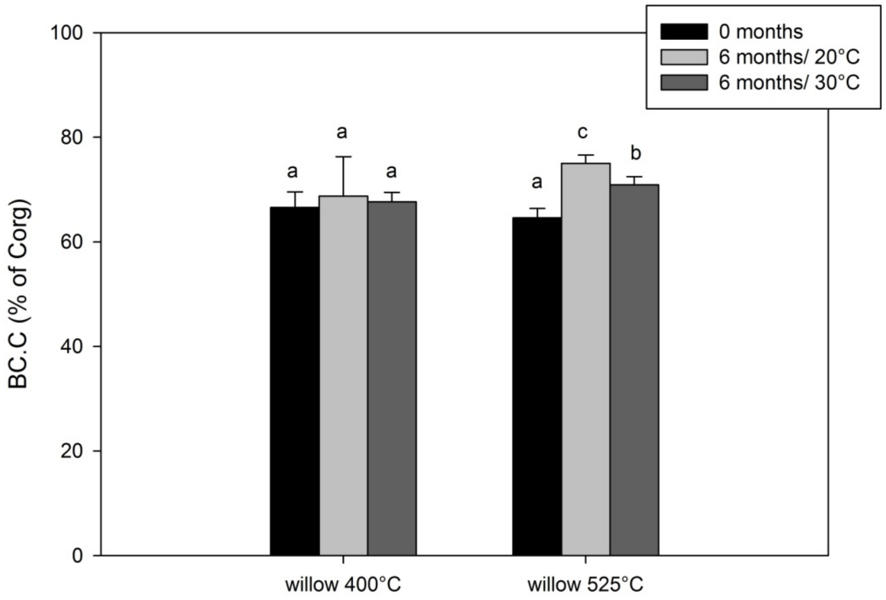

Figure 24 Effect of incubation temperature on relative amount of pyrogenic C for willow-derived BC (n=3) in the Planosol. Incubation time: 6 months. Different letters indicate significant differences at $p < 0.05$.

Figure 24 shows that the incubation temperature had no influence on BC.C of willow 400°C within 6 months. Willow 525°C, however, showed that a positive priming effect occurred at both 20°C and 30°C incubation temperature. A stronger priming effect was found at an incubation temperature of 20°C, unlike expected. Microbial activity could have been inhibited at 30°C compared to 20°C, which may have caused a lower decomposition rate of the SOM.

1.1.2. Results of the ^{13}C analyses (after 24 months of incubation)

Here we present the results in form of the $\delta\ ^{13}$C values for the samples taken at 0, 6 and 24 months. Samples from the other sampling dates, as compiled in Table 3, were not analyzed for their ^{13}C labeling, because the results presented in 0 showed no decomposition of the BC after 6 months. For better comparison, the δ^{13}C values of the pure BCs are given in Table 5.

Table 5 $\delta\ ^{13}$C values of the ^{13}C labeled biochars (n=3). Values represent means. Standard deviations are given in parentheses.

Biochar	δ13C values
Willow 400°C	-37.98 (0.01)
Willow 525°C	-37.56 (0.07)
wheat husk 525°C	-40.37 (0.04)

The effect of different BC types on the δ^{13}C values within a 24 months incubation period in the Planosol is displayed in Figure 25.

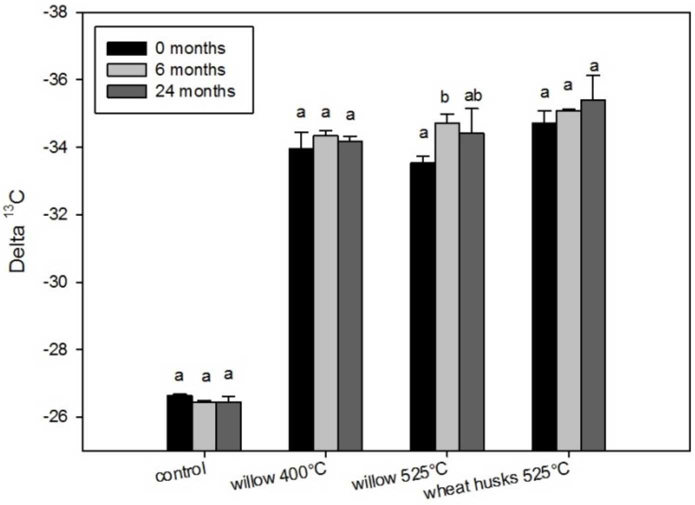

Figure 25 ^{13}C isotopic labeling of soil-biochar mixtures (3 w.-% biochar addition) sampled 0, 6 and 24 months after start of the incubation experiment (Planosol). Different letters indicate significant differences within one treatment. Numbers behind the treatment indicate the pyrolysis temperature (n=3).

The results show that the δ^{13}C value of the control (Planosol without BC) remained stable. No changes in δ^{13}C were found for the Planosol treated with willow 400°C and wheat husks 525°C, respectively. Willow 525°C, however, showed a significant shift of the δ^{13}C value towards the BC (Table 5) after 6 months incubation time. This confirms a positive priming effect, which was already found in preliminary results (Figure 23).

The effect of different BC types on the δ^{13}C values within a 24 months incubation period in the Chernozem is shown in Figure 26. Corresponding to the findings in the Planosol, the Chernozem control soil showed no change in the δ^{13}C value. In addition, the different BC treatments did not change in their ^{13}C signature within 24 months incubation time including willow 525°C, which caused a priming effect in the Planosol (Figure 25).

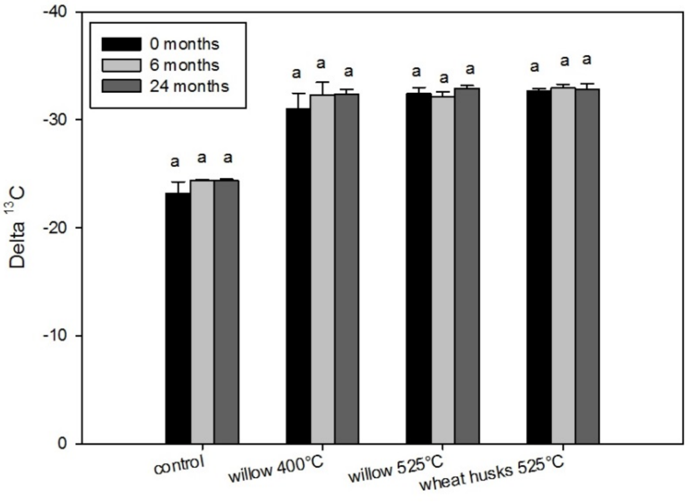

Figure 26 ^{13}C isotopic labeling of soil-biochar mixtures (3 w.-% biochar addition) sampled 0, 6 and 24 months after start of the incubation experiment (Chernozem). Different letters indicate significant differences within one treatment. Numbers behind the treatment indicate the pyrolysis temperature (n=3).

The fact that a priming effect in the Planosol occurred after willow 525°C BC addition but no effect was found in the Chernozem for the same BC treatment may be due to the different pH of the two soil types. The original pH of the Planosol was 5.4, whereas the Chernozem had a soil pH of 7.4. Since pH of the Chernozem was already in the alkaline range, we presume that pH did not significantly change after BC addition, whereas previous studies (WP5, Kloss et al., 2013, in review) showed that BC application to the more acidic Planosol caused a considerable liming effect. This, in turn, is likely to affect microbial activity and composition, which is responsible for BC and SOM degradation.

The effect of incubation temperature (20°C and 30°C) on the $\delta^{13}C$ values of the Planosol treatments is displayed in Figure 27.

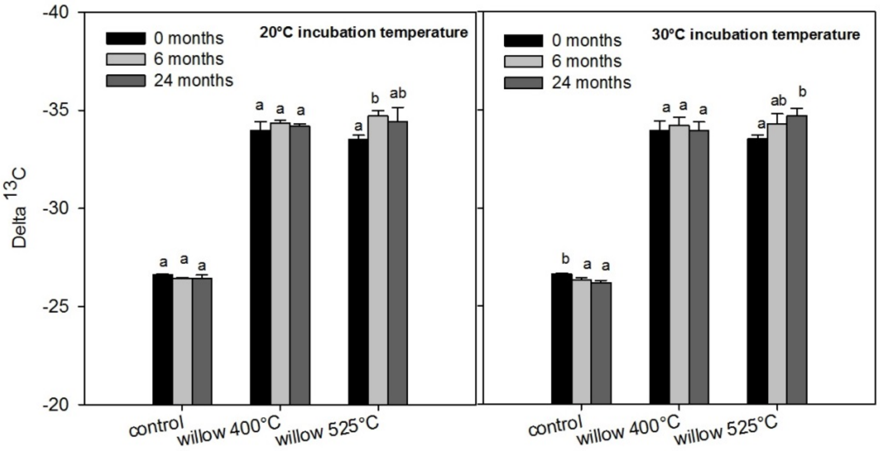

Figure 27 Effect of incubation temperature on ^{13}C isotopic labeling of soil-biochar mixtures (3 w.-% biochar addition) sampled 0, 6 and 24 months after start of the incubation experiment (Planosol). Different letters indicate significant differences within one treatment ($p < 0.05$). Numbers behind the treatment indicate the pyrolysis temperature.

Figure 27 shows that an incubation temperature of 20°C caused no alteration of the $\delta^{13}C$ values of the control and willow 400°C BC treated soil. However, a priming effect was found for willow 525°C as is was described above. The same effect (in direction and magnitude) was found for willow 525°C at an incubation temperature of 30°C.

Figure 28 shows the effect of the incubation temperature (20°C and 30°C) on the Chernozem treatments.

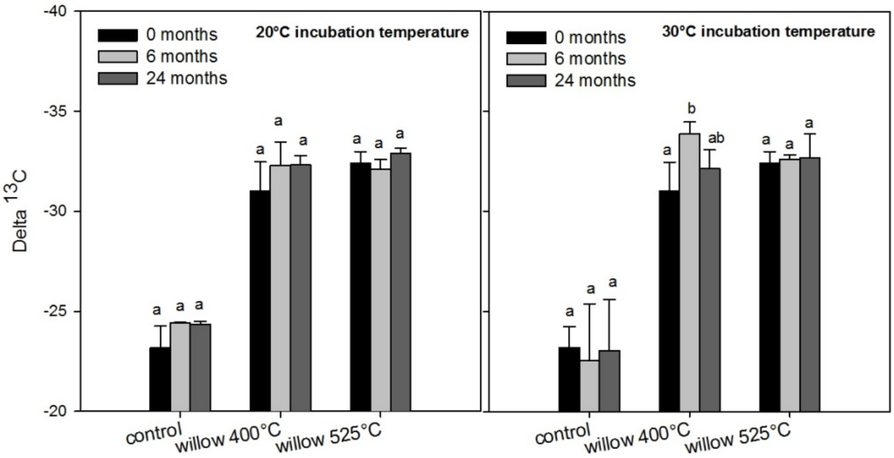

Figure 28 Effect of incubation temperature on ^{13}C isotopic labeling of soil-biochar mixtures (3 w.-% biochar addition) sampled 0, 6 and 24 months after start of the incubation experiment (Chernozem). Different letters indicate significant differences within one treatment ($p < 0.05$). Numbers behind the treatment indicate the pyrolysis temperature.

At an incubation temperature of 20°C, no effect on the $\delta^{13}C$ values was found. However, at an incubation temperature of 30°C, willow 400°C caused a significant priming effect in the Chernozem within 6 months.

Conclusions after 24 Months of Incubation

Facing global change and a modification of the carbon cycle, it is important to know how stable BCs are if added to different soils and how different soils react on BC addition, especially in view of positive priming effects, which induce an accelerated decomposition of SOM. Depending on the type of BC and specific soil characteristics, BC addition to the soil may not only potentially sequester C as intended, but also act as a C source (Zimmerman et al., 2011). Considering the results we obtained within our long-term incubation experiment until now, we saw that BC was remarkably stable in two contrasting soils and at two different incubation temperatures. We often found no effect of BC application on SOM or a slight positive priming effect, which means mineralization rates have changed after BC addition in a way that non-BC derived C was released into the atmosphere. To what extent BC acts as priming substance depends on the labile C fraction that is included in the BC. Further research beyond 24 months of incubation is needed to confirm the observed BC stability and to specify the involved priming mechanisms.

Milestones and Deliverables

M3-1 and M3-2 were completed. Based on the obtained results (no BC decomposition within the 2-year observation period; s. above), M3-3 (carbon pool modeling) could not be pursued, i.e. we could not model BC decomposition because no decomposition occurred. For D3-1 to D3-3, instead of decomposition curves, rate constants and temperature sensitivities (as originally foreseen), we have obtained experimental proof that BCs are very stable in contrasting temperate soils (acidic and calcareous) regardless of incubation temperature, and that BC application might trigger positive priming of SOM decomposition (s. above). As for changes in molecular properties, we applied FTIR spectroscopy on pure fresh and soil-aged BCs (s. WP5) and found that despite the limited decomposition, the structure of BC considerably changes in the soil over time. This opens up new research questions to be tackled (e.g. how do these aging effects change priming, nutrient retention or heavy metal sorption). The results obtained within this project will therefore be the starting point for new projects in the future. We are already planning to use the incubated samples of this project for further analyses in the future.

In WP4, we also conducted a ^{13}C labeled incubation experiment following the ^{13}C label into microbial PLFAs. Similarly to the results of WP3, we did not find significant BC decomposition; however, we were able to trace the ^{13}C label into certain microbial PLFAs and use this to estimate the mean residence time of BCs in the studied soils. These estimates were in the range of millennia (s. WP4 and associated submitted manuscripts). As for WP3, since after 2 years of incubation, we still did not find any BC decomposition, we decided to extend the incubation experiment to 5 years instead of two, as originally foreseen. The output of WP3 will be an extended peer-reviewed publication over a 5 year incubation period, including a thorough account on priming mechanisms and how they can be related to BC aging in the soil. This will add valuable (because based on longer-term observations) knowledge to the current understanding on BC stability and priming effects.

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2.4 WP 4: Response of the soil microorganisms to biochar application

WP leader: Andrea Watzinger, AIT Austrian Institute of Technology, Tulln

Work package content:

Study of the soil microbial community after biochar application and biochar degradation

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Soil microbial communities respond to the application of biochar, but this response is small in comparison to other environmental factors (e.g. soil type and sampling date, addition plant residues…) and not uniform. The variability of the microbial data increased with increasing complexity of the system (incubation < small scale pot < large scale pot). Generally, microorganisms in the sandy low pH Planosol were affected positively especially in the first 100 days after biochar application. In the good agricultural soil, microbial growth was mostly diminished by biochar amendment, especially in the long term. Stable isotopic methods confirmed that degradation of biochar is insignificant, and microorganisms are only feeding at very little extend on biochar. Consequently, the observed shifts of the soil microbial communities were mainly driven by alteration of the environmental conditions (physical and chemical soil properties) i.e. secondary effects.

Field experiment

Material and Method

Soil samples at a depth of 0-15 cm for microbial community analysis were taken from the field experiments of Kaindorf and Traismauer (for the experimental design see WP2). Kaindorf was sampled in June 2012, when the wheat was nearly full grown. In Traismauer the cultivation in 2011 was barley and in the PLFA sampling year 2012 sunflower; at the sampling day (May 2012) the sunflower was in the juvenile growing phase.

Microorganisms were investigated using phospholipid fatty acids (PLFAs) analyses. PLFAs extracted from soils samples according to the procedure of Bligh and Dyer (1959) as described by Frostegård et al. (1996). Briefly, 2 g of fresh soil were extracted in test tubes containing a mixture of chloroform/methanol/citrate buffer (pH 4.0) (1/2/0.8) at room temperature over night. Extraction was performed twice. Crude extracts of lipids were collected after phase partitioning by adding chloroform and deionized water and dried under a gentle stream of N2. Total lipids were resolved in chloroform and separated into different lipid classes using solid phase extraction columns containing 500 mg of silica. Neutral lipids, glycolipids and phospholipids were obtained by sequential elution using aliquots of chloroform, acetone and methanol, respectively. Ester-linked PLFAs were subjected to a mild alkaline transmethylation to produce fatty acid methyl esters (FAMEs), which were analyzed on an Agilent 7890A GC equipped with a flame ionization detector (FID). Analytical separation of the FAMEs was accomplished in split mode using a 60 m x 0.25 mm x 0.25 µm internal diameter HP 5-MS fused-silica capillary column ((5%-Phenyl)-methylpolysiloxane). The carrier gas was helium (1.5 ml min-1,) and the column temperature was held at 70 °C for 2 min and subsequently ramped from 70 to 160 °C at 15 °C min-1, then to 280 °C at 2.5 °C min-1. The injector temperature was held at 240 °C, the FID temperature at 320 °C. Individual compounds were identified from their relative retention time by comparison with commercially available individual FAMEs and bacterial FAME standards. Concentrations of individual compounds were obtained based on the GC response relative to that of the internal standard 19:0 fatty acid methyl ester.

Fatty acids were designated by their total number of carbon atoms:number of double bonds (i.e., a 16-carbon alkanoic acid is designated as 16:0). The position of the double bond within unsaturated fatty acids is indicated with a number closest to the aliphatic methyl end of the fatty acid molecule with the geometry of either c (cis) or t (trans). The terminal methyl-branching is indicated with i (iso) or a (anteiso). The prefix 10Me indicates a methyl group on the 10th carbon atom from the carboxyl end of the molecule, and cy refers to cyclopropane fatty acids. The sum of the saturated fatty acids i15:0, a15:0, 15:0, i16:0, i17:0, a17:0 and 17:0 are assumed to represent Gram positive bacteria. The PLFA 18:2ω6,9 is a fungal marker fatty acid. (Frostegård et al., 1993).

All analytical results were calculated on the basis of oven-dry (105°C) weight of soil. Statistical evaluation was performed with SPSS 13.0 for Windows. A one-factor ANOVA was used to analyze the effect of the biochar on individual PLFAs. Significance was accepted at p<0.05. Discriminant analysis was used to render visible shifts of those microbial communities that do not differ significantly based on the amount of single PLFAs.

Results

The different treatments, including various amounts of biochar and nitrogen fertilization, did not differ significantly in their PLFA values (Figure 29). Only the location (climate, soil, cultivation) made a significant difference. The amounts of individual PLFAs from Kaindorf were higher than those from Traismauer, except the PLFA for fungi.

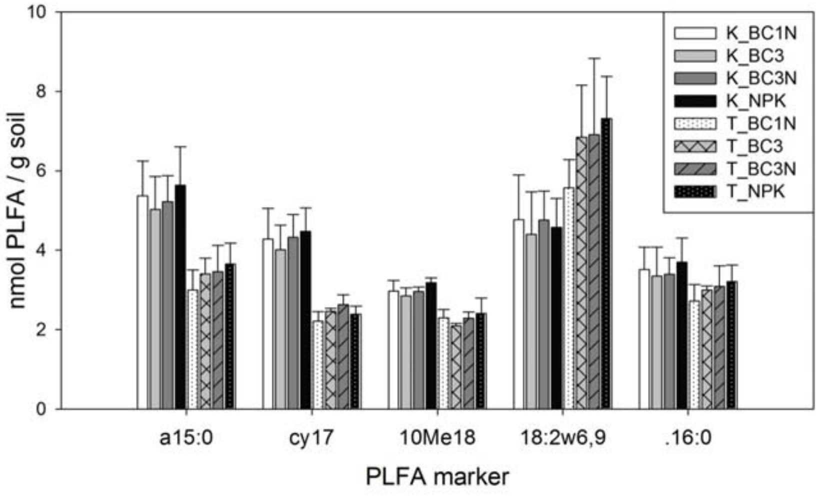

Figure 29: Means and standard deviation of individual PLFAs from the field experiments at the locations Kaindorf (K) and Traismauer (T); n = 5.

The field experiment showed no significant trends of individual PLFAs, but a clear separation of groups was evident in the discriminant analysis (Figure 30). Discriminant analysis clearly separated the treatments 3 w/w% biochar and nitrogen fertilizer (BC3N), 1 w/w% biochar and nitrogen fertilizer (BC1N), NPK fertilizer (NPK) and the treatment of only 3 w/w% biochar without fertilizer (BC3) in Kaindorf. In Traismauer the different biochar concentrations BC3N and BC1N were grouped together, while BC3 and NPK were clearly separated. The separation from soils from the field experiment (function 1) was caused by PLFAs (16:1ω5, i17:0, 17:0), whereas the separation of treatments (function 2) was additionally caused by Gram positive PLFAs (i16:0, i17:0, a15:0).

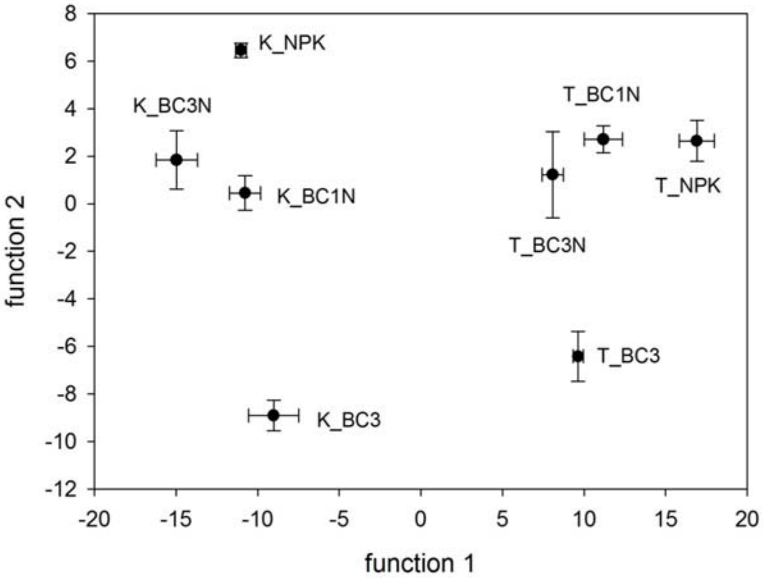

Figure 30: Discriminant function with grouping of various biochars and fertilization treatments from the field experiment. Error bars indicate standard deviation.

Pot experiment – comparison of various biochars

Material and Method

Soil samples for microbial investigations have been taken from the large scale pot experiment (WP 2) at a depth of 20-15 cm using a soil auger. Samples were frozen at -20°C until extraction. So far, samples were collected on the day of the first irrigation (start of experiment; 23.11.2010) and then after 2, 5, 10, (before fertilization; 3.12.2010), 51 (after fertilization; 13.01.2011) and 86 (after harvest; 17.02.2011) days. Two more samples were taken during grain maturation of barley (170 days, 12.5.2011) and during vegetative clover development at a height of 30 cm (297 days, 16.09.2011) (Figure 31).

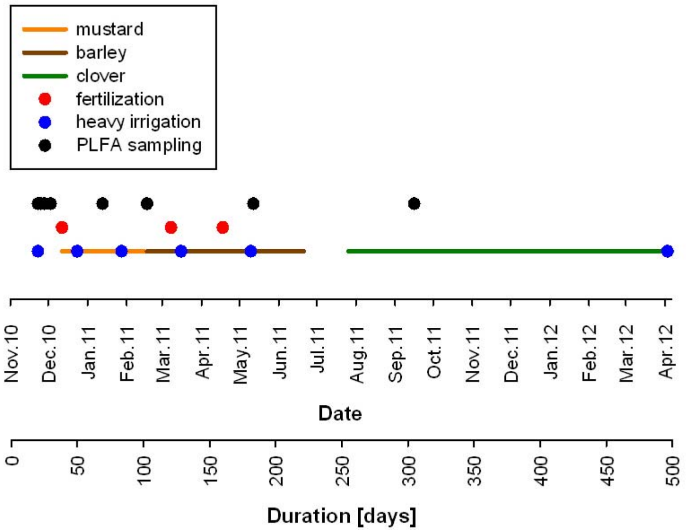

Figure 31: Schematic timeline of the pot experiment; Vegetation cover and events of sampling, fertilization and heavy irrigation are indicated.

Microorganisms were investigated as described above using phospholipid fatty acids (PLFAs) analyses.

Calculation of results and statistical evaluation was performed as described above; except a univariate analysis of variance (ANOVA) was used for the greenhouse experiment. This analysis was selected because there were more treatments for Eschenau (seven) than for Traismauern and Kaindorf (two treatments each), and normal variance analysis, which is cross calculated, was therefore not possible. Accordingly, the soil was treated as a treatment itself, yielding eleven different treatments; these were tested for significant differences of individual PLFAs. Finally, a correlation was done separately for each soil with biochar and without biochar. We calculated the mean amount from each treatment and analyzed individual PLFAs with the factors of soil characteristics (N-content, C-content, C/N ratio, water content), leachate composition (pH-value, DOC, ammonium, nitrate, electron conductivity) and plant performance (weight of dried plant material) with the Spearman correlation (=S.c.). The PLFAs considered were: i14:0, 14:0, i15:0, a15:0, 15:0, i16:0, 16:1ω7c, 16:1ω6c, 16:1ω5c, 16:0, 10Me16:0, i17:0, a17:0, 17:1ω8c, cy17:0, 17:0, 10Me17:0, 18:2ω6.9, 18:1ω9c, 18:1ω7/9c, 18:0, 10Me18:0, 12Me18:0, cy19:0, 19:1.

1.1.3. Results

The temporal development of PLFA sums, which can be taken as an indicator for microbial biomass, is shown in Figure 32. The first ten days included 4 sampling days (23.11., 25.11., 28.11. and 3.12.2010). In this initial phase, the microbial community showed high sums but chaotic trends. After the fourth sampling date, the sampling intervals were extended to one month or more. The microbial community in Eschenau soil showed an increasing trend until day 86 (17.02.2012); the Eschenau soil amended with vineyard pruning pyrolised at 400°C showed an increase until day 170 (12.05.2011). The following 6 months were characterized by a stabilizing process with a slight decrease. The PLFA sums of the soils from Kaindorf and Traismauer developed similarly, but with different sum levels. In both soils, the PLFA sums of treatments with biochar were slightly lower compared to the controls.

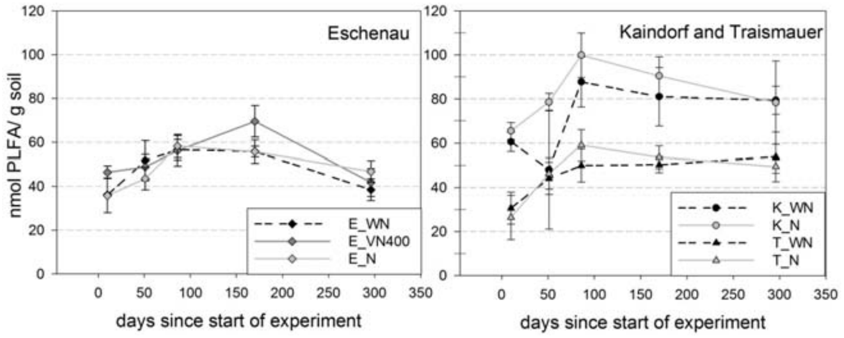

Figure 32: *PLFA sums of different treatments with the soil of Eschenau (left) and Kaindorf and Traimauer (right). Error bars indicate standard deviation; n = 5; E = Eschenau soil, T = Traismauer soil, W = wood biochar, V400 = wineyard pruning biochar pyrolized at 400°C, N = nitrogen fertilizers.*

We focused on individual PLFAs but also investigated five microbial groups: Gram positive bacteria, actinomycetes, Gram negative bacteria, fungal and unspecific PLFAs. In Figure 33, we selected one representative fatty acid for each soil microbial group. The Gram positive bacterial PLFA a15:0 and the Gram negative bacterial PLFA cy17:0 remained on a similar level as at the beginning of the experiment. The actinomycete PLFA 10Me18:0 showed, on days 170 and 297, an increase compared to the PLFA amount on days 10 and 51. The saprophytic fungi biomarker PLFA 18:2ω6,9 decreased over time. Unspecified PLFAs (i.e. 16:0) decreased by more than half until day 170 and did not rise again until the end of the experiment. The PLFA analysis showed only few significant trends. Many PLFAs showed a significant difference between the three soils (Eschenau, Kaindorf, Traismauer), but only the treatment with vineyard pruning biochar pyrolised at 400°C from Eschenau soil showed a significant increase compared to the control and the other biochar treatments of Eschenau (Figure 32 and Figure 33). In this treatment, the PLFAs for actinomycetes (10Me17:0), Gram positive bacteria (i16:0), Gram negative bacteria (cy17:0, 17:1ω8, cy19:0), fungi (16:1ω5c, 18:1ω9c, 18:2ω6,9) and unspecific organisms (18:0, 15:0, 16:0, 17:0, 16:1ω6c) increased on several sampling days. The other biochar treatments from Eschenau were not significantly different from their control. Additionally, there were no significant differences in individual PLFAs between biochar and the control soil from Traismauer and Kaindorf. Generally, PLFA concentrations of Kaindorf were highest and those of Traismauer lowest.

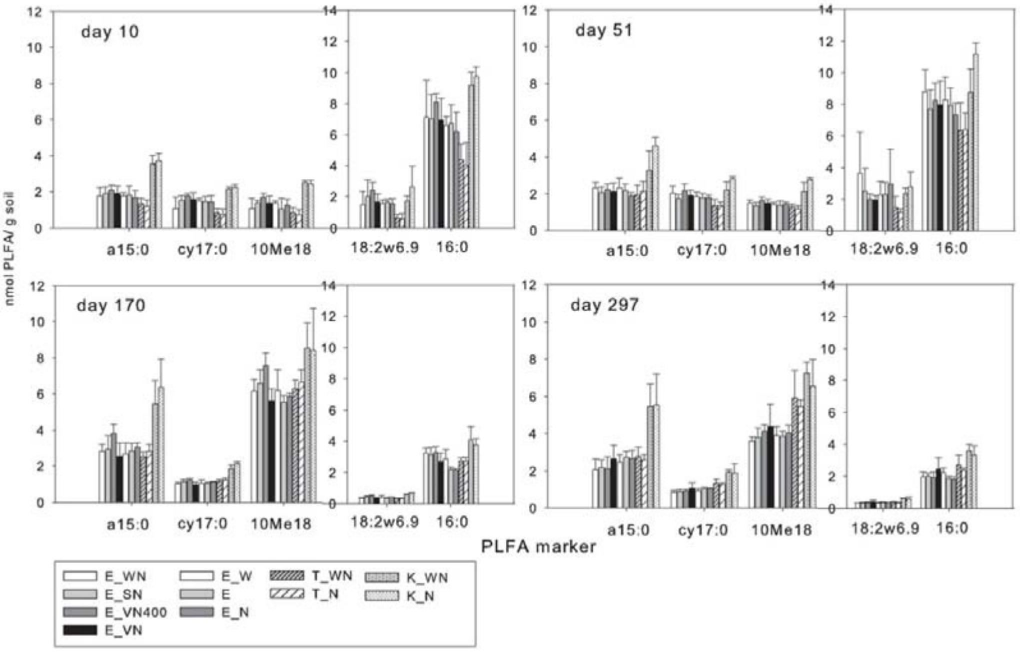

Figure 33: Five PLFAs (a15:0, cy17:0, 10Me18:0, 18:2ω6.9 and 16:0) of the treatments on four different sampling days. Error bars indicate standard deviations; n = 5; E = Eschenau soil, T = Traismauer soil, W = wood biochar, S = straw biochar, V = wineyard pruning biochar, V400 = wineyard pruning biochar pyrolized at 400°C, N = nitrogen fertilizers.

For discriminant analysis we selected four sampling days. This provided insights into the shifts in the microbial community and into potential dominant drivers (specific PLFAs or organism groups) of these shifts. The discriminant analysis of the greenhouse experiment showed a significant grouping of the treatments. The treatments from Eschenau showed a separation between groups of treatments with biochar and those without; especially the above-mentioned biochar treatment E_VN400 showed a large separation (Figure 34). The treatments from Kaindorf and Traismauer also showed a separation between the treatment with and without biochar (Figure 35). Kaindorf showed a greater separation between the treatment groups than Traismauer. This group separation from Kaindorf and Traismauer was similar to the group separation from the field experiment (Figure 30). Basically, the highest influence on the grouping of treatments was shown by PLFAs that belong to the group of Gram positive bacteria and many unspecific PLFAs. In the greenhouse experiment, additionally the PLFAs for actinomycetes (10Me16:0) and Gram negative bacteria (16:1ω7c) influenced the grouping. Nonetheless, the results showed no specific PLFAs or organism group which operated as a dominate driver for shifts. Accordingly, the separation is apparently not driven by any microbial group or a single PLFAs.

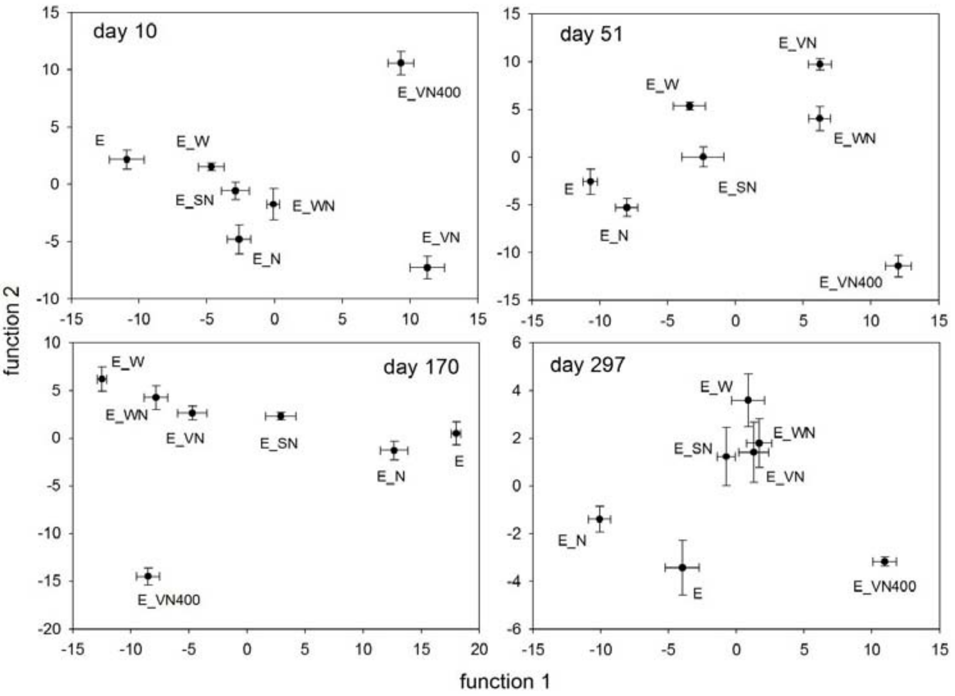

Figure 34: Discriminant functions with grouping of various biochar and fertilization treatments for Eschenau. Error bars indicate standard deviation. E = Eschenau soil, T = Traismauer soil, W = wood biochar, S = straw biochar, V = wineyard pruning biochar, V400 = wineyard pruning biochar pyrolized at 400°C, N = nitrogen fertilizers.

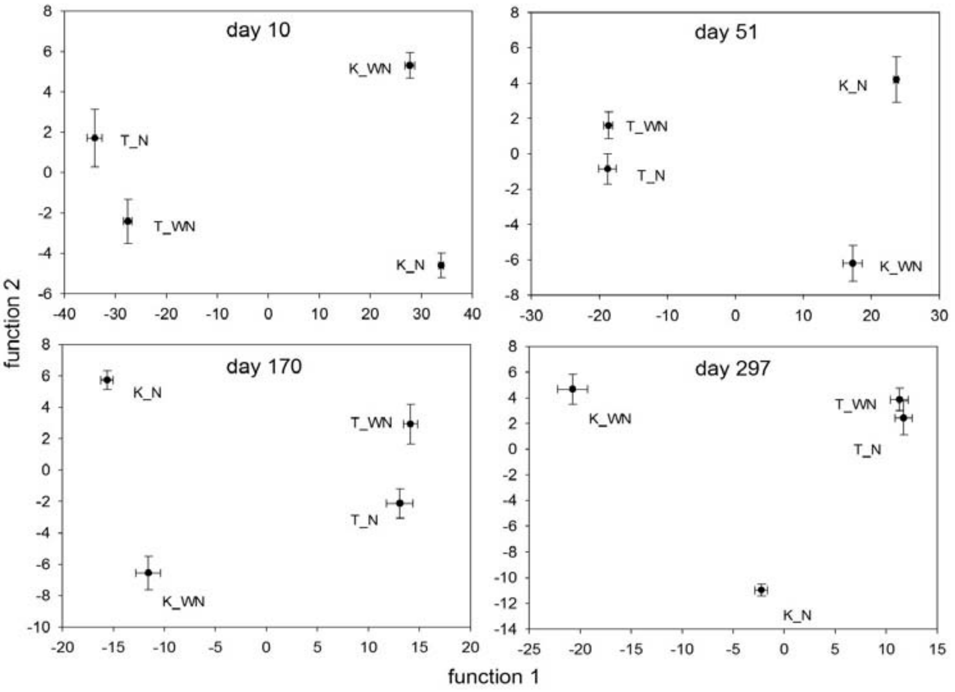

Figure 35: Discriminant functions with grouping of biochar treatment for Kaindorf and Traismauer. Error bars indicate standard deviation. E = Eschenau soil, T = Traismauer soil, W = wood biochar, S = straw biochar, V = wineyard pruning biochar, V400 = wineyard pruning biochar pyrolized at 400°C, N = nitrogen fertilizers.

The correlation analysis from the greenhouse experiment showed many significant correlations between PLFAs and soil properties, seepage water characterization and plant biomass. The C/N ratio in the soil increased after adding biochar (Table 6). Between day 51 and 170 the C/N ratio from Eschenau biochar treatments increased to values between 33 and 37. The C/N ratio from the Kaindorf and Traismauer treatments with biochar increased to over 20. The C and N contents were also the only parameters determined for the soil samples which were used for PLFA analysis. All other parameters were reported from different samples and time points (Kloss et al. 2013 unpublished, Brücker 2012). We found many correlations between PLFAs and the soil C/N ratio; note, however, that the PLFAs reacted differently to the analyzed factors, depending on soil type. In Kaindorf many PLFAs correlated negatively with the C/N ratio, but the opposite trend occurred in the Traismauer treatments: many PLFAs correlated positively with the C/N ratio. PLFAs from Eschenau correlated positively and negatively with the C/N ratio. Many positive correlations between pH-value and PLFAs were found in treatment T_N and Eschenau treatments with biochar. The other factors (sulphate, chloride, nitrate, DOC, EC) correlated with diverse PLFAs, but no general pattern was evident. The Eschenau treatments without biochar showed a strong positive correlation with all PLFAs and with the growth of mustard, barley and clover. In the treatment with biochar, only the first crop (mustard) correlated with many PLFAs from different microbial groups.

Table 6: Mean and standard deviation of C_{org} and N_{tot} in the soil on four selected days during the greenhouse experiment; n=5.

	Day 2		Day 51		Day 170		Day 297	
	C_{org}	N_{tot}	C_{org}	N_{tot}	C_{org}	N_{tot}	C_{org}	N_{tot}
E_WN	2.8±0.6	0.14±0.01	3.1±0.3	0.20±0.04	2.8±0.4	0.08±0.03	2.8±0.4	0.1±10.01
E_SN	2.6 ± 0.2	0.15±0.01	2.9±0.3	0.18±0.02	2.8±0.5	0.08±0.01	2.6±0.4	0.09±0.01
E_RN400	3.3±0.4	0.17±0.01	3.2±0.3	0.20±0.02	3.2±0.3	0.09±0.01	3.1±0.2	0.11±0.01
E_RN	3.1±0.5	0.16±0.01	3.4±0.2	0.17±0.00	3.5±0.2	0.09±0.00	3.5±0.2	0.11±0.00
E_W	2.5±0.1	0.15±0.01	3.1±0.8	0.16±0.00	3.0±0.3	0.08±0.01	2.8±0.4	0.10±0.01
E	1.1±0.1	0.14±0.01	1.1±0.1	0.14±0.00	1.1±0.1	0.05±0.01	1.4±0.9	0.08±0.01
E_N	1.0±0.1	0.13±0.00	1.1±0.2	0.13±0.00	1.0±0.3	0.07±0.00	0.9±0.2	0.09±0.02
K_WN	3.6±0.1	0.25±0.00	4.3±0.1	0.27±0.01	4.4±0.1	0.21±0.02	4.3±0.0	0.25±0.00
K_N	2.4±1.5	0.25±0.06	2.4±0.7	0.25±0.05	2.3±0.4	0.22±0.01	2.0±0.3	0.19±0.01
T_WN	5.2±0.3	0.20±0.00	5.3±0.5	0.21±0.02	5.2±0.2	0.13±0.00	5.0±0.1	0.17±0.00
T_N	3.5±0.2	0.18±0.01	3.5±0.1	0.17±0.01	3.5±0.1	0.13±0.01	3.3±0.4	0.12±0.05

E= Eschenau; T=Traismauer; K=Kaindorf; WN= wood biochar with nitrogen; SN= straw biochar with nitrogen; RN400= vineyard pruning biochar with pyrolysis temperature 400°C with nitrogen; RN= vineyard pruning biochar with nitrogen; W= wood biochar without nitrogen; E= without biochar without nitrogen; N= without biochar with nitrogen; Corg = soil organic carbon content, Ntot = total nitrogen content.

Discussion

This study investigated possible effects of biochar on microbial communities. It was designed to identify (1) the influence of biochar on the soil microbial communities, (2) the differences in the biochar effects caused by different application rates in soil, different pyrolysis temperature and feedstock of biochar, (3) the biological or physical factors causing shifts within the communities and (4) the difference between short- and medium-term effects on microorganisms.

Effects of biochar on the soil microbial biomass and community structure

PLFA analysis of the greenhouse experiment showed little significant evidence for a positive effect of biochar on microbial biomass. The analysis of the field experiment showed no significant difference of PLFA amounts between the treatments. The absence of effects of wood biochar on soil microorganisms had already been documented by Castaldi et al. (2011). Like Quilliam et al. (2012), we found that biochar amendment in nutrient-rich soils gave only transient or recurrent rather than significant advantages; we also found no significant negative effect of biochar amendment on total microbial biomass in temperate soils. Nevertheless, our discriminant analysis of the greenhouse and field experiments separated the treatments into groups and visualized shifts in the microbial community. This rendered visible changes in microbial community structure that could not be detected by comparing single PLFAs or the total microbial community. If microbially available carbon sources (e.g. plant residues, vegetable oil, …) are added to the soil, then soil microorganisms tended to react by increasing their biomass (Stemmer et al. 2007, Mellendorf et al. 2010). As we generally did not observe such an increase, we hypothesize that changes in microbial communities were largely caused by altered soil characteristics, as already proposed by, Mašek et al. (2011) and Lehmann et al. (2011). The behavior of the PLFA pattern also supports findings of O´Neil et al. (2009) and Anderson et al. (2011) that the biomass shifts apparently occurred on the level of single families, genera and species, and not on total microbial biomass.

Linking soil microbial community changes to the soil properties in the greenhouse experiment

Biochar-induced changes in the C/N ratio, water holding capacity, pH-value and nutrient availability affected the soil fertility and the microbial community (Mao et al. 2012, Pietikäinen et al. 2000, Liang et al. 2010, Kolb et al. 2009). Soil samples from the greenhouse experiment were collected and analyzed at the start of the experiment and after seven months (Kloss et al. 2013). Adding biochar to the soil increased the pH-value, EC, CEC, C/N ratio and Corg in the soil of the greenhouse experiment. During the first seven months, the EC of the soil treated with biochar decreased while CEC increased. The C/N ratio increased after 51 and 170 days. We ascribe the observed increase to the absence of fertilization, which was omitted as a preparative management for the cultivation of clover. The reaction of PLFAs to the tested factors differed from soil to soil, and the correlations from the treatments with biochar differed from those without biochar. This supports a mainly indirect and complex effect of biochar on microbial communities, involving manifold effects of biochar on the soil physical and chemical factors rather than a direct interaction such as degradation of biochar by microorganisms as suggested by Mašek et al. (2011) and Lehmann et al. (2011).

Clearly, the addition of biochar influenced the C/N ratio and thus correlated with more PLFAs in the biochar treatments. One explanation for the observed strong correlation is that C/N is the only parameter which was determined on the same samples as the PLFA analysis. Beyond this, it is known that an increasing C/N ratio changes the soil microbial community, e.g. favors fungal growth but limits bacterial abundance (Eiland et al. 2001). Generally, carbon is the main limiting factor for bacterial growth in soil, but only under the condition that all other limiting nutrients are available (Demoling et al. 2007). Demoling et al. (2007) also stated that a low level of a second limiting nutrient and an increasing carbon pool does not promote the growth of bacterial communities. Jindo et al. (2012) found that a high C/N ratio even reduced microbial biomass by inducing N limitation for the decomposition of organic compounds such as hemicelluloses and cellulose. In contrast to this general model, we found increasing microbial biomass with increasing C/N ratio (Traismauer), as well as a positive correlation of the C/N ratio with bacterial versus negative correlation with fungal

PLFAs (Eschenau). This mismatch can be explained by the fact that C/N ratios do not visualize the availability of C or N. Depending on the soil and its nutrient status and dynamics, the processes of adsorption, immobilization, nitrification and mineralization will considerably affect nutrient availability and consequently soil microorganisms (Nelissen et al. 2012, Anderson et al. 2011).

The correlations also showed that in the Planosol (Eschenau) many microorganisms benefited from the higher pH-value. We found an increase of actinomycetes after 5 month of the experiment. This probably partly reflects their sensitivity to low pH-values (Giri et al. 2013). The decrease and low amount of fungal PLFAs could also have been a consequence of higher pH, because fungi normally grow optimally in acidic soils (Aciego Pietry and Brookes, 2009). The pH-value increase in the Cambisol (Kaindorf) and the Chernozem (Traismauer) showed no beneficial effects on microorganisms. In both soils, the pH-value was close to neutral and its increase after biochar application was small, which might explain the lack of response of the soil microorganisms.

A high pyrolysis temperature increases the micro-porosity in biochar and the fraction of finer biochar particles (Abit et al. 2012), and decreases the cation exchange capacity (CEC) of biochar (Lehmann et al. 2011). The process temperature also determines how much char, condensable liquid and gas will ultimately result from the pyrolysis. With increasing pyrolysis temperature the fractions of stable biochar compounds increase; this yields biochars with longer residence times in the soil, but with less labile compounds to encourage metabolism by microorganisms (Mašek et al. 2011, Lehmann et al. 2011). It is possible that the low pyrolysis temperature in treatment E_VN400 produced a larger labile C fraction; this, in turn, might have increased microbial PLFAs while the other investigated biochar treatments showed stagnation or decreasing effects. Nelissen et al. (2012) also reported increased activity of soil microorganisms in biochar pyrolysed at 350°C versus 550°C. They attributed this to the larger labile carbon fraction in the lower-temperature biochar. Our greenhouse experiment provided no proof that they were involved in biochar degradation. One example of increased PLFA was 10Me17:0, actinomycetes PLFA. The individual reproduction of actinomycetes is slow and they prosper in nutrient-limited soil. Actinomycetes can also degrade persistent and complex substrates and tend to build more stable populations within the microbial community (Metting, 1993). Additionally, Rodococcus and Mycobacterium, members of the actinomycetes, are known degraders of aromatic compounds (Johnsen et al. 2002, Ringelberg et al. 2001). Nonetheless, some of the volatile organic compounds can be toxic (e.g. PAHs). Moreover, high salt levels from the labile biochar fraction could decrease microbial biomass (Lehmann et al. 2011, Spokas et al. 2011). Taghizadeh-Toosi et al. (2011) described VOCs from biochar as possible nitrification inhibitors. Kloss et al. (2013 unpublished) and Deenik et al. (2011) found that the detrimental effects of VOCs in biochar-enriched soils were temporary. In our experiment, the stability of the total microbial biomass after biochar amendment confirmed that biochar toxicity played a minor role. Discriminant analysis of the microorganism community, however, did show a decreased effect of biochar with time, which might also be attributed to the loss / leaching of salts and the labile carbon fraction of the biochar.

Linking soil microbial community and plant growth in the greenhouse experiment

The first crop (mustard) of Eschenau showed strong differences between the biochar treatments and the control, but these differences were reduced and insignificant in the second (barley) and third crops (clover) (Kloss et al. 2013 unpublished). This pattern of a decreased effect of biochar with time was also reflected in the discriminant analysis of the microorganism community. Generally, the biochar application decreased the plant biomass of the first two crops (mustard and barley) in all soils. This might be related to shifts in micronutrient availability, toxic effects of VOCs and/or polycyclic aromatic hydrocarbons (PAHs) (Kloss et al. 2013 unpublished). The microbial PLFAs only partly reflected these findings. In the Planosol (Eschenau) without biochar, PLFAs correlated with all three crops, whereas the treatment with biochar correlated only with the mustard crop. One interpretation is that, in the sandy Planosol without biochar, the interaction between plants and microorganisms is closed and has a stronger impact. This direct connection seemed to be decoupled through the biochar amendment.

Effects of biochar onto soil microorganisms in the field

In the field experiment, the C/N ratio increased significantly after biochar addition, while the soil parameters pH-value, EC and CEC were not influenced by this addition in the second vegetation period, when PLFA samples were collected (Karer et al. 2013 unpublished). In Kaindorf, the yield of wheat (dry biomass) fell significantly under BC3 treatment compared with the other three treatments. The yield of sunflower in Traismauer showed a lower difference between the BC3 and the NPK treatment (Karer et al. 2013 unpublished). The microorganism PLFAs showed the same distribution pattern in the discriminant analysis as the crop yield of the corresponding treatments. The disadvantage of treatment BC3 was most likely caused by the increasing C/N ratio without any fertilizer, pointing to the importance of nutrient availability (Anderson et al. 2011, Demoling et al. 2007, Nelissen et al. 2012). The same biochar caused visibly different trends in the two soils, which is clearly linked to the different physical and chemical properties of the soil and/or to a difference in microbial communities. The trends and the separation of the treatments in the field experiment were comparable with those from the greenhouse experiment.

Small scale pot and incubation experiment – use of ^{13}C labeled biochar

Material and Method

Biochar characterisation

Two different feedstocks were selected for biochar production. During growth, wheat *(Triticum aestivum)* and willow *(Salix alba)* were ^{13}C depleted by combusting methane in the glasshouse. Methane combustion is a usual method for CO_2-enrichment in horticultural glasshouse production. Additionally, methane from natural gas is characterized by an isotopic carbon composition of -40 to -60 ‰ (Mango and Elrod, 1999). By burning pure methane with a $\delta^{13}C$ value of -48 ‰ in a C.A.P. CO2 Generator (GEN-1), R & M Supply, USA to keep average CO_2-concentrations in the glasshouse at 650±50 ppm, we generated a significantly ^{13}C-depleted atmosphere and produced ^{13}C depleted plant biomass. CO_2-enrichment was active daily from 9 a.m. to 5 p.m. during 80 % of the growth period of the plants. Leaves and wood from the willow branches as well as wheat husk were chosen for the experiments. The non-pyrolysed material had $\delta^{13}C$ values of -37.3 ± 0.3 ‰ (willow wood), -40.3 ± 1.8 ‰ (willow leaves) and -40.2± 1.3 ‰ (wheat husks), respectively. The feedstocks were pyrolyzed at a maximum temperature of 525°C. The heating rate was 2°C min^{-1} with a dwell time at the maximum temperature of 8 hours. The furnace was flushed continuously with argon before, during and 2h after pyrolysis to provide a low-oxic atmosphere. The physical and chemical characteristics of the biochars are listed in Table 2. Differential scanning calorimetry and Fourier-transform infrared spectroscopy (DSC and FTIR; performed according to methods described in Kloss *et al.*, 2012) showed that pyrolysis led to a loss of labile, aliphatic compounds and cellulosic materials accompanied by an enrichment of more stable, aromatic structures (indicated by DSC peak temperatures of >400°C; Table 7). The FTIR spectra (not shown) of the willow biochars exhibited several distinct bands (especially in the fingerprint region from 1600 to 900 cm-1), whereas the wheat husk biochar barely showed any notable bands; the band at 875 cm^{-1}, which may be assigned to carbonate formation upon pyrolysis (Kloss *et al.*, 2012) was only found for biochars from willow leaves and wood but not from wheat husks.

Table 7: Characterization of the used biochars produced from wheat husk, willow leaves and willow wood.

biochar parameters	wheat husks	willow leaves	willow wood
C [a] / %	57.5	51.6	76.0
N [a] / %	3.2	4.2	2.4
H [a] / %	2.4	2.1	2.8
ash content / g/100g	20.7	24.8.	8.7
sum 16 PAHs [b] / mg kg^{-1}	1.73	0.61	12.7
BET surface [c] / m^2 g^{-1}	1.87	0.99	4.49
exothermic DSC peaks [c] / °C	395, **448**	375, **456**	**426**, 445
$\delta^{13}C$ / ‰	-41.3	-38.3	-37.9

[b] PAH = polycyclic aromatic hydrocarbons (U.S. EPA method 610), [c] BET = Brunauer-Emmett-Teller - N_2 surface area (DIN 66131), [c] DSC = differential scanning calorimetry; temperature of maximum exothermic reaction in bold. [a] Carbon (C), nitrogen (N) and hydrogen (H) content was measured by elemental analysis (EA1108, Carlo Erba Instruments)

The effect of biochar on soil properties such as extractable potassium and phosphorus (ÖNORM L 1087), pH, electric conductivity (ÖNORM L 1092) and the cation exchange capacity (ÖNORM L 1086-1) was determined after mixing of soil and biochar (Table 8).

Table 8: Changes of the chemical soil characteristics in the soil after biochar amendment; + increase and – decrease; E = Planosol, T = Chernozem.

soil parameters	wheat husks biochar		willow biochar [a]	
	E	T	E	T
pH-value (H_2O)	+ 0.8	- 0.1	+ 1.1	+ 0.4
EC [b] / µS cm^{-1}	+ 726	+ 637	+ 407	+ 411
CEC [c] / $mmol_c$ kg^{-1}	+ 49	+ 20	+ 22	+ 12
K [d] / mg kg^{-1}	+ 1523	+ 1446	+ 952	+ 856

P ^{d} / mg kg^{-1}	+ 222	+ 102	+ 84	+ 47

[a] The biochar consisted of 60% willow leaves and 40% wood, [b] EC = electrical conductivity, [c] CEC = cation exchange capacity, [d] extracted by CAL (calcium-acetate-lactate) solution.

Experimental design

An incubation experiment was conducted using 2 mm sieved biochar derived from 13C depleted wheat husks and 2 mm sieved Planosol and Chernozem. After 10 days of pre-incubation of the soil, 96 Erlenmeyer flasks (4 treatments, 4 replicates, 6 sampling dates) were filled with 50 g soil or with 50 g biochar amended soil (3 g biochar 100 g-1 dry soil), respectively. The addition of 3 % (w/w) biochar corresponded to a field application rate of 90 t ha-1, which lies at the upper range of field experiments. This application rate has also been used in the model assumptions of Woolf et al. (2010). The four treatments were Planosol (E), Planosol with biochar (E +BC), Chernozem (T) and Chernozem with biochar (T +BC). Samples were watered to reach 50 % of the water holding capacity and incubated at 20 °C and 95 % relative humidity. Soil samples for phospholipid fatty acid (PLFA) and 13C PLFA analyses were taken after 0, 2, 4, 7, 14, 37 and 100 days and frozen immediately. Furthermore, total nitrogen content (Ntot), total carbon content (Corg) and δ13Corg of the soil samples were determined on day 0, 2, 14, 37 and 100.

For the pot experiment, 1.5 cm of coarse sand (0.5-2 mm) followed by 1.5 cm of fine sand (0.4-0.8 mm) were filled on the bottom of a 15 cm (inner diameter) and 20 cm high PE pot supplemented with a drainage tube. As control treatments, 3500 g of air-dried, sieved (2 mm) Planosol (E) or Chernozem (T) were filled into the pots and compacted to reach a dry weight bulk density of 1.40 g cm-3 (E) and 1.32 g cm-3 (T). For the biochar amended soil, 3 g of labelled willow (60% leaves and 40% wood) biochar per 100 g of dry sieved soil was mixed and compacted to a density of 1.37 g cm-3 (E +BC) and 1.29 g cm-3 (T +BC). The mixed willow biochar had a calculated δ13C value of -38.1 ‰. Limited amounts of labelled biochar only allowed the set up of 8 pots (4 treatments, 2 replicates). At each time interval, two samples per pot were collected and analysed. The pots were irrigated using artificial irrigation water until drainage occurred (Chernozem: ~1300 ml; Planosol: ~1100 ml; biochar amended soil required approx. 10 % more water). Germinated barley (Hordeum vulgare cultivar: Xanadu) was planted and covered with 2 cm of dry soil. Irrigation was designed to ensure optimal plant growth. Soil moisture fluctuated between 63 and 34 % of the water holding capacities (WHC). An adjustment to 70 – 80 % WHC was done two days before sampling. A standard fertilization rate of 50 kg N, 48 kg P2O5 and 80 kg K2O ha-1year-1 was applied at day 22 (tillering stage) and another 50 kg N at day 49 (shooting stage) (Figure 36).

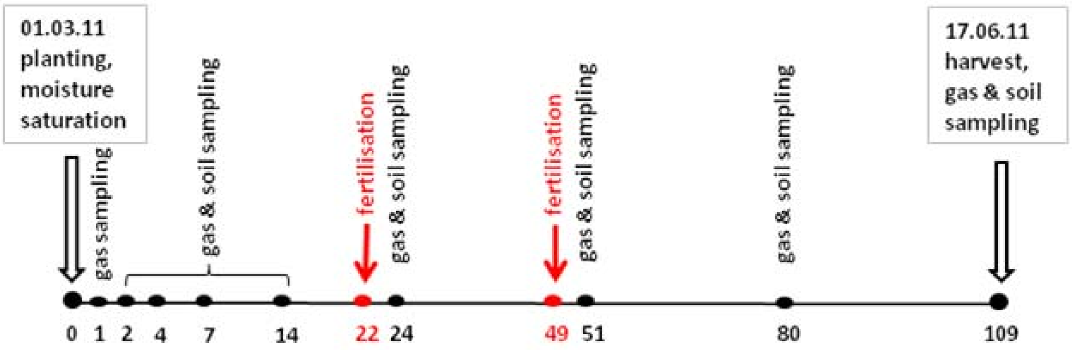

Figure 36: Schematic timeline of sampling and fertilization events in the planted pot experiment.

In the pot experiment, soil samples for PLFA, 13C PLFA, Corg, Ntot and 13Corg analyses were taken on day 2, 4, 7, 14, 24 (2 days after fertilization, at tillering state), 51 (2 days after fertilization, shooting of barley), 80 (maturation of barley) and 109 (harvest) (Figure 1). Samples were frozen immediately at -20 °C. Soil gas fluxes (CO2, CH4 and N2O) were determined manually on day 1, 2, 4, 7, 14, 24, 51, 80 and 109 by the closed chamber technique (Kitzler et al., 2006) (Figure 1). To this end, the pots were tightly closed with PVC chambers (0.4 l until day 24 and then 8.4 l to accommodate for plant growth). 24 ml of gas was extracted with a 60 ml syringe at 0, 5, 10 and 20 min and injected into sealed pre-evacuated 20 ml vials. Additionally, the growth of barley was monitored by determining stage of development and measuring plant height at several points of time. Barley was harvested at the end of the experiment on the 17th June 2011 (Figure 1) and the wet and dry plant biomass was determined.

Analysis of phospholipid fatty acids, soil organic carbon and gas fluxes

Microorganisms were investigated using PLFAs analyses. PLFAs were extracted from soils samples according to the procedure of Bligh and Dyer (1959) and Frostegård et al. (1996) as described above. The δ13C values of PLFAs were determined using the instrumental settings described in Watzinger et al. (2007). In contrast to earlier methods, analytical separation of the FAMEs was accomplished in split mode using a 60 m x 0.25 mm x 0.25 µm internal diameter HP 5-MS fused-silica capillary column (5% diphenyl 95% dimethylpolysiloxane) for both gas chromatography - flame ionisation detector (GC-FID) and gas chromatography – combustion – isotopic ratio mass spectrometry (GC-C-IRMS) measurements.

The 13C/12C ratio and content of the soil organic carbon (Corg) and the biochar, as well as the Ntot of the soil were measured by EA-IRMS (elemental analysis - isotopic ratio mass spectrometry; Carlo Erba EA 1108 equipped with a WLD and connected to a Finnigan MAT 251 via a Conflow II). The 13C/12C ratio of the plant material before pyrolysis was measured by a Delta XP (Thermo Fisher) IRMS with a Vario EL III (Elementar) EA and a Conflow III (Thermo Fisher). All samples were ball milled before analysis. Calibration was done using the international IAEA Standard NBS 22. The isotopic composition of C is reported in the delta (δ) notation relative to the Vienna Pee Dee Belemnite (V-PDB) standard. The precision (standard deviation) of the δ13C measurements was ≤ 0.2 ‰. The carbonate of the soil was released before measurement by repeated addition by 6 mol l-1 HCl solution (ratio of about 1 g soil to 1 ml acid). Because of inhomogenity, measurement of the soil organic carbon content was repeated using a LECO RC-612 elemental analyser (ÖNORM L 1080).

Gas samples were analysed according to the method of Kitzler et al. (2006) (see the supporting information for the detailed description of the method). The δ13C value of CO2 was measured by GC-C-IRMS. The GC-C-IRMS is comprised of a HP5890 Series II connected to a Delta S (Finnigan) via a Combustion II Interface (Finnigan). The GC was equipped with a CP Poraplot capillary column (25 m x 0.32mm). He pressure was kept constant at 70 kPa. The split flow was 15 ml min-1 and the purge flow was 5 ml min-1. Injection temperature was 120 °C. 50 to 100 µl of gas sample were injected manually. Oven temperature was kept constant at 40 °C for 4 min, and then ramped at 50 °C min-1 to 110 °C for 2 min. The δ13C of the CO2 emitted from the soil was calculated using the mass balance calculation (equation 1). The glasshouse had a concentration of 517 +/- 121 ppm CO2 and a δ13C = -10.6 +/- 0.9 ‰. These values were used to calculate the emitted CO2.

$$\delta^{13}\mathrm{C\ CO}_{2\ \mathrm{emitted}} = \frac{(\mathrm{conc\ CO}_{2\ 20\mathrm{min}} * \delta^{13}\mathrm{C\ CO}_{2\ 20\mathrm{min}}) - (\mathrm{conc\ CO}_{2\ \mathrm{glasshouse}} * \delta^{13}\mathrm{C\ CO}_{2\ \mathrm{glasshouse}})}{(\mathrm{conc\ CO}_{2\ 20\mathrm{min}} - \mathrm{conc\ CO}_{2\ \mathrm{glasshouse}})} \qquad (1)$$

where $\mathrm{conc\ CO}_{2\ 20\mathrm{min}}$ is the concentration of CO2 at the end of the sampling interval (20 min) and $\delta^{13}\mathrm{C\ CO}_{2\ 20\mathrm{min}}$ is its corresponding δ13C value, $\mathrm{conc\ CO}_{2\ \mathrm{glasshouse}}$ is the concentration of CO2 in the glasshouse (0 min) and $\delta^{13}\mathrm{C\ CO}_{2\ \mathrm{glasshouse}}$ is its corresponding δ13C value.

To determine the amount of biochar carbon respired from the soil we used the simplified mass balance calculation (equation 2), assuming that degradable biochar constituents (e.g. volatiles) had the same δ13C to that of the bulk biochar.

$$C_{BC}(\%) = \frac{(\delta^{13}\mathrm{C\ CO}_{2\ \mathrm{soil+BC}} - \delta^{13}\mathrm{C\ CO}_{2\ \mathrm{soil}})}{(\delta^{13}\mathrm{C}_{\ \mathrm{BC}} - \delta^{13}\mathrm{C\ CO}_{2\ \mathrm{soil}})} * 100 \qquad (2)$$

where $C_{BC}(\%)$ is the fraction of carbon derived from biochar, $\delta^{13}\mathrm{C\ CO}_{2\ \mathrm{soil+BC}}$ the δ13C value of the CO2 emitted from the biochar amended soil, $\delta^{13}\mathrm{C\ CO}_{2\ \mathrm{soil}}$ the δ13C value of the CO2 released by the control soil and $\delta^{13}\mathrm{C}_{\ \mathrm{BC}}$ the δ13C value of the biochar.

Statistical analysis

All analytical results were calculated on the basis of oven-dry (105 °C) weight of soil. Statistical evaluation was performed with SPSS 13.0 for Windows. A 1-factor ANOVA (factor: biochar) was used to analyse the effect of biochar on individual PLFAs. Significance was accepted at the $p \leq 0.05$ value of probability.

Results

Effect of biochar on the soil water content and plant growth

The actual water content of the incubation experiment was below the target value of 50 %

water holding capacity (WHC). In the Planosol the water content was kept constant at 47 ± 2 % and in the Chernozem at 45 ± 1% of the WHC. The water content in the pot experiment was increased under biochar amendment in the Planosol owing to the increased WHC. In the Chernozem, the WHC was not increased significantly by biochar addition. Plant height measurements indicated a slower growth rate of the control plants compared to the biochar-amended plants on the Chernozem. Hence, less transpiration caused a higher water content of the control soils on day 51 and lower water content on the days 80 and 109. Plant dry biomass measurements revealed that plants on the Planosol produced more aboveground biomass than on the Chernozem. Plant growth of barley was positively affected by the application of biochar in both soils. Biochar led to an increase of aboveground dry matter of 6.6 % on the Planosol and 9.1 % on the Chernozem (data not shown).

Effects of biochar amendment on the soil microbial community

The behaviour of the soil microbial community depended on the soil, the type of biochar used and the experimental design (Figure 37: Behaviour of total microbial biomass after 3 % (w/w) biochar application (BC) in the incubation experiment, (A) Planosol and (C) Chernozem, and in the pot experiment, (B) Planosol and (D) Chernozem. Error bars indicate standard deviation (incubation experiment n = 4; pot experiment n = 2 + 2). Significant differences ($p \leq 0.05$) are indicated by an asterisk.Figure 37). In the incubation experiment, amendment of biochar made from wheat husks increased total microbial biomass (total amount of PLFAs). This positive effect of biochar was more pronounced in the slightly acidic sandy Planosol than in the calcareous Chernozem. In the absence of biochar, total microbial biomass strongly increased in the Chernozem at the end of incubation (100 days). In general, the microbial biomass decreased during the duration of the incubation. In contrast, the soil microbial community was barely affected by amendment of biochar produced from willow leaves and wood in the pot experiment. A negative effect of biochar on the total microbial biomass was found after the second fertilization event (day 51) in the Chernozem.

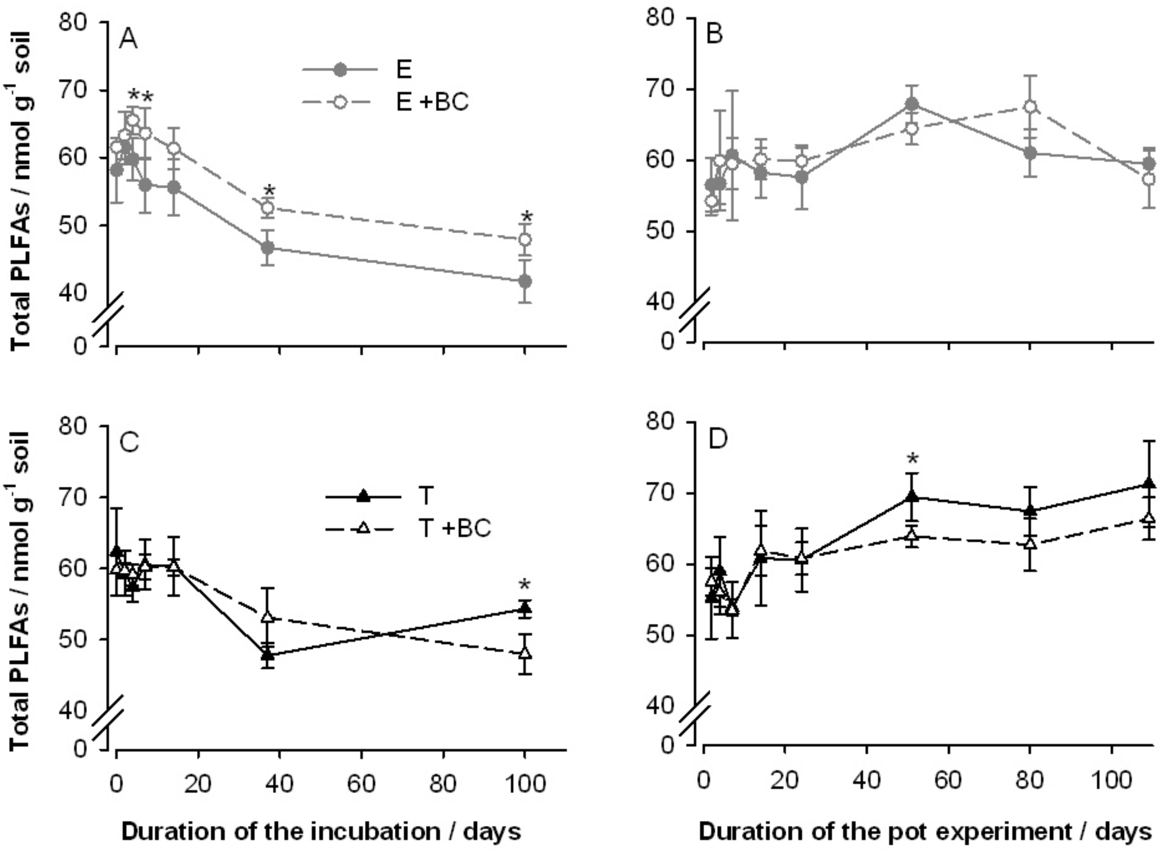

Figure 37: Behaviour of total microbial biomass after 3 % (w/w) biochar application (BC) in the incubation experiment, (A) Planosol and (C) Chernozem, and in the pot experiment, (B) Planosol and (D) Chernozem. Error bars indicate standard deviation (incubation experiment n = 4; pot experiment n = 2 + 2). Significant differences ($p \le 0.05$) are indicated by an asterisk.

The native soil microbial community of the Planosol was relatively fungal-dominated whereas the native community of the Chernozem contained relatively more PLFAs indicative for Gram negative bacteria and actinomycetes. The amount of Gram positive bacterial PLFAs differed marginally between the soils. Biochar addition affected various PLFAs differently.

In the incubation experiment many PLFAs were significantly increased after biochar addition in the Planosol after day two and onwards (Figure 38). Especially, unsaturated, straight-chain and cyclopropyl as well as methyl branched PLFAs indicative for Gram negative bacteria and actinomycetes, respectively, showed the strongest positive responses. The fungal specific fatty acid 18:2ω6,9 was less affected. In the Chernozem biochar treatment, some PLFAs representative of actinomycetes, Gram negative bacteria and fungi, were significantly elevated on day 37. However, on the last sampling date, most PLFAs were significantly reduced by biochar addition, especially Gram positive bacterial PLFAs (Figure 39). The PLFAs 10Me17:0 and 10Me18:0 indicative for actinomycetes were significantly elevated in both soils. In addition, 10Me18:0 was significantly depleted in ^{13}C in the biochar-amended soil, thus indicating microbial metabolism of labelled biochar (Figure 39).

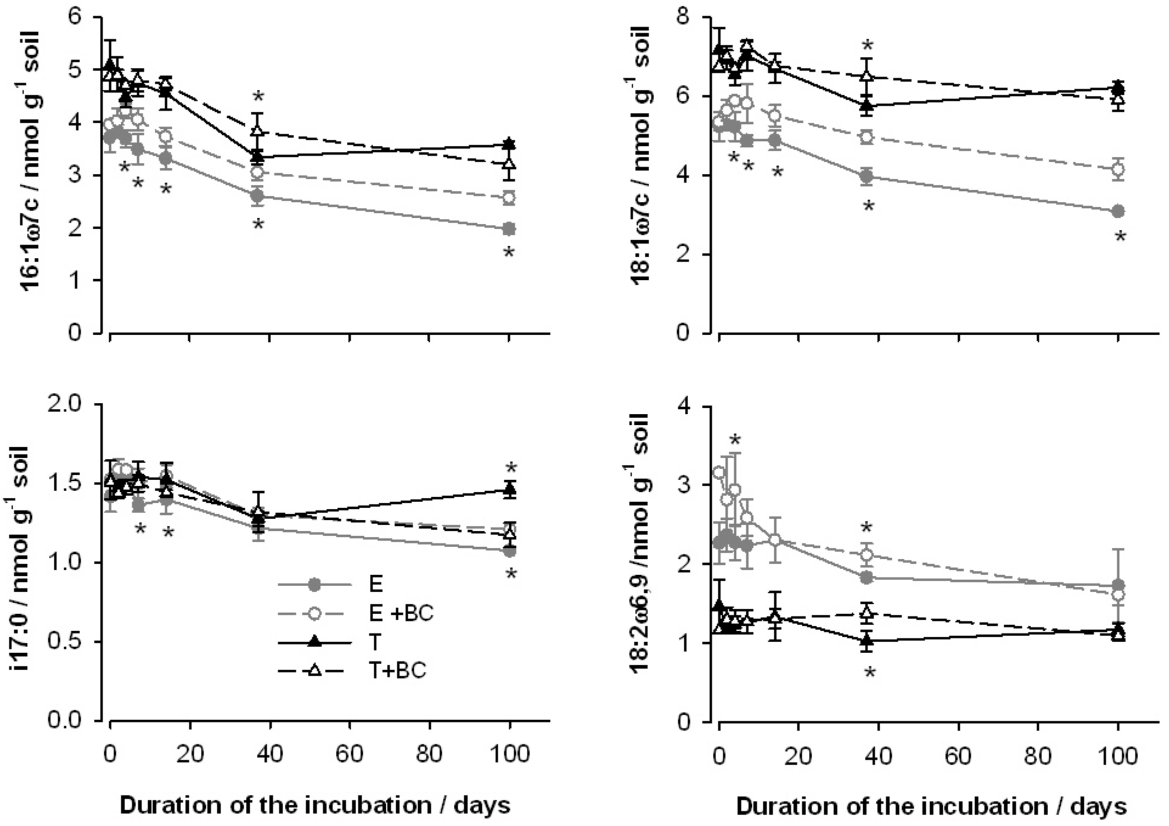

Figure 38: Behavior of the single PLFAs representing various microbial groups (Gram negative bacterial PLFAs 16:1ω7c and 18:1ω7c, Gram positive bacterial PLFA i17:0 and fungal PLFA 18:2ω6,9) after 3 % (w/w) biochar application (BC) in the incubation experiment; E = Planosol and T = Chernozem. Error bars indicate standard deviation (n = 4). Significant differences (p ≤ 0.05) are indicated by an asterisk.

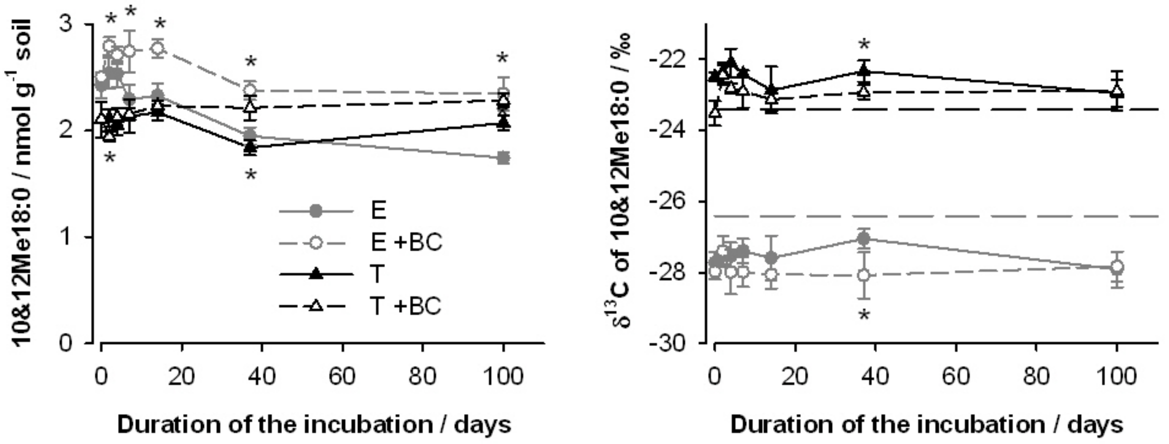

Figure 39: Concentration of the actinomycetal PLFAs 10&12Me18:0 after 3 % (w/w) biochar application in the incubation experiment and its δ^{13}C value. Error bars indicate standard deviation (n = 4). Significant differences (p ≤ 0.05) are indicated by an asterisk.

In the pot experiment, significant differences, based on single PLFAs, between biochar treated and untreated soils were mainly detected at the last three sampling dates (see the supporting information for a list of significantly affected PLFAs). In the Planosol 60% and in Chernozem 100% of all significant reactions to biochar amendment were negative.

Negatively affected PLFAs in the Planosol were mainly Gram positive bacterial and actinomycetal PLFAs, whereas Gram negative bacterial and fungal PLFAs were positively affected (Figure 40).

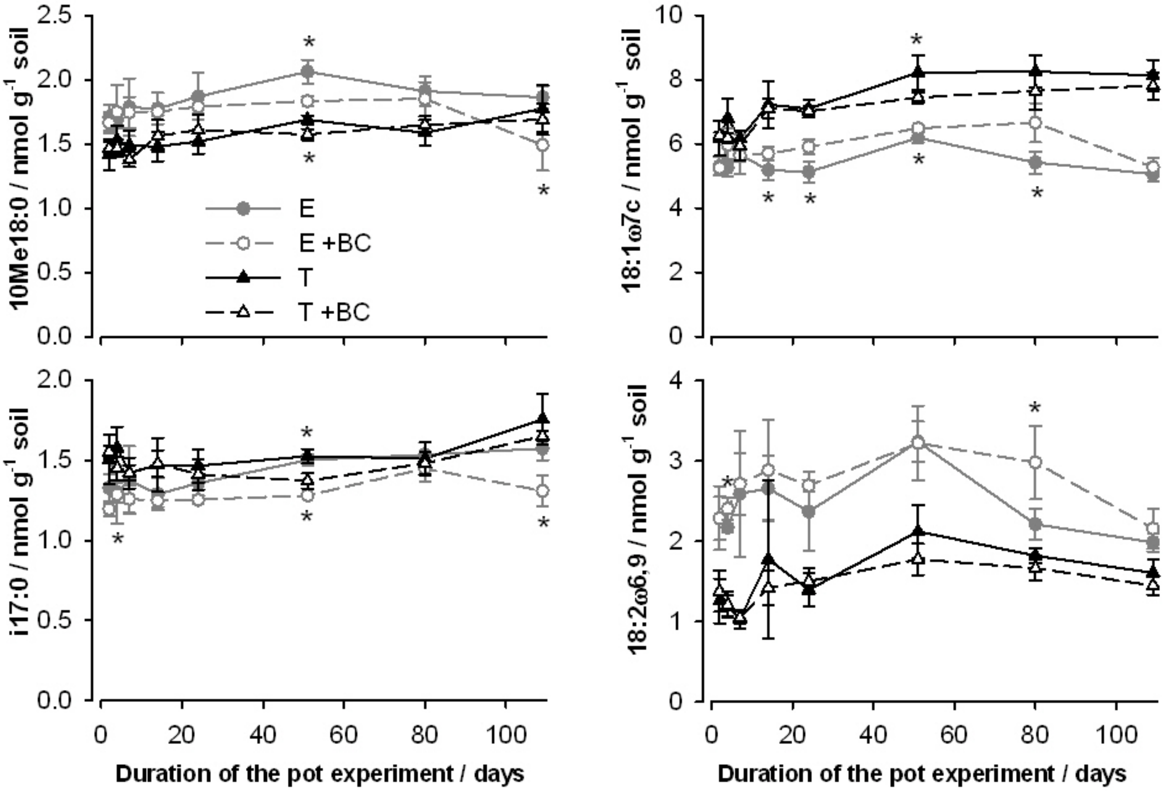

Figure 40: Behavior of single PLFAs representing various microbial groups (actinomycetal PLFA 10Me18:0, Gram negative bacterial PLFA 18:1ω7c, Gram positive bacterial PLFA i17:0 and fungal PLFA 18:2ω6,9) after 3 % (w/w) biochar application (BC) in the pot experiment; E = Planosol and T = Chernozem. Error bars indicate standard deviation (n = 2 + 2). Significant differences ($p \leq 0.05$) are indicated by an asterisk.

Generally, the uptake of the labelled biochar carbon into the microbial PLFAs was very low and occurred earliest after 5 weeks. ^{13}C labelling of single PLFAs was more frequently observed in the pot experiment compared to the incubation experiment, even though in the incubation experiment, it appeared from the concentration data that microbial groups profited from biochar application. In the pot experiment, negative labelling (i.e. increase of δ^{13}C PLFAs) was mainly observed in the Chernozem, where maize (typical δ13C of C4 plants is -13‰) was cultivated in the years prior to soil collection (Figure 41). In those soils the δ13C increased in many PLFAs in the first week of incubation (independently of biochar treatment). In some PLFAs (16:1ω5c, 18:1ω9c, 18:1ω7c) this increase was also observed in the biochar treatments at a later stage of the experiment. In the Planosol, uptake of ^{13}C labelled biochar in PLFAs was observed towards the end of the experiment (after about 51 days). The strongest labelling was observed in the Gram negative bacterial PLFA 16:1ω6&7 (Δ^{13}C by 1.2 and 2.0 ‰ at the last three sampling points) (Figure 6). Additional decreases in δ^{13}C were found in the PLFAs 16:1ω5 (Figure 6), 18:1ω9c, 10Me16:0 & i17:1ω8 and i17:0.

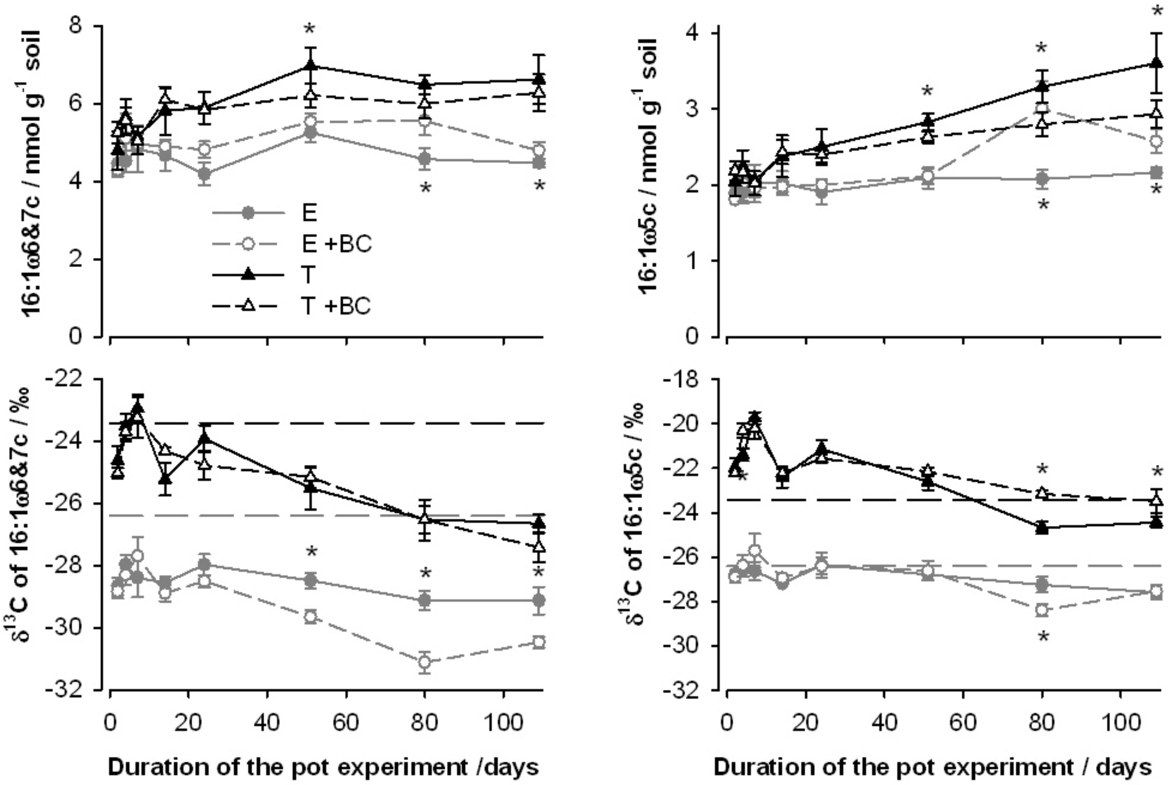

Figure 41: Behaviour of the PLFAs 16:1ω6&7c and 16:1ω5c after 3 % (w/w) biochar application in the pot experiment and their δ^{13}C value. Horizontal lines in indicate the δ^{13}C of the Planosol (grey) and Chernozem (black). Error bars indicate standard deviation (n = 2+2). Significant differences (p ≤ 0.05) are indicated by an asterisk.

Biochar and soil organic matter degradation

The addition of 3 % (w/w) biochar increased the soil organic carbon content (C_{org}) of the soils and decreased the δ^{13}C value (Figure 42). The C_{org} and its δ^{13}C value did not alter throughout the experiments.

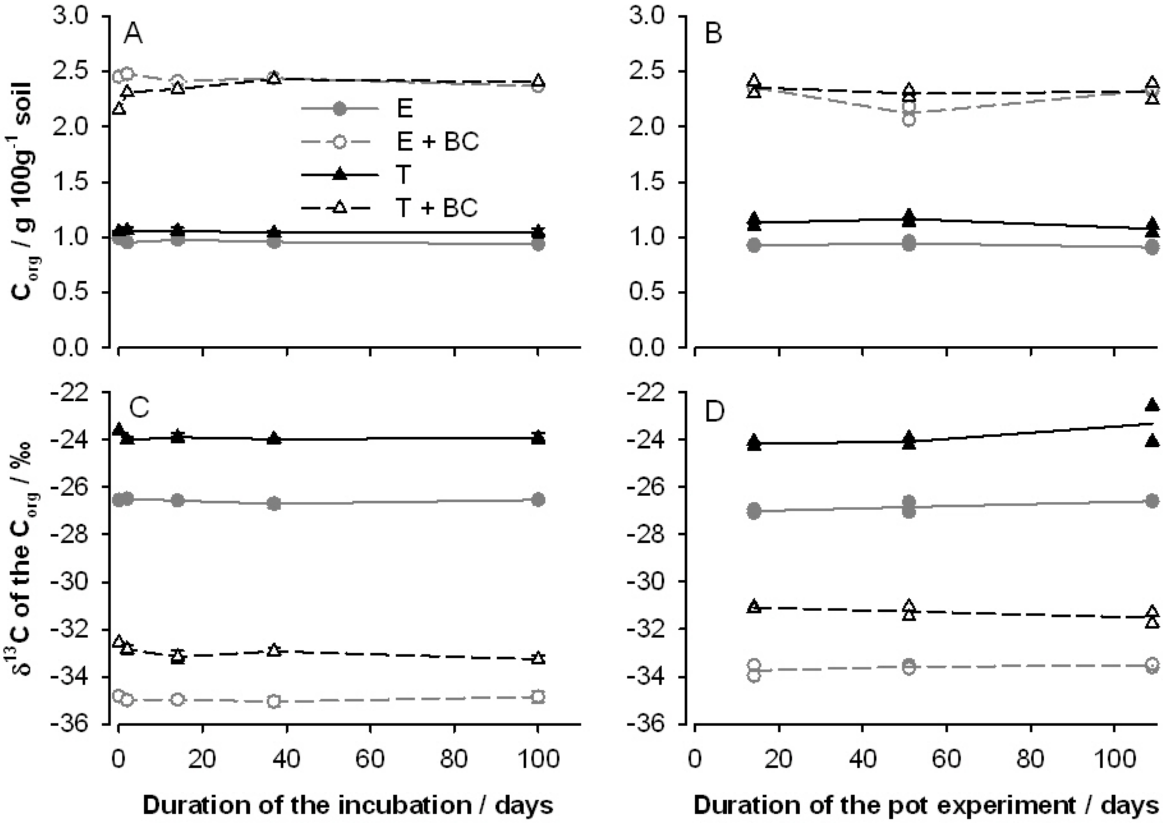

Figure 42: Time behaviour of the soil organic carbon content and its δ^{13}C value in the incubation (A and C) and pot (B and D) experiment of the Planosol (E) and Chernozem (T) and amended with 3 % (w/w) biochar (+BC). Error bars in the incubation experiment indicate standard deviation (n = 4).

Application of biochar decreased CO_2 emissions in the first two weeks (Figure 43). Only in the Chernozem did the δ^{13}C of the CO_2 decrease during that time. Using the simplified mass balance calculation 19.7, 12.9, 31.6 and 20.6 % of the emitted CO_2 was derived from biochar on day 1, 2, 4 and 7 respectively. Results from the single pots ranged from 0 to 42 % biochar carbon. The δ^{13}C value of CO_2 released from the Chernozem was generally high, but this could have been attributable to the prior maize cropping as discussed above or to the presence of carbonates with a δ^{13}C of -10.2 ‰ in the soil. In the Planosol, the δ^{13}C of CO_2 was increased under biochar treatment. Low amounts of carbonates were found in the Planosol amended with biochar; these had an initial δ^{13}C value of about -25.6 ‰. After two weeks microbial respiration was masked by root respiration. Maximum soil respiration was measured when barley was in milk ripeness on day 80. On this day and after the first fertilisation on day 22, the biochar amended pots of the Planosol emitted notably more CO_2 than the control plots.

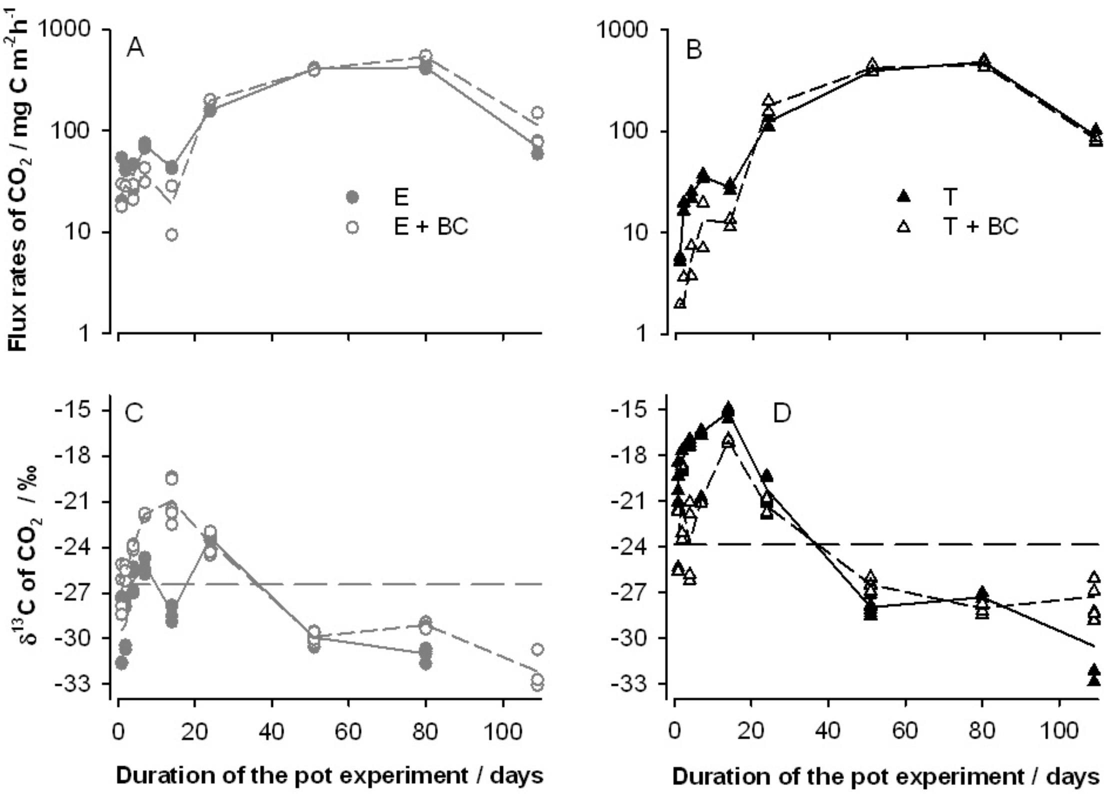

Figure 43: CO_2 emissions (A, B) and $\delta^{13}C$ value (C, D) emitted from a Planosol (E) and a Chernozem (T) treated with biochar (+BC). Dashed line indicated the $\delta^{13}C$ value of the Planosol (grey) and Chernozem (black) soil.

N_2O emissions decreased from up to 800 µg N_2O – N m^{-2} h^{-1} down to about 100 µg N_2O – N m^{-2} h^{-1} after about 10 days. Fertilization increased N_2O emissions. Biochar amendment did not clearly affect N_2O emissions. Furthermore, CH_4 emissions were not altered by biochar addition.

1.1.4. **Discussion**

Incubation of wheat husk biochar under constant incubation conditions (20 °C, 50 % WHC) increased microbial PLFAs relative to the control. This increase was more pronounced in the Planosol. Addition of biochar increased available phosphate and potassium concentrations as well as the cation exchange capacity and the water holding capacity in both soils, while the increase of the pH value was much more apparent in the Planosol. We hypothesize that the improved nutritional and physical conditions and above all the increase of the pH in the slightly acidic Planosol promoted microbial growth. The absence of biochar uptake into most microbial PLFAs together with unaltered soil organic carbon content and its $\delta^{13}C$ value confirmed that biochar was not a significant carbon source for the microbial community. Observed microbial community shifts after addition of wheat husk biochar in the incubation experiment supported the importance of pH effects on microorganisms: Actinomycetes, which are sensitive to low pH (Giri *et al.*, 2005), increased most dramatically in the Planosol.

Additionally, fungal PLFAs, which are more abundant in acidic soils (Aciego Pietry and Brookes, 2009), showed less response to biochar application compared to bacteria.

At the beginning of the pot experiment, soil microorganisms responded minimally to the addition of willow biochar, only after 50 days did microbial biomass decrease in the biochar treatments compared to the control, coinciding with the second N fertilization event. In accordance with our data, no or even negative effects of wood biochar on soil microorganisms had been documented (Castaldi *et al*., 2011; Dempster *et al*., 2012; Santos *et al.*, 2012), although the interaction of biochar and N cycling has been reported previously (Singh *et al.* 2010, Anderson *et al*. 2011). The within treatment variation was higher in the pot experiment than in the incubation experiment and the impact of the biochar appeared to be less in the pot experiment, possibly due to the fact that pot was more heterogeneous and continually changing over time, due to plant growth and root development, as well as cracks in the soil, resulting in uneven and changing distributions of nutrients, redox potential, water content, pore space and consequently soil microorganisms. For example, the concentration of the PLFA 16:1ω5c, also present in arbuscular mycorrhiza (AM), increased throughout the experiment in the Chernozem, which might be linked to the plant growth. It increased to a lesser extent in the biochar treatment which is in accordance with the behavior of AM reported by Warnock *et al.* (2010). In Planosol, 16:1ω5c increased suddenly and significantly incorporating biochar carbon, as AM are unlikely to metabolize biochar, other microorganisms must have been involved.

Was there an influence of the biochar type used? Willow biochar contained much higher amounts of polycyclic aromatic hydrocarbons (PAHs), predominantly naphthalene (10 mg kg^{-1}), which possibly prevented microbial growth. However, low concentrations of PAHs were also detected in the wheat husk biochar – but might have been degraded, as indicated by labeling of actinomycetal PLFAs. Members of actinomycetes (*Mycobacterium, Rodococcus*) are notorious degraders of aromatic compounds (Johnson *et al*., 2002, Ringelberg *et al*., 2001, Margesin *et al*., 2003) and were already found in the rhizosphere and bulk soil of wood biochar amended soil (Kolton *et al*., 2011; Khodadad *et al*., 2011). Wood biochar contained more volatiles – substances, which were released at 950°C (Enders *et al.,* 2012) - than straw biochar (unpublished data). A high volatile content might explain the higher microbial incorporation of willow compared to wheat husk biochar evident from the ^{13}C PLFAs. However, the increase of fungi in the willow biochar amended soil cannot be attributed to biochar degradation, because fungi did not assimilate biochar carbon. Wheat husk biochar application also did not promote degraders of complex organic matter, such as fungi, but rather Gram negative bacteria. These results are only impartial agreement with the observed microbial shifts in the rhizosphere communities (Kolton *et al*., 2011) and following addition of yeast derived hydrochar (Steinbeiss *et al*. 2009), where *Proteobacteria* were reduced and fungi enhanced. The main difference between their and our experiments was the slower degradation of our biochar.

Generally, the uptake of biochar carbon was low compared to the metabolisation of plant residues (e.g. Stemmer *et al.*, 2007). Additionally, we have a lack phase of biochar metabolisation of 5 weeks. In comparison, the metabolization of maize straw residues, which were present in the Chernozem, occurred within a week. Obviously, the soil microbial communities had to adapt in order to degrade biochar. Besides labeling of actinomycetial biomarkers (10&12Me18:0 and 10Me16:0 & i17:1ω8), the PLFAs 16:1ω6&7c, 16:1ω5c, 18:1ω9c and i17:0 were only labelled after 50, 80 and 109 days in the Planosol and pot experiment, which is in slight contrast to Santos *et al.* (2012), who found an uptake of charcoal carbon into all, but primarily Gram positive bacterial PLFAs. The PLFAs with the highest biochar uptake (16:1ω6&7c, 16:1ω5c) are not especially known for their ability to degrade soil organic matter. The strongest label in 16:1ω6&7c corresponded to a 6 to 18 % of the PLFA carbon being derived from biochar i.e. 0.002 % of the total biochar carbon available. This Figure was determined using mass balance equations; assuming that the fractionation during metabolic conversion of biochar carbon into PLFA carbon is constant to the fractionation factor between soil organic carbon and PLFA in the control soil (Δ = -1.5 ‰ for 16:1ω6&7c), in addition it was assumed that degradable biochar components have the same $\delta^{13}C$ than the bulk biochar. Similarly, Steinbeiss *et al*. (2009) found an uptake of about 10 to 15 % hydrochar carbon in bacterial PLFAs, but up to 60 % in fungi. The uptake of biochar into PLFAs for all labelled PLFAs was summed for the respective days and related to the total PLFAs. The amount of biochar label into the total microbial biomass was in the range of 0.6 – 3.5 %. In accordance Kuzyakov *et al*. (2009) reported a total microbial uptake of 1.5 to 2.6 % biochar carbon after 624 days using ^{14}C labelling and total microbial biomass determination by the fumigation - extraction method. To estimate whether degradation of biochar proceeds at time scale of decades or millennia, we assumed that biochar carbon in microorganism was released at comparable rates to other carbon sources. Consequently the biochar content in microorganisms would be the same as in CO_2. Total CO_2 emissions were approximately 50 mg C m^{-2} h^{-1} using results from CO_2 measurements at the beginning of the experiment, where root respiration was absent, and from a similar pot experiment conducted at the same time (unpublished data). 0.3 to 1.9 mg C m^{-2} h^{-1} of biochar carbon were lost as CO_2. Assuming exponential simple first order degradation of biochar, the mean residence time (MRT) was estimated in the range of millennia (mean value of 3000 years). Similar biochars had a MRT of 2000 (Kuzyakov *et al*., 2009) and 500 to 1600 years (Singh *et al.*, 2012). From the MRT perspective, it was logical that degradation of wheat husk and willow biochar were not detectable from the soil organic carbon values in our short term experiments (109 days).

Interpretation of the $\delta^{13}C$ of the CO_2 was complicated by the presence of labile soil organic matter in the form of maize residues in the Chernozem and the presence of carbonate in the biochar amended Planosol. In the Chernozem, the presence of biochar decreased the $\delta^{13}C$ of the CO_2. Attributing the reduction of the $\delta^{13}C$ value to biochar only, an average of 21 % of the emitted CO_2 derived from biochar. Assuming exponential simple first order degradation of biochar, the average MRT in the first week was estimated 3000 years, which is similar to the one calculated using PLFA labelling. However, the shift in the $\delta^{13}C$ of the CO_2 of the

Chernozem may also have been influenced by a negative priming effect on the labile soil organic matter (maize carbon). Positive (Luo *et al.,* 2011; Jones *et al.*, 2011) and negative priming (Keith *et al.,* 2011; Liang *et al.,* 2010) were reported in literature. Reduction of respiration was noted after willow biochar amendment, which supported the hypothesis of a negative priming effect. If we estimate the resulting $\delta^{13}C$ of the CO_2 assuming that reduction of degradation is mainly due to the diminished labile matter degradation, we could explain the measured $\delta^{13}C$ values. Higher maize residue uptake into some PLFAs was estimated later in the experiment under biochar treatment. (1) Decrease of $\delta^{13}C$ of CO_2 emitted under biochar treatment, (2) corresponding decrease of CO_2 emission, (3) prolonged degradation time of maize residues and last but not least (4) mismatch of the occurrence of PLFA labelling and CO_2 labelling indicate that negative priming of the labile organic matter was indeed occurring. Decreased mineralisation of labile organic matter has often been attributed to the adsorption on biochar (Liang *et al.,* 2010, Keith *et al.*, 2011) and inactivation of enzymes (Bailey *et al.,* 2011, Jones *et al.,* 2011).

Also in the Planosol, release of biochar labelled CO_2 was not detected: In contrast, biochar-amended soil released ^{13}C enriched CO_2. One possible explanation is the interference with the inorganic carbon cycling. This effect is not unknown. Release of inorganic carbon was already noted by Jones et al. (2011) and Chen et al. (2011) and after addition of biochar. Measurements of biochar amended Planosol yielded low carbonate contents with a $\delta^{13}C$ value of -25.6 ‰. The presence of carbonate in the willow biochar was also indicated by FTIR measurements. CO_2 release likely occurred after addition of carbonated biochar to the slightly acidic Planosol, while precipitation might have occurred after soil pH value increased in the Planosol as a result of biochar addition. Both processes have an influence on the $\delta^{13}C$ of CO_2 (Mook, 2000).

1.2. Status of the WP4 and dissemination of results

All Milestones M4-1, M4-2, M4-3 have been completed in time and the results and full interpretation were presented in this report. In addition to the proposed work, PLFA samples from the two field sites (Traismauer and Kaindorf) which had received biochar amendments were investigated to check the reproducibility of results gained from the greenhouse and lab experiments.

The outcome of WP4 were presented as posters at the ÖBG (Austrian Soil Science Union), at the SINA2011 (Stable Isotope National User Group Austria) and at the Eurosoil2012 (4th International Congress of the European Soil Science Societies). An oral presentation was given at the EGU2012 (European Geosciences Union - General assembly) and at the 2nd Nordic Biochar Seminar. A poster with the final results will be presented at the BCD2013 (International Conference Biochar, Compost, and Digestates) in October 2013. Within this WP two Master theses were published and one more is under preparation. Additionally two manuscripts have been submitted to the European Journal of Soil Science and the

Agricultural and Food Sciences. Published and submitted output from the WP4 of the biochar project is listed below:

Manuscripts submitted to SCI Journals

Anders E., Watzinger A., Rempt F., Kitzler B., Wimmer B., Zehetner F., Stahr K., Zechmeister-Boltenstern S. and Soja G. (2013) Biochar affects the structure rather than the total biomass of microbial communities in temperate soils. Agriculture and Food Science (submitted)

Watzinger A., Feichtmair S., Kitzler K., Zehetner F., Kloss S., Wimmer B., Zechmeister-Boltenstern S. and Soja G. (2013) Soil microbial communities responded to biochar application in temperate soils and slowly metabolized 13C labeled biochar as revealed by 13C PLFA analyses – results from a short term incubation and pot experiment. European Journal of Soil Science (submitted)

Master Thesis:

Rempt, F. (2011) Die Verwendung von Biochar als Bodenzusatz - Auswirkungen auf Pflanzenwachstum und mikrobielle Gemeinschaftsstrukturen. Master thesis, Universität Hohenheim, p.

Feichtmair S. (2012) The effect of biochar amendment on short term dynamic of microbial community and degradation of biochar using PLFA method and 13C natural labeling. Master thesis, University of Natural Resources and Life Sciences, p74.

Anders E. (2013) Biochar affects the structure rather than the total biomass of microbial communities in temperate soils. Master thesis, University of Natural Resources and Life Sciences. (in preparation)

Oral Presentations

Watzinger A., Feichtmair S., Rempt F., Anders E., Wimmer B., Kitzler B., Zechmeister-Boltenstern S., Horacek M., Zehetner F., Kloss S., Richoz S. and Soja G. (2012) The effect of biochar amaendment on the soil microbial community - PLFA analyses and 13C labeling results. Geophysical Research Abstracts Vol14, EGU2012-1584-4. European Geosciences Union - General Assembly 2012, 22.-27. April 2012, Vienna, Austria.

Watzinger A., Feichtmair S., Kitzler K., Zehetner F., Kloss S., Wimmer B., Zechmeister-Boltenstern S. and Soja G. (2013) Soil microbial communities responded to biochar application in temperate soils and slowly metabolized 13C labeled biochar. 2nd Nordic Biochar Seminar, 14.-15. Feb 2013, Helsinki, Finland.

Posters

Feichtmair S., Watzinger A., Zechmeister-Boltenstern S., Zehetner F., Kloss S., Wimmer B., Kitzler B., Klinglmüller M. and Soja G. (2011) Quantification of Biochar degradation and identification of degrading microbial groups in 13C natural abundance experiments. Ökosystemleistungen des Bodens, Jahrestagung der ÖBG, 6.-7.Okt. 2011, St. Florian, Austria.

Rempt F., Watzinger A., Fischer H., Kloss S., Wimmer B., Stahr K. and Soja G. (2011) Biochar als Bodenzusatz - Auswirkungen auf Bodenmikroorganismen und Pflanzenwachstum. Ökosystemleistungen des Bodens, Jahrestagung der ÖBG, 6.-7.Okt. 2011, St. Florian, Austria.

Watzinger A., Feichtmair S., Horacek M., Kitzler B., Zechmeister-Boltenstern S. and Soja G. (2011) Short term biochar degradation in a 13C natural abundance experiment by measuring 13CO2, 13Corg and 13C PLFAs in the soil. SINA - Stable Isotope Network Austria, 11th Stable Isotope Network Meeting, 4.-5. Nov. 2011, Vienna, Austria.

Watzinger A. and Soja G. (2012) PLFA Extraction – Problems associated with the preparation of soil samples with unknown water content and the effect of freeze drying. In: European Confederation of Soil Science Societies, Book of Abstracts, S11.02 P -21; 4th International Congress Eurosoil 2012, 2.-6. July 2012, Bari, Italy.

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2.5 WP 5: Soil fertility after biochar application

WP leader: Franz Zehetner, University for Natural Resources and Life Sciences, Institute for Soil Science, Vienna

Work package content:

Assessment of the soil nutrient status and nutrient bioavailability after application of biochars from different sources and different production techniques. Studies of nutrient adsorption, leaching (nitrate mobility), crop growth and yield analyses.

Objectives

Biochar (BC) application to soil has inspired much interest in the recent years. A role model for BC application to soils was found in the Amazonian Terra Preta (TP) soils, which are anthropogenic soils featuring high amounts of organic C (C_{org}). Parts of the C_{org} are derived from natural and anthropogenic burning activities and are therefore of pyrogenic origin with high recalcitrance. This feature is accompanied by a higher cation exchange capacity (CEC), higher pH and nutrient content, which entailed considerably higher plant yields compared to the surrounding, rather infertile tropical soils. Therefore, depending on the particular implementation purpose, BC is seen as a useful soil additive in terms of carbon (C) sequestration (WP 3) as well as soil amendment and remediation (WP 5). The ability of realizing those three main scopes of application is based on the unique properties of BC, which we had thoroughly investigated in Kloss et al. (2012) prior to implementing BC application in glasshouse and field experiments (WP 1). The specific effects depend on a range of factors such as the choice of feedstock, pyrolysis temperature and residence time in the pyrolysis unit. Briefly, we found that pH and specific surface area (SSA) of all BCs increased while CEC decreased with increasing pyrolysis temperature.

BC application to poor tropical soils proved to be useful to enhance their quality; however, the implementation of BC application in temperate soils may vary due to differing soil properties and basic conditions such as originally higher soil pH and soil organic matter (SOM) content. This chapter will present results of glasshouse and field experiments using different temperate soils. In detail, following questions have been regarded:

- Influence of various BC types on nutrient status, leaching and plant growth on a temperate soil
- Influence of BC application rate of a specific BC on nutrient status, leaching and plant growth on three temperate soils of different characteristics
- Influence of different N fertilizer application rates on nutrient status, leaching and plant growth
- Influence of BC application on soil water and crop growth (field experiments)

Highlights of the research are presented in this chapter and have been thoroughly discussed in manuscripts that are in the state of submission and review, respectively (see appendix).

In addition to the originally proposed research of BC effects on soil nutrient status and crop yields, supplementary research (not originally foreseen in this project) on BC as a remediation tool for trace metals and pesticides has been performed. This included following aspects:

- Influence of BC on trace metal availability on different soils
- Influence of BC application to a temperate soil on pesticide sorption
- Influence of different BCs on Cd and Cu sorption potential
- Influence of BC aging on Cd and Cu sorption potential

Highlights of the additional research topics are presented in this chapter but partly overlap with WP 3. Publications in peer-reviewed journals are currently prepared and are subject to submission in summer 2013.

Materials and Methods

Glasshouse experiment

Soils and biochars

The glasshouse experiment was originally setup in Seibersdorf, NÖ at the Austrian Institute of Technology (AIT) in starting in September 2010. The setup took about two months; the pot experiment started in November 2010. In April 2011, the pots were moved to the new facility in Tulln, NÖ.

Agricultural soils from three different sites were sampled in summer 2010:

- **Chernozem** (site: Traismauer, NÖ; 48°19’52.6’’N, 15°44’20.5’’E; parent material loess; 547 mm mean annual precipitation)
- **Cambisol** (site: Kaindorf, Stmk; 47°13’46.0’’ N, 15°50’40.6’’E; parent material Tertiary sediments; 883 mm mean annual precipitation)
- **Planosol** (site: Eschenau; NÖ; 48°46’32.9’’N, 15°14’28.6 E; parent material granite, 667 mm mean annual precipitation)

Pictures of the soil profiles of the three sites are given in Figure 44.

Figure 44 Soil profiles of the Chernozem (NÖ), Cambisol (Stmk) and Planosol (NÖ).

The soils used for the experiment were taken from the top 30 cm and air-dried and homogenized after transport to Seibersdorf, NÖ.

BC was produced from three different feedstocks:

- Wheat straw (WS, *Triticum aestivum*)
- Mixed woodchips (WC)
- Vineyard prunings (VP; *Vitis vinifera*)

The three feedstocks were pyrolyzed at 525°C under argon atmosphere to provide a low-oxygen atmosphere. In addition, VP was pyrolyzed at 400°C to investigate the effect of pyrolysis temperature on soil and plant yield. The pyrolysis unit (stainless tube furnace; 2°C min^{-1} heating rate) used for VP can be seen in Figure 45. After cooling, VP was ground to < 2mm.

Figure 45 Stainless tube furnace unit in Seibersdorf, NÖ.

WS and WC were pyrolyzed at EVN Dürnrohr, NÖ in a rotary furnace (dwell time approx. 1h, 10-20°C min^{-1} heating rate). A characterization of the used soils and BCs is given in Table 9.

Table 9 Basic soil and biochar characterization (n=3). Different letters indicate significant difference within one column ($p < 0.05$; Tukey's test). EC: electrical conductivity; CEC: cation exchange; SA: Surface area; from: Kloss et al. (2013; JPNSS, in review).

soil		**texture**	**pH ($CaCl_2$)**	**EC**	**CEC**	**C/N ratio**	**carbonate**
				(µS cm^{-1})	(mmol$_c$ kg^{-1})		(w.-%)
Planosol		loamy sand	5.4 ± 0.0 a	41.2 ± 12.3 a	75.1 ± 0.4 a	14.9 ± 1.6 b	0.0 ± 0.0 a
Cambisol		clay loam	6.6 ± 0.1 b	103.9 ± 0.1 b	209.4 ± 2.2 b	13.8 ± 0.8 ab	0.0 ± 0.0 a
Chernozem		silt loam	7.4 ± 0.1 c	173.6 ± 5.2 c	208.6 ± 3.6 b	11.9 ± 0.7 a	15.8 ± 0.1 b
biochar	**pyrolysis temperature**	**ash content** (w.-%)	**pH ($CaCl_2$)**	**EC** (mS cm^{-1})	**CEC** (mmol$_c$ kg^{-1})	**C/N ratio**	**BET -N_2 SA** (m^{2}g^{-1})
straw	525°C	28.10	9.7 ±0.0 c	5.2 ± 0.1 d	148.5 ± 0.8 d	63.8 ± 1.6 c	12.26 ± 1 c
woodchips	525°C	15.20	8.9 ±0.1 b	1.6 ± 0.0 c	93.0 ± 1.9 b	58.2 ± 0.7 b	26.41 ± 1 d
vineyard pruning	400°C	4.30	8.3 ± 0.0 a	1.5 ± 0.0 b	123.5 ± 1.3 c	52.0 ± 2.4 a	1.69 ± 0 a
vineyard pruning	525°C	7.70	8.8 ± 0.1 b	1.1 ± 0.0 a	78.8 ± 1.4 a	58.0 ± 1.9 b	4.85 ± 0 b

Table 9 illustrates that the three soils differed in soil texture, CEC and pH. The BCs had different ash contents, EC, CEC and SSA. Vineyard pruning pyrolyzed at 400°C (VP400) had a lower ash content, pH, SSA than the same feedstock pyrolyzed at 525°C (VP525), but a higher CEC.

Experimental setup and sampling

Before filling the pots, the respective soil- biochar mixtures were generated in a closed cement mixer at two concentration rates: 1 w.-% and 3 w.-% BC (which would correspond to

30 and 90 t ha^{-1} at an incorporation depth of 20 cm in the field). The dimensions of the pots were the following:

- Inner diameter: 23.5 cm
- Height: 40 cm
- Surface area: 0.04335 m²
- Volume: 17.34 L

The bottom of each pot was filled with two 1.5 cm layers of quartz sand (coarse sand 0.5-2 mm; fine sand 0.4-0.8 mm); each pot was additionally equipped with an outlet to collect leachate water. Each pot contained a mesh at the bottom of the pot to prevent the soil from clogging the drainage outlet. One replicate of each treatment was additionally equipped with a moisture probe (Trase multiplex system 1 6050X1, Soil moisture equipment corp., Santa Barbara, USA and 10 HS, Decagon Devices Inc., WA, USA, respectively) to survey the water content. The pots were arranged in 4 double rows in a randomized block design. Altogether, 25 treatments with 5 replicates as well as controls were prepared. The treatments used in the manuscript of Kloss et al (2013, in review) are given in Table 10. In addition, the investigation of the leachates required the inclusion of BC treated pots that had not been planted. The term control refers to the soil without BC but with standard fertilization (Table 10).

Table 10 Summary of the treatments investigated in the pot experiment (Kloss et al., 2013; JPNSS, in review).

soil	biochar type	pyrolysis temperature (°C)	amount of biochar (wt.- %)	N fertilization (kg ha^{-1})
Planosol	-	-	0	40*/ 100#
Planosol	woodchips	525	1	40*/ 100#
Planosol	woodchips	525	3	40*/ 100#
Planosol	wheat straw	525	3	40*/ 100#
Planosol	vineyard pruning	400	3	40*/ 100#
Planosol	vineyard pruning	525	3	40*/ 100#
Planosol	-	-	0	0*/ 0#
Planosol	-	-	0	20*/ 50#
Planosol	-	-	0	80*/ 200#
Planosol	woodchips	525	3	0*/ 0#
Planosol	woodchips	525	3	20*/ 50#
Planosol	woodchips	525	3	80*/ 200#
Cambisol	-	-	0	40*/ 100#
Cambisol	woodchips	525	1	40*/ 100#
Cambisol	woodchips	525	3	40*/ 100#
Chernozem	-	-	0	40*/ 100#
Chernozem	woodchips	525	1	40*/ 100#
Chernozem	woodchips	525	3	40*/ 100#

* mustard/ # barley

The pots were planted with mustard (*Sinapis alba L.* cv. Serval; Nov 23, 2010 to Feb 17, 2011). Subsequently, barley (*Hordeum vulgare* cv. Xanadu; Feb 18 to June 20, 2011, 10 seedlings per pot) was sown, followed by red clover (*Trifolium pratense* cv. Reichersberger Neu; July 26 to Dec 13, 2011, 6 seedlings per pot). A standard fertilizer in the range of 40 kg N ha^{-1} was applied (Linzer Star, N: P_2O_5: K_2O: S = 15:15:15:3), which was later increased to 100 kg N ha^{-1} for barley. Clover was not fertilized. An additional set of pots (Planosol) was treated with 4 different N fertilization rates ranging from 0 to 80 kg N ha^{-1} (N0- N80) for mustard and N0 to N200 for barley, both with and without BC (Table 10). A picture of the setup in the glasshouse during leachate collection in Seibersdorf, NÖ is given in Figure 46.

Figure 46 Experimental setup of the glasshouse experiment in Seibersdorf. The pots are connected to cans that collect leachate water. This picture shows the growing of barley.

At each harvest, the above-ground biomass was cut off manually, dried at 80°C until constant weight was reached. Above-ground biomass was determined. In addition, barley ears were threshed to allow for separate analyses of grains and straw.

The soils of the pots were sampled on Nov 23rd, 2010 immediately after preparing the soil-BC mixtures and before filling the pots (n=3). Irrigation was carried out according to the water content of the respective treatments using artificial rainwater (3 mg Ca L^{-1}; 50 % $CaCl_2×2H_2O$, 50 % $CaSO_4×2H_2O$). The pots with TDR probes have not been sampled to avoid damages of the probes. A second soil sampling was carried out after 7 months following barley harvest (July 8th, 2011; n=4) using a small core drill. Another soil sampling was carried out after 15 months (March 2012; after the second clover harvest; n=4); at this, only selected pots containing Planosol and the four BC types plus control were sampled for adsorption experiments. A timeline is given in Figure 47, which summarizes the activities within the scope of the glasshouse experiment.

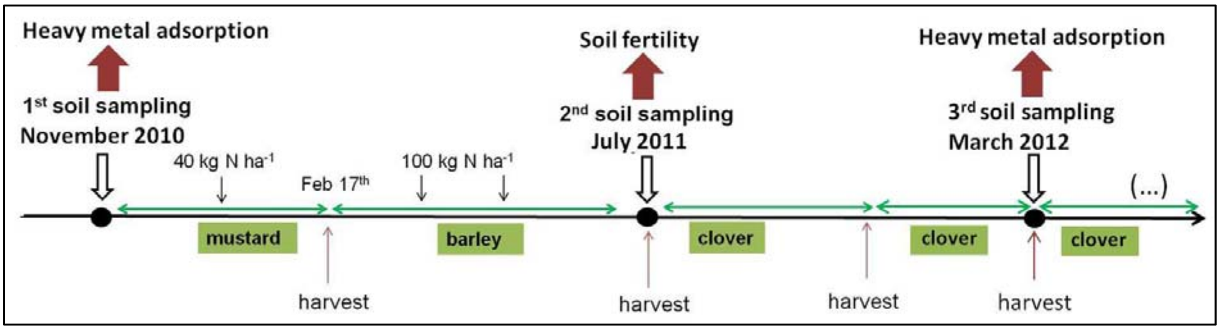

Figure 47 Timeline of the glasshouse experiment including soil sampling, planting and harvest dates and fertilization rates

The experiment was run under semi-controlled temperature conditions simulating a day-night temperature profile (night minima: 14±2 °C in winter, 18±2 °C in summer, day maxima: 20±2 °C in winter and 25±2 °C in summer).

Leachate water was collected five times:

- November 25th, 2010
- December 14th, 2010
- January 18th, 2011
- April 16th, 2011
- May 10th, 2011

At each sampling date, 200 mL of the leachate water was treated with ^{60}Co (effective dose 25.5 kGy; MEDISCAN, Seibersdorf, Austria) to avoid microbially induced changes of nitrogen and oxygen.

Analyses

Following plant analyses have been carried out after each harvest:

- Above-ground biomass
- Plant N concentration
- Elemental composition after full acid digestion (HNO_3: $HClO_4$ = 20 + 4 mL; on the basis of *ÖNorm* L 1085, 2009)

After each soil sampling, the soil was air-dried and sieved to < 2 mm. Following analyses were carried out for the 1st and 2nd soil sampling:

- pH
- electrical conductivity (EC)
- cation exchange capacity (CEC; *ÖNORM* L 1086 (2001), exchangeable cations
- Total C and N
- Calcium-acetate-lactate extractable phosphorus and potassium (P_{CAL} and K_{CAL})
- Nitrogen-supplying potential (NSP) by anaerobic incubation (*ÖNorm* L 1091 (1999)).

A more detailed description of the methodology is given in Kloss et al. (2013; JPNSS, in review; see appendix).

The leachate water was investigated for following parameters:

- pH
- EC
- NH_4^+
- NO_3^-
- Dissolved phosphorus (P_{diss})
- Dissolved organic carbon (DOC)

The third soil sampling (March 19th, 2012) was subject to various sorption experiments that were carried out within the frame of a scholarship at Cornell University, NY. The methodology is briefly described in 0.

To summarize the glasshouse experiment the dimension of a pot as well as analyses carried out within the scope of the glasshouse experiment are depicted in Figure 48.

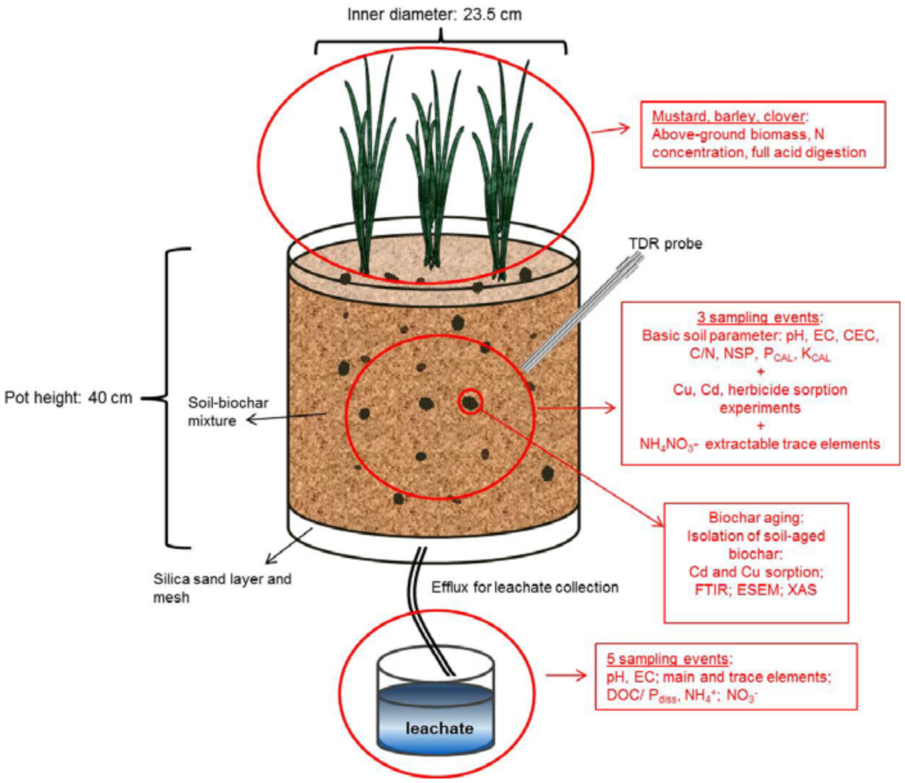

Figure 48 Scheme of the dimensions of a pot from the glasshouse experiment and realized analyses within the work package 5 (red boxes). EC: electrical conductivity; CEC: cation exchange capacity; NSP: nitrogen supplying potential; P_{CAL}/ K_{CAL}: calcium-acetate-lactate extractable phosphorus and potassium; FTIR: Fourier-Transform Infrared Spectroscopy; ESEM: Environmental Scanning Electron Microscopy; XAS: X-ray absorption spectroscopy; DOC: dissolved organic carbon; P_{diss}: dissolved phosphorus.

Field experiments

Soils and biochars

In addition to the controlled pot experiments, field experiments have been installed at the locations in Kaindorf; Styria (Cambisol; 47°13’46.0’’N, 15°50’40.6’’E; parent material tertiary sediments; 883 mm mean annual precipitation) and Traismauer, NÖ (Chernozem; 48°19’52.6’’N, 15°44’20.5’’E; parent material loess; 547 mm mean annual precipitation) to investigate the effects of BC on soil under field conditions. A detailed characterization of the two soils can be seen in 0.

BC was employed from S.C.ROMCHAR S.R.L (Romania) and produced from beech wood by slow pyrolysis (550°C; < 2 cm diameter) obtaining following basic characteristics:

- pH: 9.0
- C: 80 w.-%
- H: 1.6 w.-%
- N: 0.4 w.-%

Polycyclic aromatic hydrocarbons (PAHs) and heavy metal (HM) concentrations complied with EBC guidelines.

Experimental setup and sampling

The setup of the field experiments started in spring 2011 and was set up identically for both study sites. Four different treatments including control (plots without BC but with fertilization) were used. Each plot had a dimension of 33 m². Altogether, each site had 16 plots (n=4). The experimental plots were circular to minimize edge effects.

After applying the BC, it was mixed with the first approx. 15 cm of the soil. Figure 49 shows photographs taken during BC application at the two experimental sites Kaindorf and Traismauer.

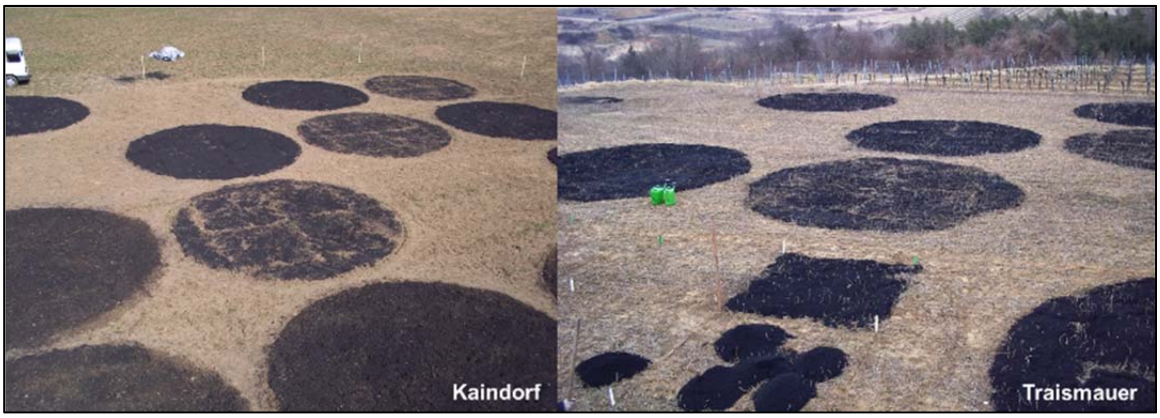

Figure 49 Biochar (BC) application at the two sites Kaindorf (Cambisol) and Traismauer (Chernozem)

In addition, three of the four treatments received additional mineral fertilization (Nitramoncal [NH_4NO_3], Linzer Star [N: P: K= 15:15:15]). BC addition rates were 30 t ha^{-1} and 90 t ha^{-1} moist mass. Water content of the BC was determined at the AIT and found to be in the range of 20 %; after correcting for the water content, BC application rates amounted to 24 and 72 t ha^{-1}, respectively. The treatments have already been summarized in the WP 2 description

Maize (*Zea mays*, 2011) and winter wheat (*Triticum aestivum*, 2012) were grown on the Cambisol, whereas the Chernozem was planted with barley (*Hordeum vulgare*, 2011) and sunflower (*Helianthus anuus*, 2012). Soil sampling was carried out subsequent to the harvests. A detailed description of the course of the experiments is compiled in Table 11.

Table 11 Temporal sequence of activities of the two field experiments in 2011 and 2012

Cambisol (Kaindorf)		**Chernozem (Traismauer)**	
2011		**2011**	
March 31st	BC application and incorporation	March 16th	BC application and incorporation
April 12th	NPK fertilization	April 11th	NPK fertilization
April 25th	sowing of maize (*Zea mays*)	April 12th	sowing of spring barley (*Hordeum vulgare*)
July 6th	Nitramoncal application	May 10th	Nitramoncal application
Sept 28th	maize harvest, soil sampling	July 21st	barley harvest, soil sampling
October 10th	sowing of winter wheat (*Triticum aestivum*)		
2012		**2012**	
March 12th	Nitramoncal fertilization	April 20th	sowing of sunflower (*Helianthus anuus*)
July 17th	wheat harvest, soil sampling	May 3rd	NPK fertilization
		Sept 26th	sunflower harvest

For following interpretations it is not unimportant to mention that during our experiments both the Traismauer and the Kaindorf region showed a severe precipitation deficit compared to the long-term mean (1971-2000, Figure 50).

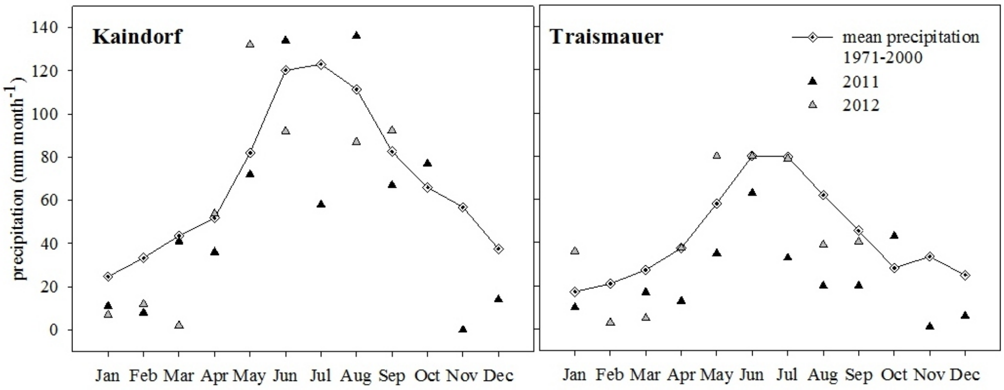

Figure 50 Monthly mean precipitation at the two study sites Kaindorf and Traismauer in 2011 and 2012 compared to the monthly long-term mean precipitation (1971-2000; Karer et al., 2013, Agricultural and Food Science, submitted)

Analyses

After determining above-ground dry mass (dried at 60°C), the harvest products were separated in grain and straw, chaffed and milled. In addition, following analyses were performed:

- Plant N concentration
- Elemental composition after full acid digestion (HNO_3: $HClO_4$ = 20 + 4 mL; on the basis of *ÖNorm* L 1085, 2009)

After each soil sampling, the soil was air-dried and sieved to < 2 mm. Following analyses were carried out:

- pH
- electrical conductivity (EC)
- cation exchange capacity (CEC; *ÖNORM* L 1086 (2001), exchangeable cations
- Total C and N
- Calcium-acetate-lactate extractable phosphorus and potassium (P_{CAL} and K_{CAL})
- Nitrogen-supplying potential (NSP) by anaerobic incubation (*ÖNorm* L 1091 (1999)).

In addition, following analyses were performed:

- Determination of bulk density
- Water holding capacity (WHC)
- pF curve

A more detailed description of the methodology is given in Karer et al. (2013; Agricultural and Food Science, submitted; see appendix).

Selected Results and Discussion

Glasshouse experiment

Results presented here are discussed in more detail in Kloss et al. (2013), which is currently in review at the Journal of Plant nutrition and soil science (appendix).
Table 12 shows the effects of the different BC types on the Planosol variants immediately after mixing soil and BC as well as after 7 months.

Table 12 Effect of different biochars (3 w.-% application rate) on soil fertility parameters of an agricultural Planosol at the start of the pot experiment (t1; n=3) and after 7 months (t2; n=4). Standard fertilization was 40 kg N ha^{-1} for mustard and 100 kg N ha^{-1} for barley. Different letters indicate significant differences within one line (p<0.05, Tukey's test). EC: electrical conductivity; NSP: Nitrogen supplying potential. HTT: highest treatment temperature during pyrolysis (Kloss et al., 2013; JPNSS, in review).

Variable	**initial soil-biochar mixtures (n=3)**				
	control	mixed woodchips (HTT 525°C)	straw (HTT 525°C)	vineyard pruning (HTT 400°C)	vineyard pruning (HTT 525°C)
pH ($CaCl_2$)	5.4 ± 0.0 a	6.8 ± 0.0 d	6.7 ± 0.0 c	6.5 ± 0.0 b	6.5 ± 0.0 b
EC / µScm^{-1}	43.1 ± 0.4 a	121.1 ± 7.6 c	188.9 ± 2.8 d	90.8 ± 0.2 b	95.2 ± 2.2 b
CEC / mmol$_c$kg^{-1}	75.1 ± 0.4 a	92.2 ± 0.8 c	84.1 ± 1.1 b	91.5 ± 1.2 c	85.9 ± 0.4 b
C/N ratio	14.9 ± 1.6 a	36.6 ± 2.5 d	27.4 ± 1.0 b	29.0 ± 3.3 cd	35.2 ± 3.3 bc
C_{org} / w.-%	1.6 ± 0.0 a	4.8 ± 0.0 e	3.4 ± 0.1 b	4.0 ± 0.1 c	4.6 ± 0.1 d
NSP / µg g^{-1} d^{-1}	2.0 ± 0.7 a	3.2 ± 0.3 bc	4.0 ± 0.5 c	2.6 ± 0.3 ab	2.4 ± 0.2 ab
P_{cal} / mgkg^{-1}	61.3 ± 0.8 a	83.8 ± 2.4 b	103.7 ± 1.4 c	82.8 ± 0.4 b	81.4 ± 1.6 b
K_{cal} / mgkg^{-1}	107.2 ± 1.7 a	339.6 ± 3.1 c	562.3 ± 5.8 d	266.4 ± 1.2 b	260.7 ± 4.8 b
	after seven months (n=4)				
pH ($CaCl_2$)	5.3 ± 0.1 a	6.9 ± 0.1 c	6.5 ± 0.1 b	6.6 ± 0.0 b	6.6 ± 0.1 b
EC / µScm^{-1}	34.5 ± 3.6 a	74.7 ± 2.7 b	71.8 ± 5.5 b	66.0 ± 4.0 b	68.7 ± 6.2 b
CEC / mmol$_c$kg^{-1}	75.1 ± 2.4 a	101.1 ± 1.5 c	94.0 ± 1.1 b	97.2 ± 1.3 bc	96.5 ± 1.8 b
C/N ratio	17.2 ± 1.9 a	31.4 ± 4.0 ab	36.6 ± 3.7 ab	37.0 ± 10.2 ab	43.1 ± 16.3 b
C_{org} / w.-%	1.6 ± 0.5 a	3.5 ± 0.6 ab	4.6 ± 0.9 b	3.3 ± 2.0 ab	4.3 ± 1.4 b
NSP / µg g^{-1} d^{-1}	2.1 ± 0.2 a	3.4 ± 0.5 b	3.5 ± 0.5 b	1.4 ± 0.7 a	3.6 ± 0.6 b
P_{cal} / mgkg^{-1}	54.5 ± 2.2 a	92.5 ± 1.8 b	95.5 ± 1.8 b	92.2 ± 8.1 b	88.0 ± 2.1 b
K_{cal} / mgkg^{-1}	73.2 ± 1.8 a	289.9 ± 20.3 b	462.5 ± 47.8 c	260.8 ± 13.0 b	285.8 ± 21.4 b

Application of BC showed significant increases in pH, EC, CEC, C/N, P_{CAL}, K_{CAL}, and NSP compared to the control for all BC types. WS initially showed the highest values of EC, P_{CAL}, K_{CAL} and NSP, whereas the WC treatment had the highest pH, CEC and C/N. Initially discriminative differences between single BC types evened out after 7 months and showed no significant differences anymore for EC and P_{CAL}; however, they still were slightly different from the controls. Table 12 shows that CEC significantly increased after 7 months (t_2) for each BC type compared to the CEC measured at the beginning of the pot experiment (t_1), whereas the CEC of the control did not change during this time. The highest increase in CEC was found for VP525 (in the range of 12 %), followed by WS. Pyrolysis temperature (comparing VP400 and VP525) did not significantly affect the soil nutrient status (except for NSP, t=1) despite the fact that the BC characterization showed significant differences for many parameters between the pyrolysis temperatures (Table 9).

The effect of different BCs on plant yield is shown in Figure 51.

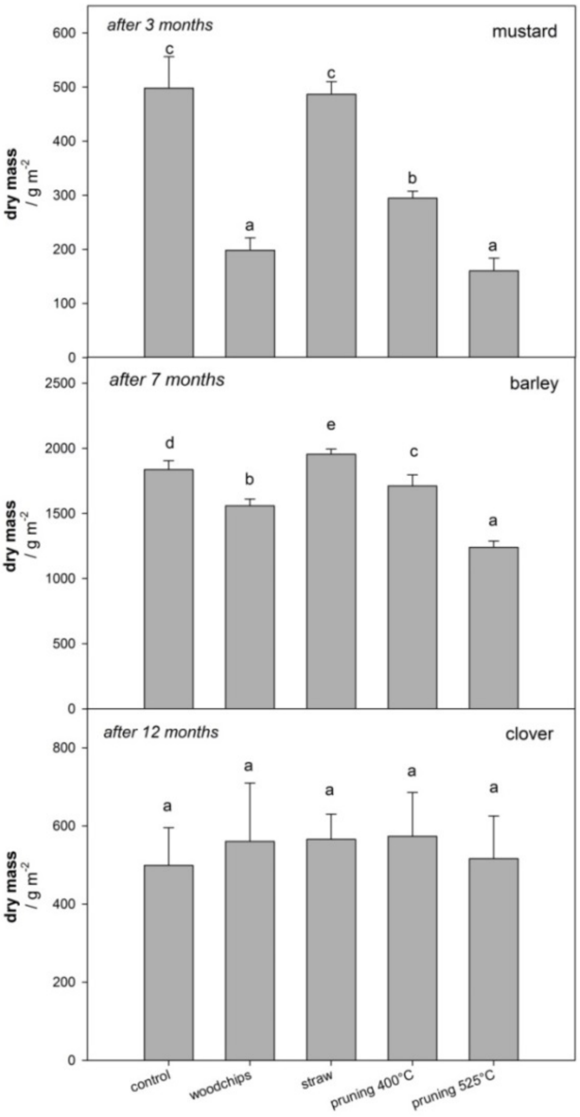

Figure 51 Effect of different biochars on above-ground dry matter production of three successive crops (mustard, barley, clover). Standard fertilization: 40 kg N ha-1 for mustard and 100 kg N ha-1 for barley. Control: standard fertilization without biochar. Different letters indicate significant differences at $P < 0.05$ (Tukey's post hoc test; n=5; Kloss et al., 2013, JPNSS, in review).

Mustard as the first crop showed that all BC types except WS led to a significant decrease of plant yield. The lowest mustard yields were found for VP525, where the decrease was 68% (161 ± 23 g m^{-2}) compared to the control (498 ± 58 g m^{-2}). The yield of barley as the second crop was also significantly depressed by BC application; however, the differences were less severe compared to mustard and showed even a significant increase with WS (by 6 %). Unlike the results of the soil analyses, Figure 51 shows that plant yield was initially affected by pyrolysis temperature showing significantly lower plant yield at higher HTT. After one year, no more significant differences were found for clover. Figure 52 displays the effect of different BC application rates on crop yields for three different agricultural soils.

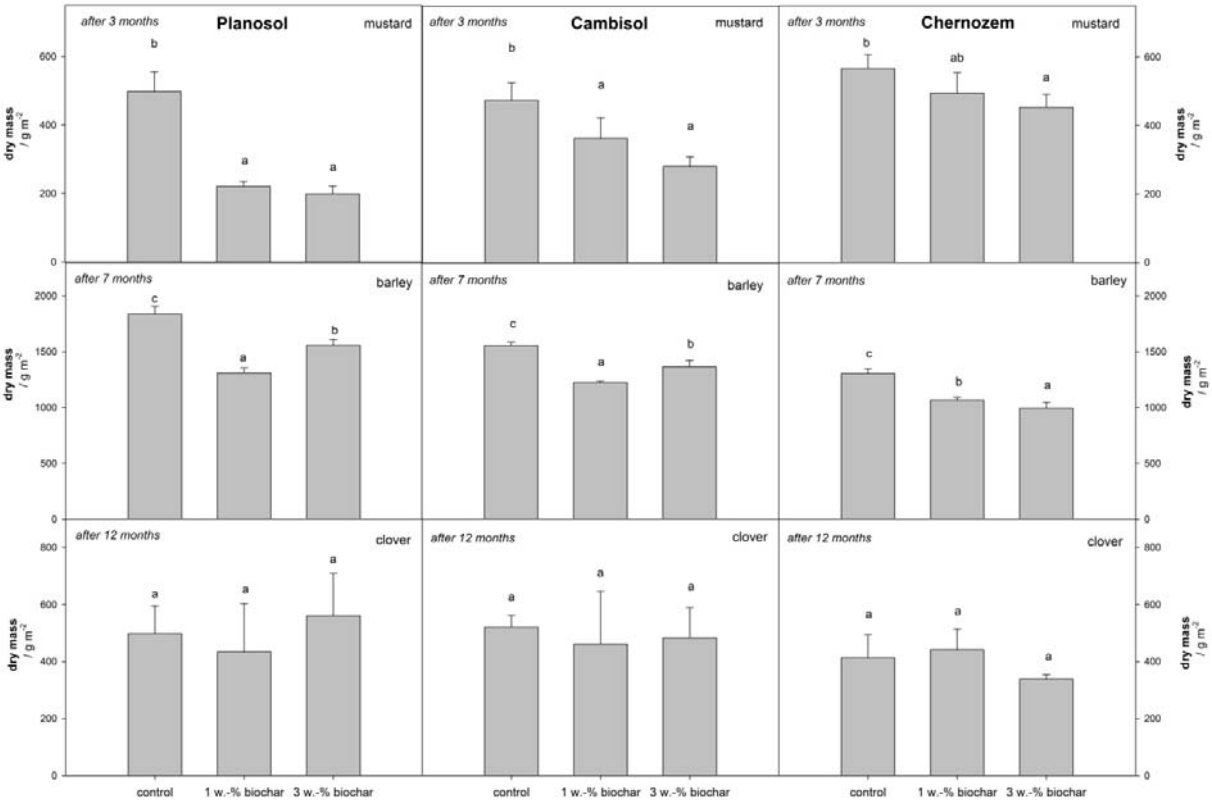

Figure 52 Effect of different biochar application rates on above-ground dry matter production of three successive crops (mustard, barley, clover) on three different agricultural soils (Planosol, Cambisol, Chernozem). Different letters indicate significant differences at $P < 0.05$ (Tukey's test; n=5; Kloss et al., 2013, JPNSS, in review).

Initial yield depressions for mustard were strongest in the Planosol, followed by the Cambisol and Chernozem. In all three soil types, decreased yields through BC were still observed for the second crop (barley) whereas for the third crop (clover) the yields in BC-amended soils were similar to those of the controls.

The results presented here indicate that the effects of BC on soil and especially crops are dependent on a variety of factors. Hence, we performed multivariate analyses of variances (MANOVA) to assess the influence of (i) BC type, (ii) soil type and BC application rate, and (iii) N fertilization and BC application on plant growth at different stages of the pot experiment. We determined the relative importance (indicated by % of R^2) of each of the above mentioned factors including interactions with the test of between-subject effects (Typ III sum of squares). The results are given in Table 13.

Table 13 Results of multivariate analyses of variance (MANOVA) investigating the effects of (i) biochar (BC) type, (ii) soil type and BC application rate as well as (iii) BC application and N fertilization on crop growth 3, 7 and 12 months after start of the pot

Biochar types

	mustard[a]		barley[b]		clover[c]	
	% of R²	p	% of R²	p	% of R²	p
BC type	95.5	**0.000**	97.5	**0.000**	9.8	0.801
unexplained	4.5		2.5		90.2	
	R²= 0.955	0.000	R²=0.975	0.000	R²=0.098	0.801

Soil types and Biochar application rates

	mustard[a]		barley[b]		clover[c]	
	% of R²	p	% of R²	p	% of R²	p
soil	40.3	**0.000**	76.5	**0.000**	12.4	0.133
BC application rate	42.1	**0.000**	14.7	**0.000**	1.9	0.718
soil x BC application rate	9.4	**0.000**	6.5	**0.000**	8.7	0.561
unexplained	8.2		2.3		77.0	
	R²= 0.918	0.000	R²= 0.977	0.000	R²= 0.230	0.453

Biochar application and N fertilization

	mustard[a]		barley[b]	
	% of R²	p	% of R²	p
BC application	65.3	**0.000**	1.5	**0.000**
N-fertilization	27.1	**0.000**	96.0	**0.000**
BC application x N-fertilization	0.9	0.352	1.7	**0.000**
unexplained	6.6		0.7	
	R²= 0.934	0.000	R²=0.993	0.000

[a]after 3 months
[b]after 7 months
[c]after 12 months

Table 13 summarizes our observations and shows that mustard and barley yield were largely dependent on BC type, whereas the BC type effect disappeared after 12 months, which is reflected by similar clover yields in the different treatments (Figure 51). MANOVA with the factors BC application rate and soil type revealed that both equally influenced mustard yield, whereas later barley yield was primarily influenced by soil type. The interaction of soil type and BC application rate was only of minor importance. MANOVA with the factors BC application and N fertilization rate showed a major effect of BC application rather than N fertilization rate on mustard growth, whereas barley yield was primarily influenced by N fertilization rate. The interaction of BC application and N fertilization was only of minor importance.

Conclusions

More results and corresponding discussion are presented in the manuscript Kloss et al., 2013 (JPNSS, in review; see appendix). The results of our study show that the effect of BC application is not only dependent on BC type and application rate, but may strongly vary with the amended soil type. The most remarkable effects, including an increase in CEC, were found for an acidic Planosol. The highest nutrient input was caused by WS. Nitrogen immobilization was found to be of minor importance. Initially depressed crop yields may have been caused by shifts in micronutrient availability and short-term BC-induced growth inhibiting effects. Only WS was able to initially maintain crop yields similar to the control and to increase yields beyond the control in the medium-term. The initially detrimental effects of the other BCs disappeared over time, which makes BC application to the soil a reasonable tool for C sequestration in the longer term. Ultimately, the combination of factors, such as micronutrient availability, N immobilization and growth-inhibiting effects seem to be crucial for crop growth on BC-amended temperate soils. This points out that post-treatments of BC prior to soil incorporation are needed to avoid initial growth-inhibiting effects.

Leachates

Selected results of the leachate characteristics are presented below and are prepared for submission (Buecker et al., 2013, AGEE). Previously, the data had been obtained within the scope of a Master thesis.

Figure 53 displays DOC concentrations of the leachates for different soil types and BC application rates from the 1st (Nov 25th, 2010) and 5th (May 10th, 2011) sampling date.

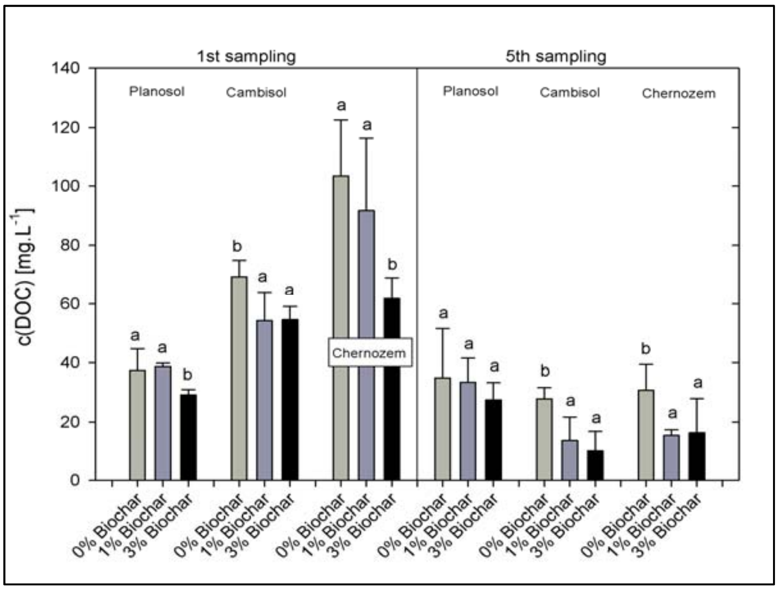

Figure 53 Dissolved organic carbon (DOC) concentrations of leachates for different soil types and biochar concentrations. Columns show means ± s.d.; Different letters indicate significant differences (n=5; $p<0.05$). (Buecker et al., in preparation).

Figure 53 shows that DOC concentrations in all soil types decreased after BC application, which may be due to an enhanced sorption of DOC on biochar surfaces or a decreased release of root exudates into the soil solution due to the lower plant production (Figure 52). Overall, DOC concentrations in the leachate decreased over time and were still significantly lower after 6 months. Concentrations of P_{DISS} for the different soil types and BC application rates are represented in Figure 54.

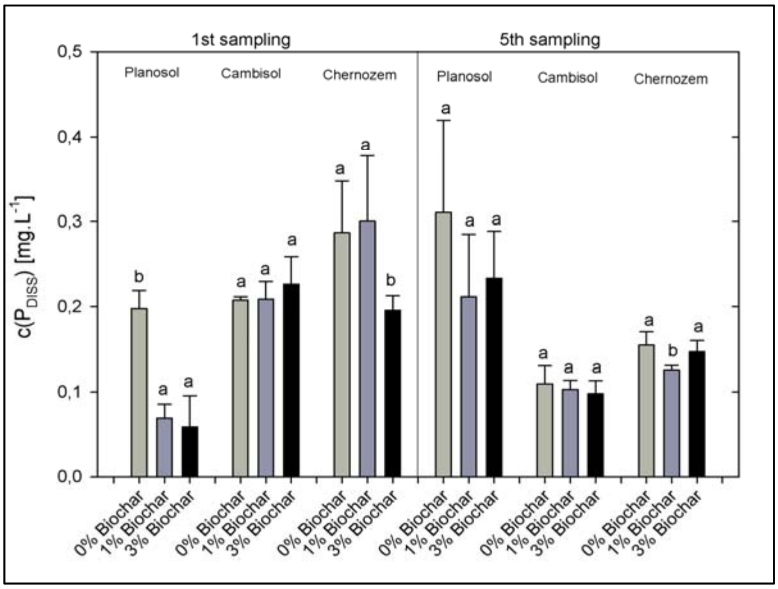

Figure 54 P_{DISS}-concentrations in leachates for different soil types and varying biochar concentrations (from woodchips); Columns show means ± s.d. Different letters show significant difference ($p<0.05$). (Buecker et al., in preparation).

We observed significantly decreased concentrations of P_{DISS} in the leachates of treatments with Planosol and biochar application at the 1st sampling (Figure 54). The application of 3 % BC to the Chernozem resulted in a significant decrease of P_{DISS}-concentrations in the leachates. At the end of the micro-lysimeter experiment, available amounts of P_{DISS} in the leachates of all biochar-amended treatments were lower compared to the control without biochar, but the differences were not significant with the exception of 1 M-% biochar-amended treatments with Chernozem. During the last three samplings, leachates from the Planosol showed significantly higher P_{DISS}-concentrations for both BC application rates than the leachates from the Cambisol and the Chernozem.

Field experiment

Selected results of the effects of BC application to soil on a field scale are presented below. Detailed effects on the soil can be taken from the manuscript of Karer et al. submitted to Agricultural and Food Science (see appendix).

Special attention within the course of the field experiments has been paid to the soil water as BC is expected to increase water holding capacity. Hence, pF curves were generated. They represent the relation between volumetric water content and the pF value, which is the logarithmic value of the matric potential (pF= log cm water column, hPa). Differences in the curve pattern are caused by differences in pore size distribution. Water-holding capacity is strongly related to SOM, which is increased by BC application in the soil. In addition, the extended pore system of BC may contribute to a higher WHC, which may be reflected in higher crop yields (Karhu et al., 2011; Jeffery et al., 2011) Hence, pF curves are expected to be different after BC application.

Figure 55 shows the pF- curves for BC treated soil in Traismauer and Kaindorf.

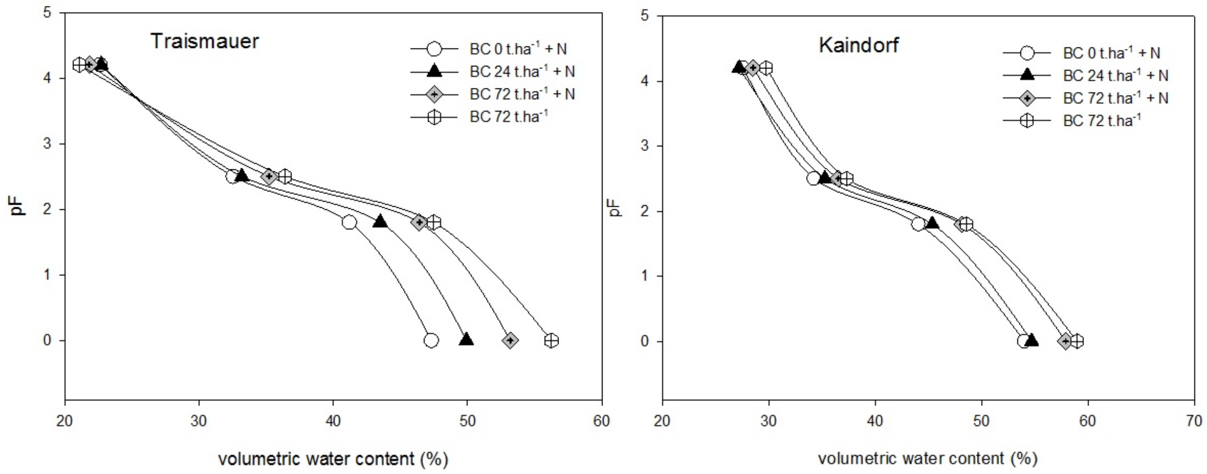

Figure 55 pF curves of the Chernozem (Traismauer) and the Cambisol (Kaindorf) soil (n=4). Volumetric water contents were determined at pF 0, 1.8, 2.5 and 4.2.

The pF curves for the two soils (Figure 55) show that both BC 72 t.ha^{-1} treated plots had significantly higher volumetric water contents at pF 0 and pF 1.8 compared to the fertilized control. There was no significance for the water contents at pF 2.5 while at pF 4.2 the BC 72 t.ha^{-1} treatment showed significantly higher volumetric water contents than BC 24 t.ha^{-1} + N application. Plant-available water (PAW) was calculated as the difference between pF 1.8-4.2 (in %) and is given in Table 14.

Table 14 Plant-available water (PAW) from the two sites Traismauer (Chernozem) and Kaindorf (Cambisol). PAW was calculated as the difference between 1.8-4.2 pF, in % (n=4).

	Plant-available water (%)	
	Traismauer	Kaindorf
BC 0 t.ha^{-1} + N	18.6 a	16.5 a
BC 24 t.ha^{-1} + N	20.8 a	18.2 ab
BC 72 t.ha^{-1} + N	24.6 a	19.6 b
BC 72 t.ha^{-1}	26.4 a	20.1 b

For Kaindorf, PAW was significantly higher after 72 t.ha^{-1} BC amendment both with and without N fertilization. However, in the Chernozem soil, the effects on PAW were not significant, whereas the pF curve (Figure 55) shows, similar to the Cambisol soil, that both BC 72 t.ha^{-1} treated plots had significantly higher volumetric water contents at pF 0 compared to the fertilized control. At pF 1.8 the BC 72 t.ha^{-1} treated plots in the Chernozem soil were higher compared to the control plot, but not at a significant level (0.059). There was no significance in the water contents at pF 2.5 and 4.2. Similarly, PAW was not affected by the varying treatments (Table 14).

Effects of BC application on straw and grain yields of the two field plots are given in Figure 56.

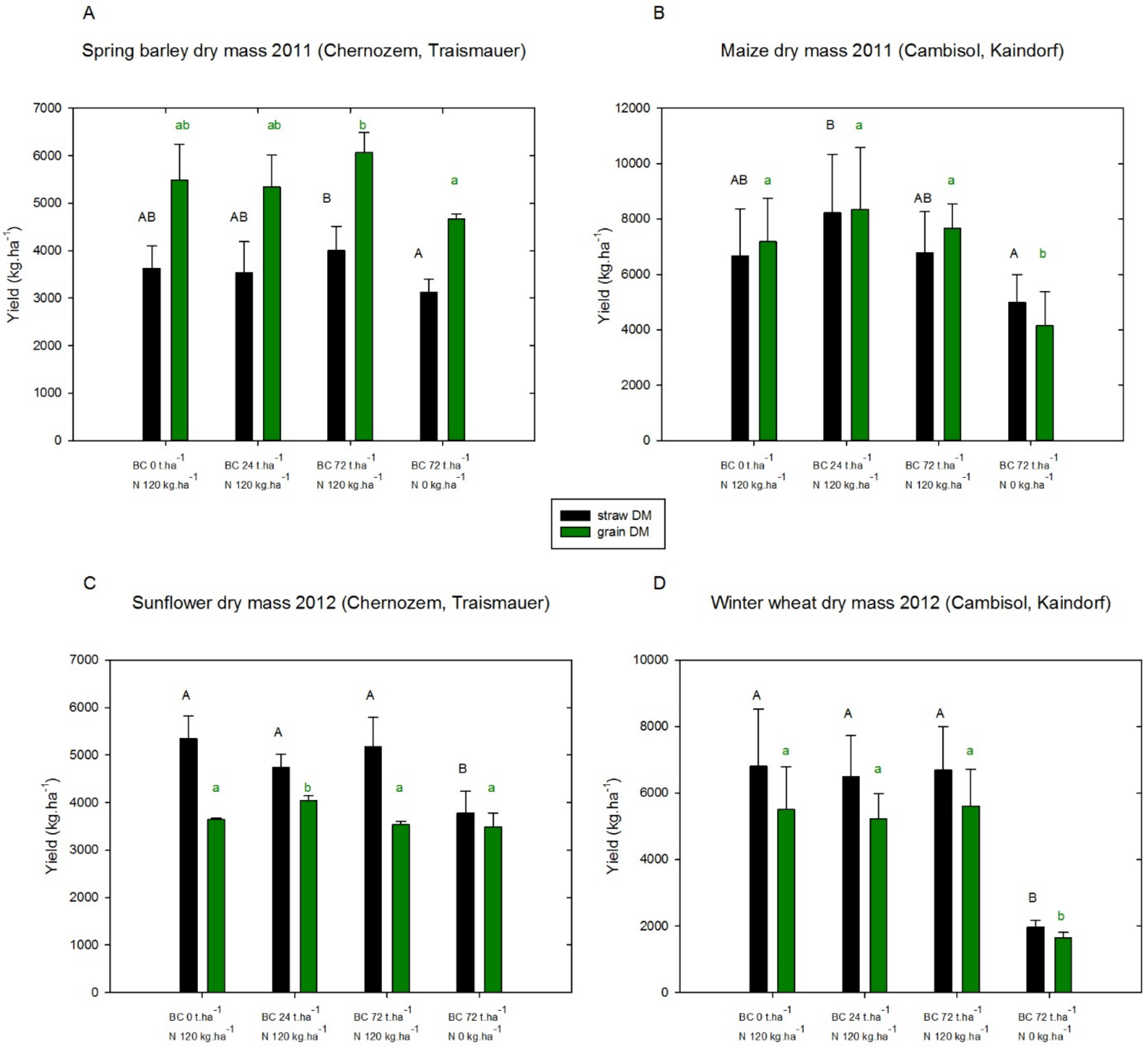

Figure 56 Grain and straw yield (dry matter (DM) of spring barley (A), sunflower (B), maize (C) and winter wheat (D) at varying biochar and nitrogen application rates. BC rates include 20 % water content, lower and upper case characters indicate significant differences ($p < 0.05$; Duncan's multiple range test).

In 2011, maize corn yield (Cambisol) was significantly reduced after 72 t.ha^{-1} BC application compared to the fertilized control (- 42 % decrease). Similarly, total barley yield (after 72 t.ha^{-1} BC) showed a significant decrease of 23 % when N application was absent. On the contrary, if N was added to 72 t.ha^{-1} BC, barley grain yield could significantly increase by 30 %. In 2012, total winter wheat yield decreased significantly (-71 %) after 72 t.ha^{-1} BC without N application. Similarly, sunflower total yield decreased significantly after 72 t.ha^{-1} BC application if N was missing, namely by 16 %. On the contrary, sunflower grain yield increased significantly after 24 t.ha^{-1} BC + N application (+ 11 %).

We found positive effects on the crop yields of our study for the Chernozem when BC was combined with a supplemental N fertilization, which is congruent with the results of Jeffery et al. (2011), Powlson et al. (2011b) and Atkinson et al. (2010). This points out the importance of investigating N limitation after BC application (Atkinson et al., 2010). We believe that the positive effects of BC on crop yield are most likely caused by the increased water holding capacity and the related increased PAW, from which the plants profited during the dry period (Figure 50).

Conclusions

The most distinct effect of BC on our investigated agricultural soils was an increase in WHC, accompanied by an increase in PAW. In particular, the increase of WHC was found to be beneficial in Traimauer, where a severe precipitation deficit occurred in 2011 (Figure 50). This shows that BC application may be a promising strategy to combat drought stress in dry regions.

Supplementary work

Besides the above-mentioned work on BC use as a soil amendment, we performed additional work focusing on BC as a potential measure for soil remediation. BC is increasingly considered for remediation purposes because of its high SSA and sorption potential as well as due to indirect effects such as an increase of soil pH. We concentrated on pesticides as well as heavy metals (HM). The former was tested using soil samples of the field experiments; the latter was tested more closely in terms of sorption mechanisms as well as considering altering HM behavior in the soil caused by BC aging using the soil samples from the glasshouse experiment.

Biochar as a remediation tool

Sorption of heavy metals and binding mechanisms

Heavy metals (HM) are metals that have a density of more than 5 g cm^{-3}. Some of them are toxic even at low concentrations such as cadmium (Cd), arsenic (As), lead (Pb) and mercury (Hg) and are therefore of concern for the environment. They occur naturally; however, human activities such as excessive agriculture, mining and industry partly tremendously increased HM concentrations in the soil. Moreover, depending on the HM and its speciation, the mobility of HM may vary. For instance, Cd is highly mobile and can therefore be easily taken up by plants. In general, the solubility of HM is largely controlled by pH. At pH > 6, Cd is immobilized in the soil by precipitation and sorption. Cu, on the other hand, strongly interacts with organic substances in the soil and is less mobile than Cd. In contrast to organic pollutants, HM are not biologically degradable.

Due to BCs high pH as well as high SSA and CEC, respectively, BC may be considered as a potential tool for HM retention in the soil. The extent of HM sorption is dependent on the properties of the BCs such as O/C ratios and recalcitrance. In addition, sorption is expected to further change with time as BC aging in the soil may increase O containing surface functional groups such as carboxyl groups.

Therefore, the purpose of this additional study was to

- investigate Cd and Cu adsorption behavior in the Planosol treated with different BC types

- investigate the effects of BC aging within a 15 months period in the soil on Cd and Cu adsorption
- elucidate sorption mechanisms in terms of BC aging using Environmental Scanning Electron Microscopy (ESEM), Fourier-Transform-Infrared Spectroscopy (FTIR) and X-ray absorption spectroscopy (XAS)

The adsorption experiments were carried out at the Department of Crop and Soil Sciences, Cornell University, Ithaca, NY under supervision of Prof. J. Lehmann.

Materials and Methods

Sorption experiments were conducted with selected pots from the glasshouse experiment as described in 0/ Figure 47. The pots were sampled in March 2012, 15 months after start of the pot experiment and included following treatments:

- Planosol control (no BC)
- Planosol + 3 w.-% WS
- Planosol + 3 w.-% WC
- Planosol + 3 w.-% VP400
- Planosol +3 w.-% VP525

In addition, the original soil-BC mixtures from the start of the pot experiment (November 2010) were used (n=3). These included following treatments:

- Planosol control (no BC)
- Planosol + 3 w.-% WS
- Planosol + 3 w.-% WC

Stock and working solutions

Cd and Cu stock solutions were prepared using $CdCl_2$ and $CuCl_2$, respectively. 8 concentration steps were chosen for the adsorption experiments ranging from 0 to 200 mg L^{-1} for Cd and 0-400 mg L^{-1} for Cu. All solutions were produced with 0.01 M $CaCl_2$ as a background electrolyte.

Adsorption procedure and measurement

4 g of soil was weighed into acid washed centrifuge tubes and treated with 40 mL of the respective working solution. The tubes were shaken for 24 h on a horizontal shaker and filtrated. The filtration process is shown in Figure 57.

Figure 57 Filtration of samples after 24 h adsorption

Cd/ Cu concentration was measured using an Atomic Absorption Spectrometer (AAS; Buck Scientific Atomic Absorption Spectrometer Model 210 VGP; air-acetylene method). Cd was measured at a wavelength of 228.9 nm, Cu at 324.7 nm. Standard solutions were prepared ranging from 0 to 2 ppm. A calibration curve was fitted using the standard solutions and the given absorbance value, which was then transferred into ppm using the quadratic equation:

$$f = y0 + ax + x^2$$

Calibrations curves for Cd and Cu are given in Figure 58.

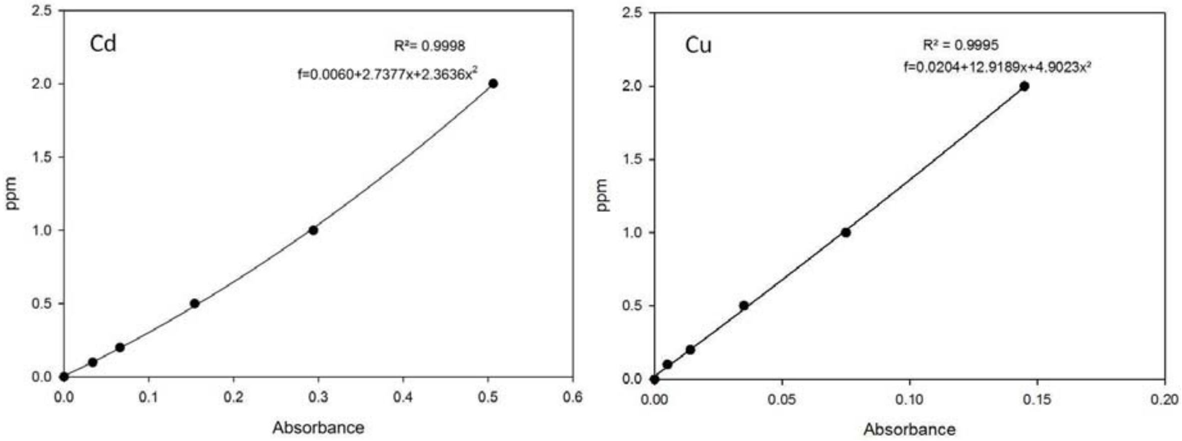

Figure 58 Calibration curves for Cd and Cu

The AAS is displayed in Figure 59.

Figure 59 Atomic absorption spectrometer

The amount of adsorbed Cd/ Cu was calculated by subtracting the concentration of the Cd/ Cu in the solution from the concentration of Cd/ Cu in the blanks. The unit ppm was then transferred into mg kg^{-1}. Adsorption isotherms were obtained by plotting the amount adsorbed to the soil-BC mixtures against the concentration in the solution. In addition, pH of the filtrates was measured prior to stabilizing the filtrates with one drop of HNO_3.

Results and discussion

Different biochar types

Results of pH of the soils used for the sorption experiments are given in Figure 60.

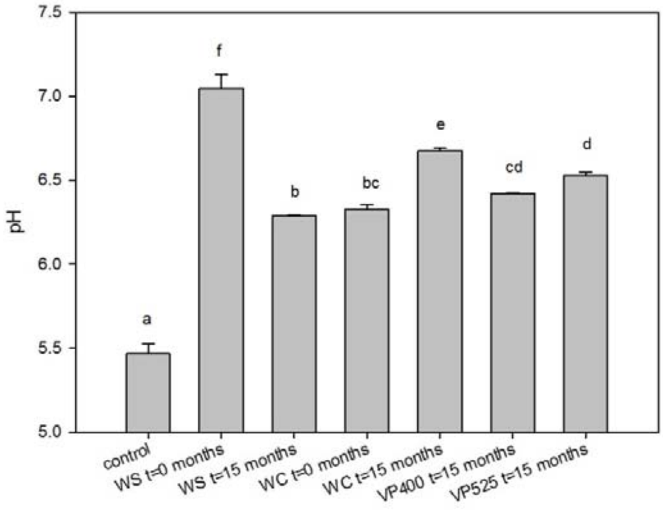

Figure 60 pH measurements of the soil samples used for sorption experiments. Biochars: WS: wheat straw (treatment temperature 525°C); WC: woodchips (525°C); VP400: vineyard pruning (400°C); VP525: vineyard pruning (525°C) (t=0: 0 months; t=1: 15 months after start of the pot experiment). Control: Planosol without biochar.

The results show that all BC treatments had a significantly higher pH after BC application compared to the control (Planosol). The pH in WS (t=0) was initially highest due to the high alkalinity (Table 9); however, much of the alkalinity was lost within 15 months after start of the pot experiment, probably due to leaching or plant uptake, which therefore considerably decreased pH. For WC, however, the opposite trend was found. Here, pH was significantly higher after 15 months compared to the initial soil-BC mixtures. It is yet unclear why pH increased for the WC treated soil. One possibility could be a slower release of basic cations compared to the WS treated soil, which then over time increased pH.
Adsorption isotherms for the different BC types in the Planosol are given in Figure 61.

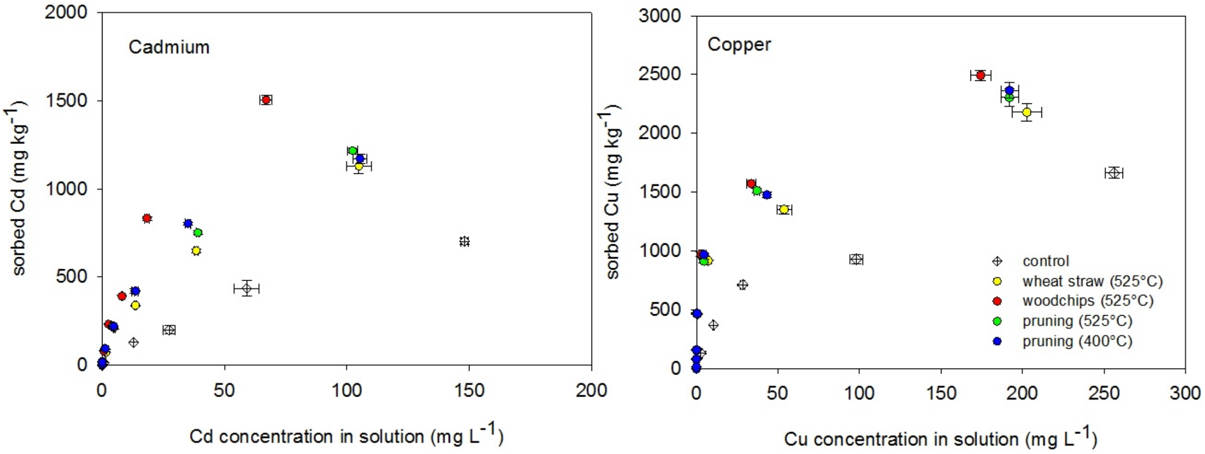

Figure 61 Adsorption isotherm for Cd (left) and Cu (right) for the different biochar treatments (Planosol; 3 w.-% BC application rate; 15 months after start of the pot experiment).

Both Cd and Cu adsorption considerably increased for all BC treated soils. We found no clear difference in sorption isotherms in face of pyrolysis temperature. A characteristic feature of BC application to soil is the increase in soil pH, at which the extent of pH increase is dependent on the initial soil pH as well as on the pH of the used BC (Rondon et al., 2006). Comparing pH of the individual BCs, WS showed the highest pH with 9.7, followed by WC with 8.9 (Table 9). The high pH was also found in the filtrates after adsorption (data not shown). However, sorption isotherms were highest for WC treated soils both for Cd and Cu, followed by VP525. Hence, sorption mechanisms other than a pH effect must be anticipated.

The results show that sorption is predominantly dependent on the feedstock type and less on the pyrolysis temperature, which is unlike the findings of Uchimiya et al. (2010) who found a clearly higher sorption potential for low-temperature BC due to a higher abundance of functional groups remaining after pyrolysis. By relating CEC to SSA (Table 9), the surface charge density can be calculated (data not shown). The charge densities were 12.11 µmol$_c$m^{-2} for WS, 3.52 µmol$_c$m^{-2} for WC, 73.08 µmol$_c$m^{-2} for VP400 and 16.25 µmol$_c$m^{-2} for VP525. The two latter results show that surface charge density for VP525 is considerably lower than for VP400, which can be attributed to a loss of surface functional groups at a higher pyrolysis temperature, which, however, is not effective enough to affect sorption behavior (Figure 61). In addition, despite the lowest surface charge density for WC (3.52 µmol$_c$m^{-2}), WC obtained the highest sorption isotherm. This shows that Cd and Cu adsorption in BC treated soils may not controlled by SSA. This was also found by Cao et al. (2009), who compared Pb sorption to BC and activated char. In addition, despite the highest pH of WS (Table 9), sorption on WS treated soil was lowest after 15 months (Figure 61) compared to the other feedstocks, which may be due to plant uptake and leaching of alkaline substances and is also shown in the decrease of pH with time (Figure 60). On the other hand, pH of the WC treatment in the filtrate after Cd adsorption shows that pH of WC is only slightly higher than WS and yet shows the highest adsorption isotherm, which shows that Cd adsorption on WC treated soils may not only be controlled by pH.

Effect of biochar aging in the soil on Cd and Cu sorption

The effect of BC aging of WS and WC, i.e. differences in Cd and Cu sorption at 0 months and 15 months after start of the pot experiment, is displayed in Figure 62.

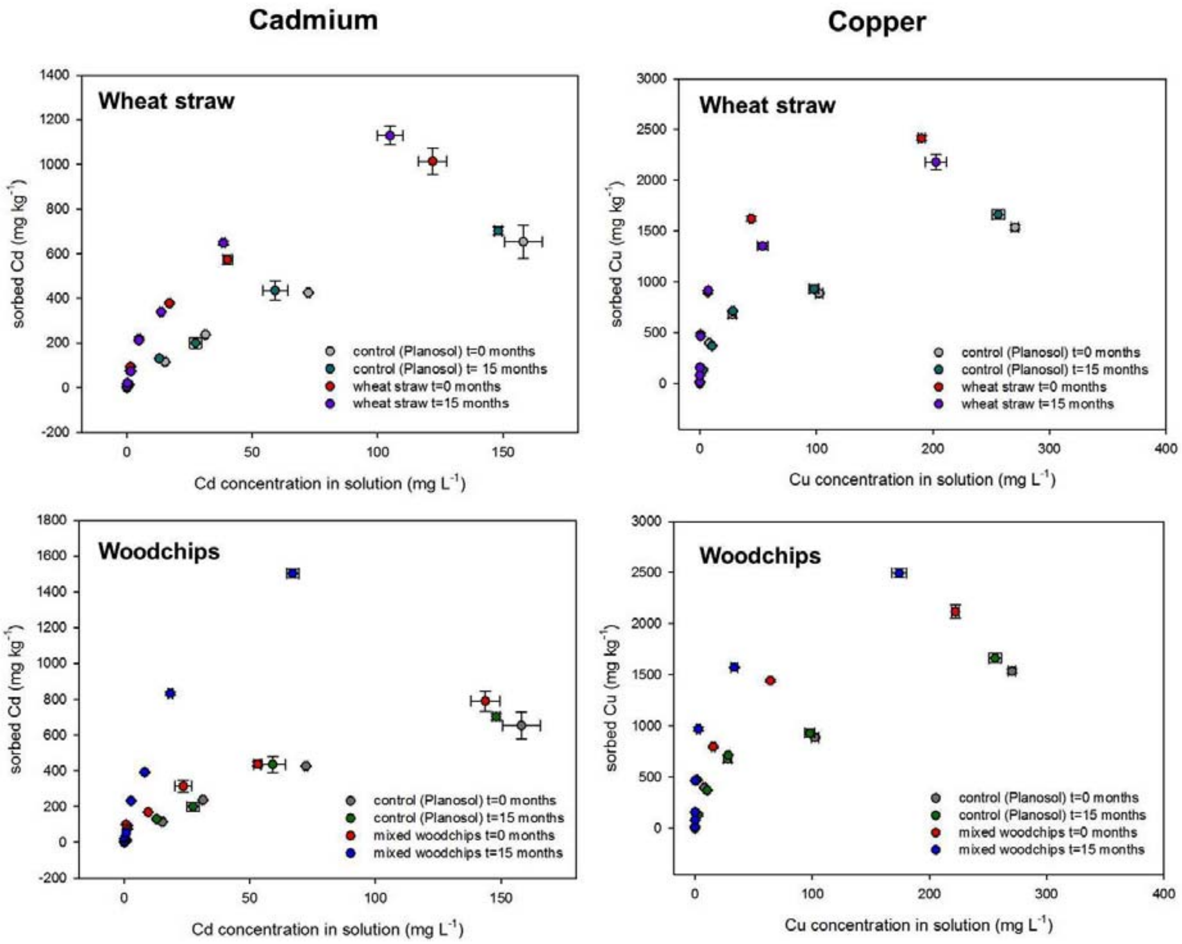

Figure 62 Effects of wheat straw and woodchips derived BC aging in the soil on Cd and Cu sorption behavior (0 and 15 months after start of the pot experiment)

Associated with the results shown in Figure 61, sorption capacity of WS-treated soil was considerably higher both at t=0 months and t=15 months compared to the control (Figure 62). Cd adsorption isotherms showed that sorption capacity in WS-treated soils was higher after 15 months compared to the start of the pot experiment, which shows that BC sorption capacity improved over the time interval of 15 months even though we found a decrease of pH (Figure 60). For Cu, however, we found an opposite trend where Cu sorption decreased after 15 months. This may prove that Cu sorption is more pH dependent whereas sorption potential for Cd, independently from the pH decrease, increased after 15 months. In addition, it is also possible that our WS contained high amounts of P, which was previously found in WS-derived BC compared to other feedstocks (Kloss et al., 2012). BC-derived P and Cu may have interacted and formed insoluble Cu-phosphates. Cao et al. (2009) found that Pb in P-rich BC treated soils precipitated as phosphates and was therefore immobilized. The long-term loss of P due to leaching and plant uptake, which was observed by Kloss et al. (2013) may have decreased precipitation as Cu phosphates and may have therefore caused the reduction of Cu immobilization. In addition, the long-term effect of BC application to soil on heavy metal sorption was found to be a function of recalcitrance. Straw-derived BC is less recalcitrant than wood-derived BC (Kloss et al., 2012) and may therefore, especially in the long-term, be less suitable for heavy metal immobilization.

Unlike for WS-treated soils, Cd and Cu adsorption was congruent on WC-treated soils (Figure 62). The isotherms show that Cd adsorption highly increased within 15 months whereas the initial WC-soil mixture was only slightly higher than the control. Cu adsorption isotherms accordingly showed an increase of the sorption behavior compared to the initial WC soil mixture. Despite Cu adsorption on WS-treated soils that showed a decrease in sorption potential over time, an increase in sorption potential within the 15 months period was observed. It was often found that oxidation of BC increases the formation of surface functional groups (Cheng et al., 2006; Cheng et al., 2008; Uchimiya et al., 2012) although over a long period of time, BC was suggested to be highly stable in the soil (Seiler and Crutzen, 1980; Kuhlbusch, 1998). Degradation of BC may occur abiotically through chemical oxidation, photo-oxidation and solubilization as well as biotically through microbial incorporation or oxidative respiration of C (Zimmerman, 2010). Uchimiya et al. (2012) oxidized different BCs and detected an increase in O/C of the oxidized BC compared to the untreated BC; BC oxidation was confirmed by FTIR spectra that showed an increase in C=O stretching of carboxyl functional groups as well as increases in the bands assigned to C=O stretching of conjugated ketones and quinones and C-O stretching of phenols, which overall increased stabilization potential for Pb, Cu and Zn. As Figure 62 generally showed an increase in sorption potential for Cd and Cu despite decreases in pH to a different extent, the oxidation of our BCs in the soil is likely.

Synchrotron-based techniques

To gain mechanistic insights into heavy metal binding in relation to speciation as well as reactive functional groups, we applied synchrotron-based x-ray absorption spectroscopy (XAS). XAS spectra give information about the chemistry of an element and are divided into 2 energy regions:

- X-ray absorption near edge spectroscopy (XANES)/ near edge X-ray absorption fine structure (NEXAFS): covers the spectra from the pre-edge region to approx. 50 eV above the specific absorption edge, followed by
- extended X-ray absorption fine structure (EXAFS). EXAFS spectra display interferences and backscattering of neighbouring atoms and give information about the identity of surrounding atoms, bond distances and coordination numbers (Koningsberger and Prins, 1988; Lombi and Susini, 2009).

At this, sorption experiments on the pure, fresh woodchips-derived BC (WC_0) were carried out and compared with sorption behavior of soil-aged BC, which stayed in the pots for 15 months (WC_{15}). Prior to the conducting XAS measurements, the latter was isolated using tweezers (Figure 63).

Figure 63 Biochar isolated from the soil 15 months after start of the pot experiment.

Subsequently, the aged BC was treated with ultrasound to remove any soil particles from the surface to avoid measurement interferences and interpretation difficulties. For better comparison, the original BC was also treated with ultrasound.

Afterwards, Cu adsorption at a micro-scale (0.05 g BC, 10 mL solution) with 2 concentrations, 5 mg L^{-1} and 100 mg L^{-1}, was carried out. During adsorption, pH was adjusted to 4 several times. After 24 hours, pH was adjusted again and the BCs were filtered using a membrane filter and washed with distilled water several times. XAS was carried out at the National Synchrotron Radiation Research Center, Hsinchu, Taiwan, in cooperation with Prof. Shan-Li Wang from National Taiwan University (NTU) in Taipei, Taiwan. Due to the fragility of WS, this could only be performed with WC.

Preliminary results can be presented for Cu; Cd measurements will be carried out in June at the facility mentioned above.

Figure 64 shows an EXAFS spectrum for Cu including fresh (red line) and soil-aged (green line) BC.

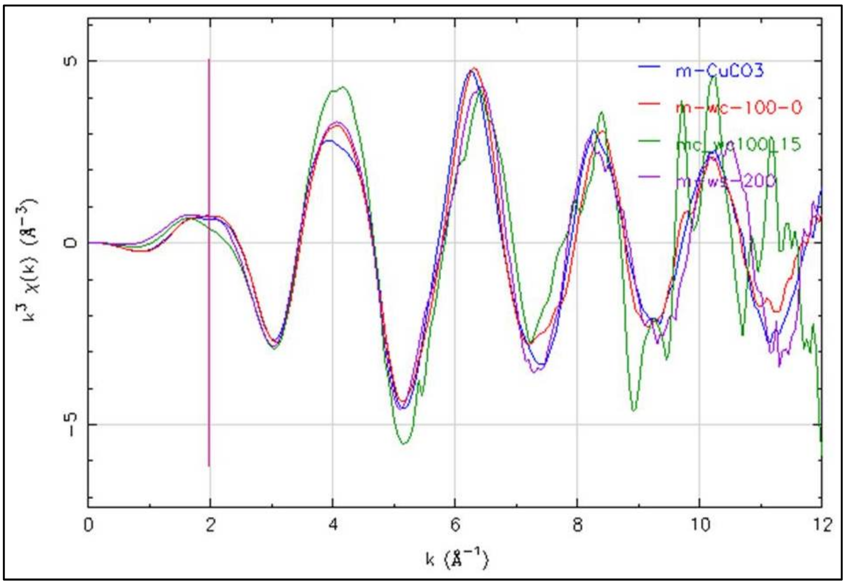

Figure 64 Derivation of EXAFS spectrum (Cu) of fresh (red line) and soil-aged (green line) woodchips-derived biochar

The pattern of WC_{15} (green line) is clearly different from the spectrum of WC_0, which proves that aging in the soil changed the sorption mechanisms of Cu on BC surfaces. Figure 65 shows 2 EXAFS spectra of fresh and aged WC in comparison to selected pure Cu species. Comparing WC_0 with WC_{15} Figure 65 highlights that fresh WC resembles $CuCO_3$, whereas soil-aged BC is rather similar to CuC_2O_4 (oxalate), which is related to the formation of –COOH groups and give therefore information on oxidation processes that occurred in the soil within 15 months.

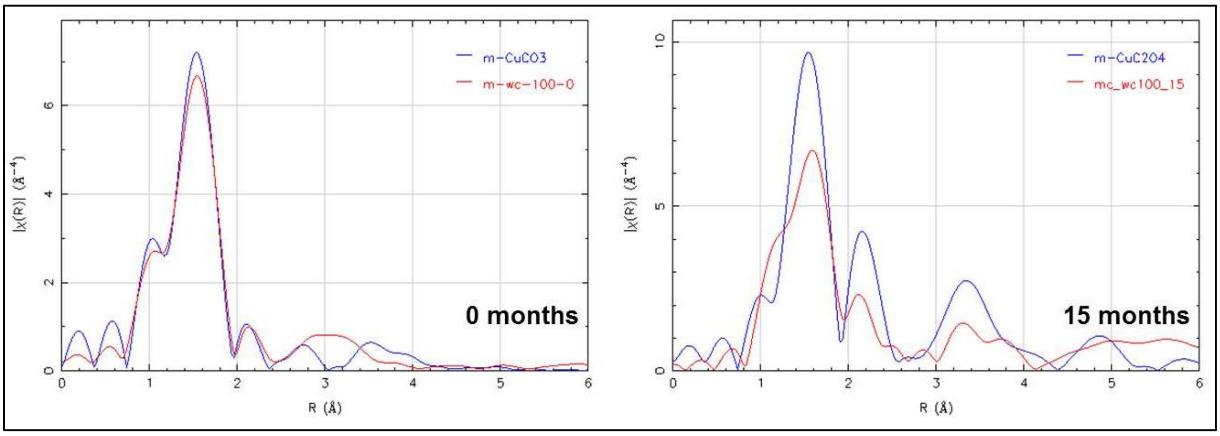

Figure 65 EXAFS spectra (Cu) of fresh (left picture) and aged (right picture) BC in relation to Cu speciation.

To follow these aging-induced changes, Environmental Scanning Electron Microscopy (ESEM) and FTIR measurements have been additionally carried out.

To obtain FTIR spectra, WC_0 and WC_{15} were first ground in a ball mill for 5 min at 1500 rpm. Then, 0.15 mg of the BC was mixed with KBr in a ball mill for 2 min at 1200 rpm and pressed to 200 mg KBr pellets (1.3 mm diameter). FTIR spectra were obtained by measuring the absorbance at a resolution of 2 cm^{-1} with 16 scans per sample (Tenor 27 SN 1683; Bruker, Austria). The spectra were corrected against a pure KBr spectrum. Results of the FTIR are given in Figure 66.

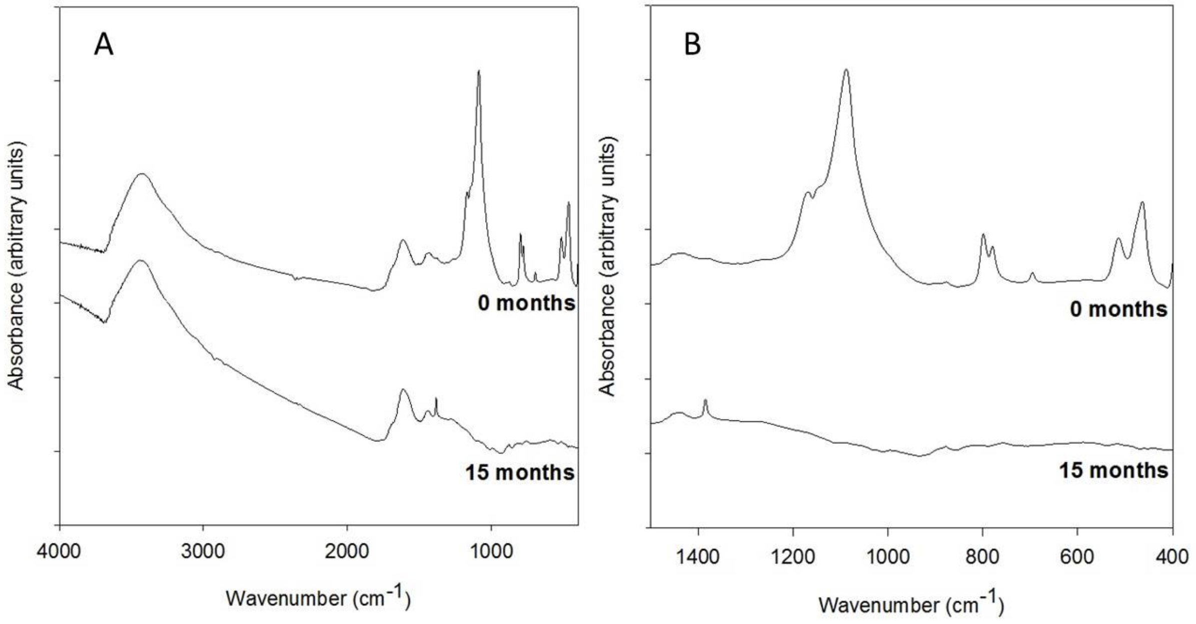

Figure 66 Fourier-Transform Infrared Spectroscopy (FTIR) spectra of fresh (0 months) and soil-aged (15 months) Woodchips-derived biochar. One increment of the y-axis corresponds to 0.1 absorbance units (n=1). A) Full spectra from 4000 to 400 cm^{-1}; B) fingerprint region from 1500 to 400 cm^{-1}.

Figure 66 shows that especially the fingerprint region (B; 1500- 400 cm^{-1}) showed considerable peak reductions and disappearances for WC_{15} compared to WC_0. WC_0 obtained a main peak between 1133 and 1055 cm^{-1} with a peak maximum at 1087 cm^{-1}, which may be attributed to the C-O-C symmetric stretching characteristic for carbohydrates (Haberhauer and Gerzabek, 1999; Schwanninger et al., 2004). The fact that the C-O-C peak disappeared within 15 months may be a sign that BC in the pots has been decomposed. In more detail, carbohydrates that have remained in the BC belong to the more easily degradable fraction in the BC, which then decomposed. Hence, this technique may also prove to be useful for the long-term incubation experiment in WP 3. In addition, Figure 66 shows that a new peak occurred for WC_{15} in the range of 1398- 1367 cm^{-1} with a peak maximum at 1384 cm^{-1}. It is yet unclear what this peak represents; further research on this is necessary and will be followed within the following weeks.

Figure 67 gives the pictures obtained by ESEM at two resolutions (150 and 1000 fold magnification) for WC_0 (A, B) and WC_{15} (C, D).

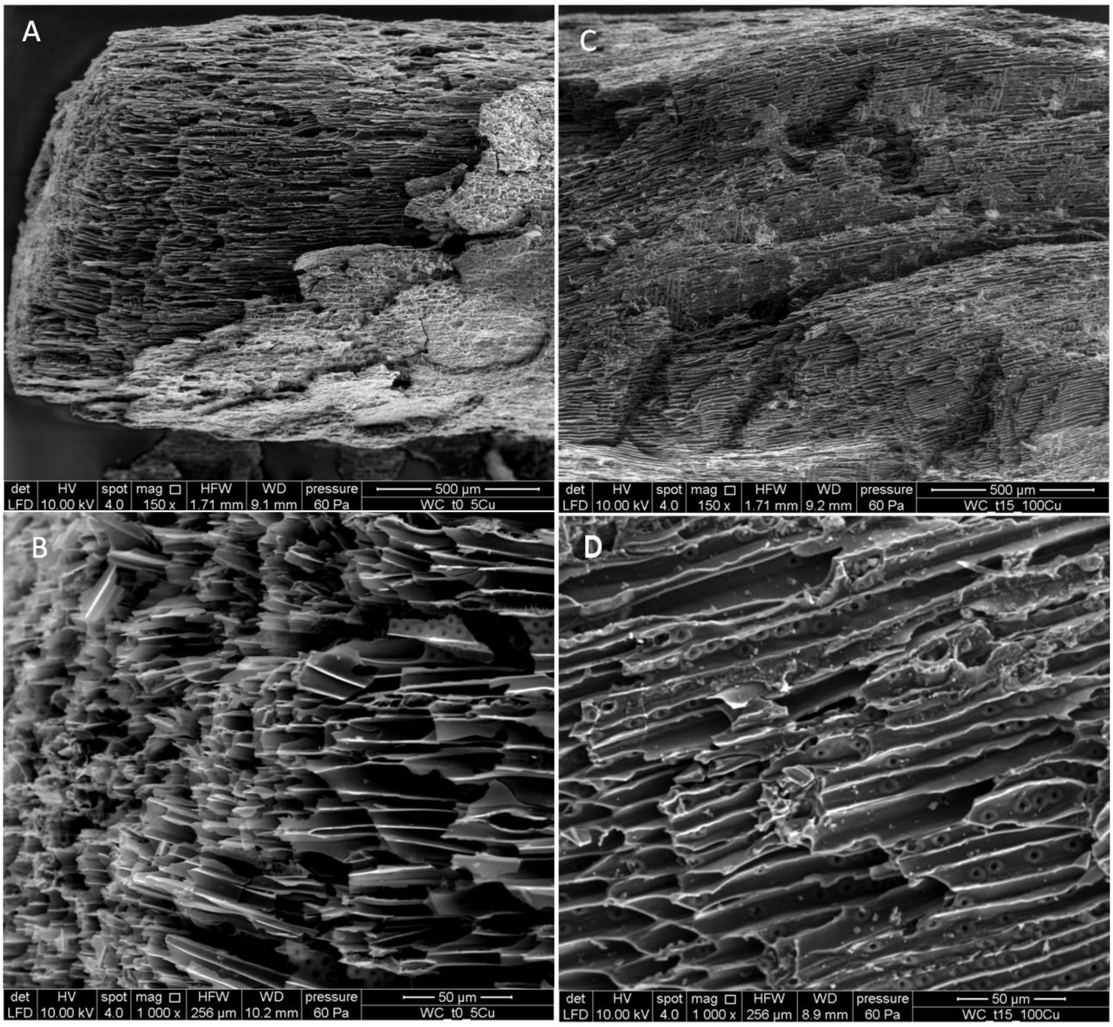

Figure 67 Environmental Scanning Electron Microscopy (ESEM) pictures of fresh, woodchips-derived biochar (A: 150 x magnification; B: 1000 x magnification) and 15 months soil-aged woodchips-derived biochar (C: 150 x magnification; D: 1000 x magnification).

Figure 67 shows that WC biochar has a distinct microporosity, which may offer microorganisms habitats. The surface of WC_{15} is more disordered than WC_0, which may have been caused by interactions in the soil and points out that BC is not inert in the soil as it has been stated for a long time. In detail, this may include physical decomposition and fragmentation to smaller particles, which then offer a higher surface where chemical and biological changes may occur (Cheng et al., 2006; Hammes and Schmidt, 2009). Within the scope of our pot experiment, this may on the one hand be the partial decomposition of smaller BC particles, on the other hand the penetration of plant roots and fungal hyphae as well as the formation of organo-mineral complexes (Lehmann et al., 2003; Hammes and Schmidt, 2009). In fact, we found the latter sporadically in our ESEM pictures despite ultrasound treatment.

Sorption of herbicides

Chloridazone and terbuthylazine are both selective herbicides. Their application is relevant to the environment as they may also affect non-target organisms and may be subject to leaching and therefore pose danger to the surrounding water bodies.

Sorption experiments including the generation of desorption isotherms using BC treated soils from the field sites (Kaindorf and Traismauer) were performed with the above-mentioned herbicides. The experiments have been carried out at the Institute of Sanitary Engineering, and Water Pollution Control (BOKU). Results of the adsorption isotherms for chloridazone and terbuthylazine are presented in Figure 68.

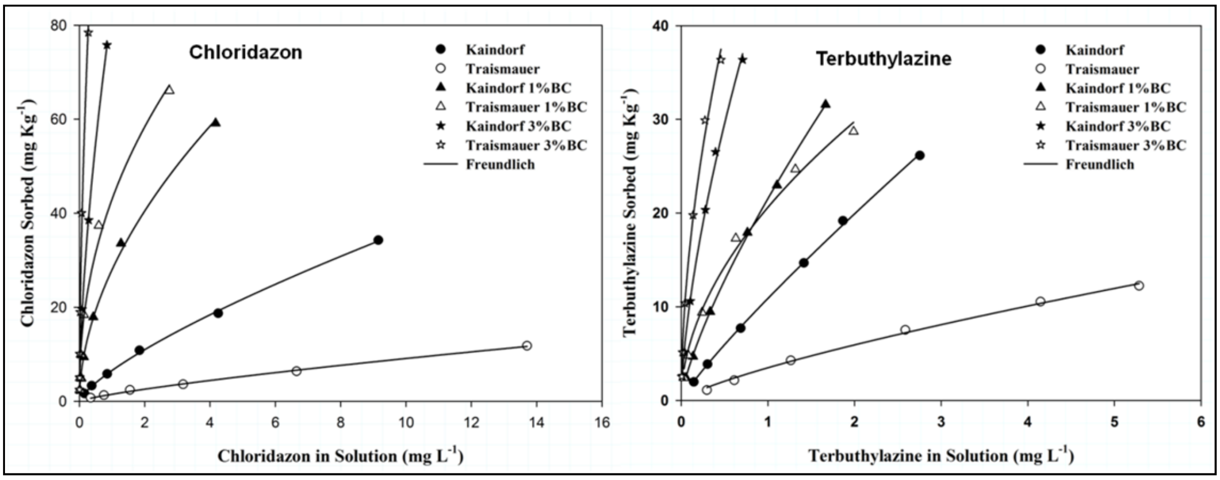

Figure 68 Freundlich adsorption isotherms for chloridazone and terbuthylazine for biochar (BC) treated soils from Kaindorf and Traismauer. 1% BC equals 24 t ha^{-1}, 3 % equals 72 t ha^{-1} application rate (dry weight).

Figure 68 shows that the sorption potential of both herbicides is considerably improved for the BC treated soils at both sites. Also, sorption potential was always higher at higher BC application rates.

After each adsorption step, desorption isotherms were subsequently generated by desorbing the investigated soils six times with water followed by a final desorption step with methanol. Figure 69 shows the desorption isotherms for chloridazone for both field sites (Kaindorf left, Traismauer right); analogous, Figure 70 shows the desorption isotherms for terbuthylazine. Desorption isotherms are different from the included adsorption isotherm showing a hysteresis effect for the control soils Traismauer and Kaindorf. About 50-65 % of the herbicides could be removed by desorption. Figure 69 and Figure 70 show that BC application to soil considerably increased the hysteresis effect; desorption of the two herbicides ranged from merely 1-7 %. The results therefore show that herbicides are much more strongly bound to the soil-BC mixture, and BC may therefore be useful as a soil remediation measure for herbicide-polluted soils.

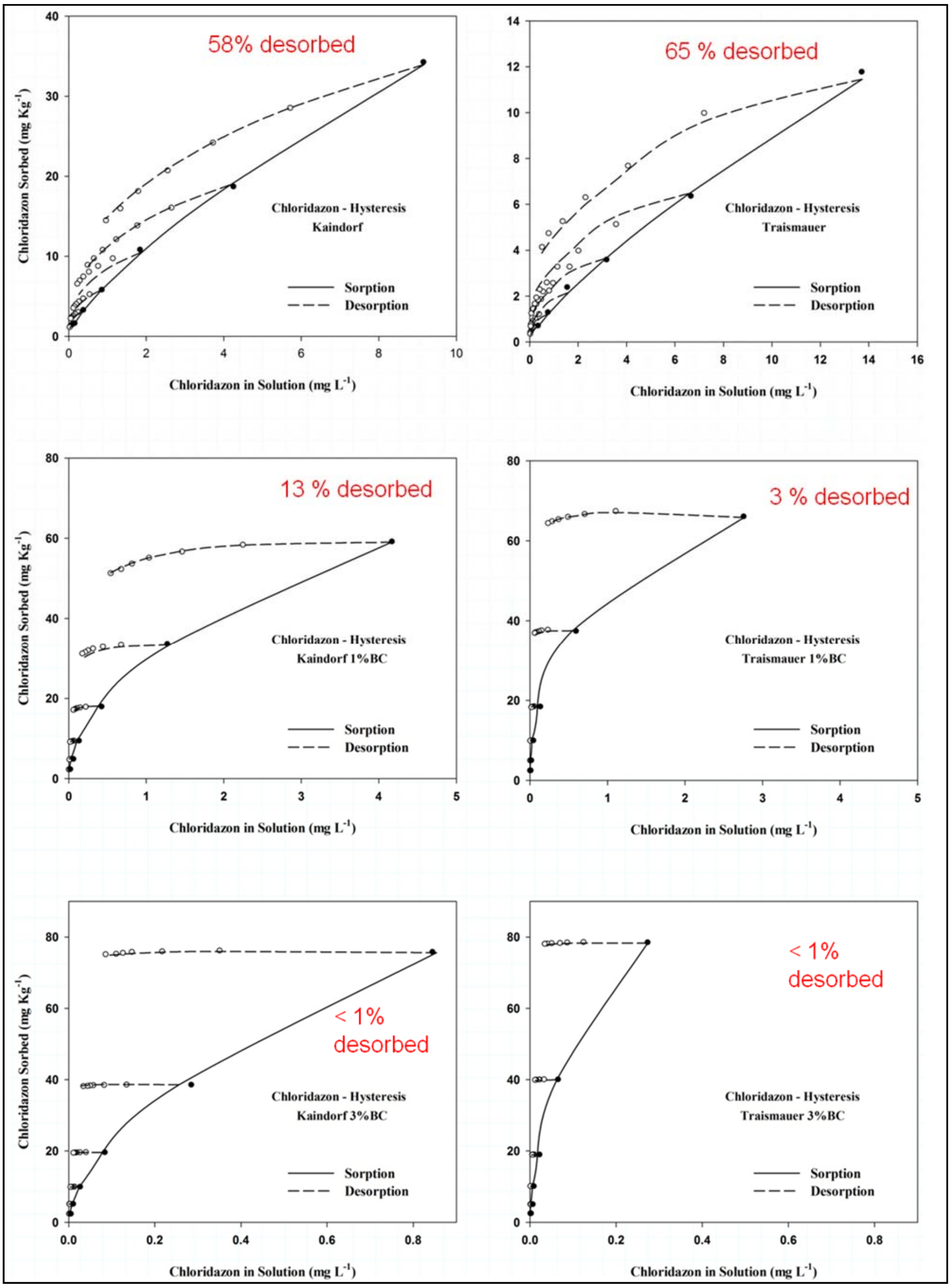

Figure 69 Chloridazone desorption isotherms of the soils with 0, 1 (24 t ha^{-1}) and 3 (72 t ha^{-1}) w.-% BC application for Kaindorf (left column) and Traismauer (right column).

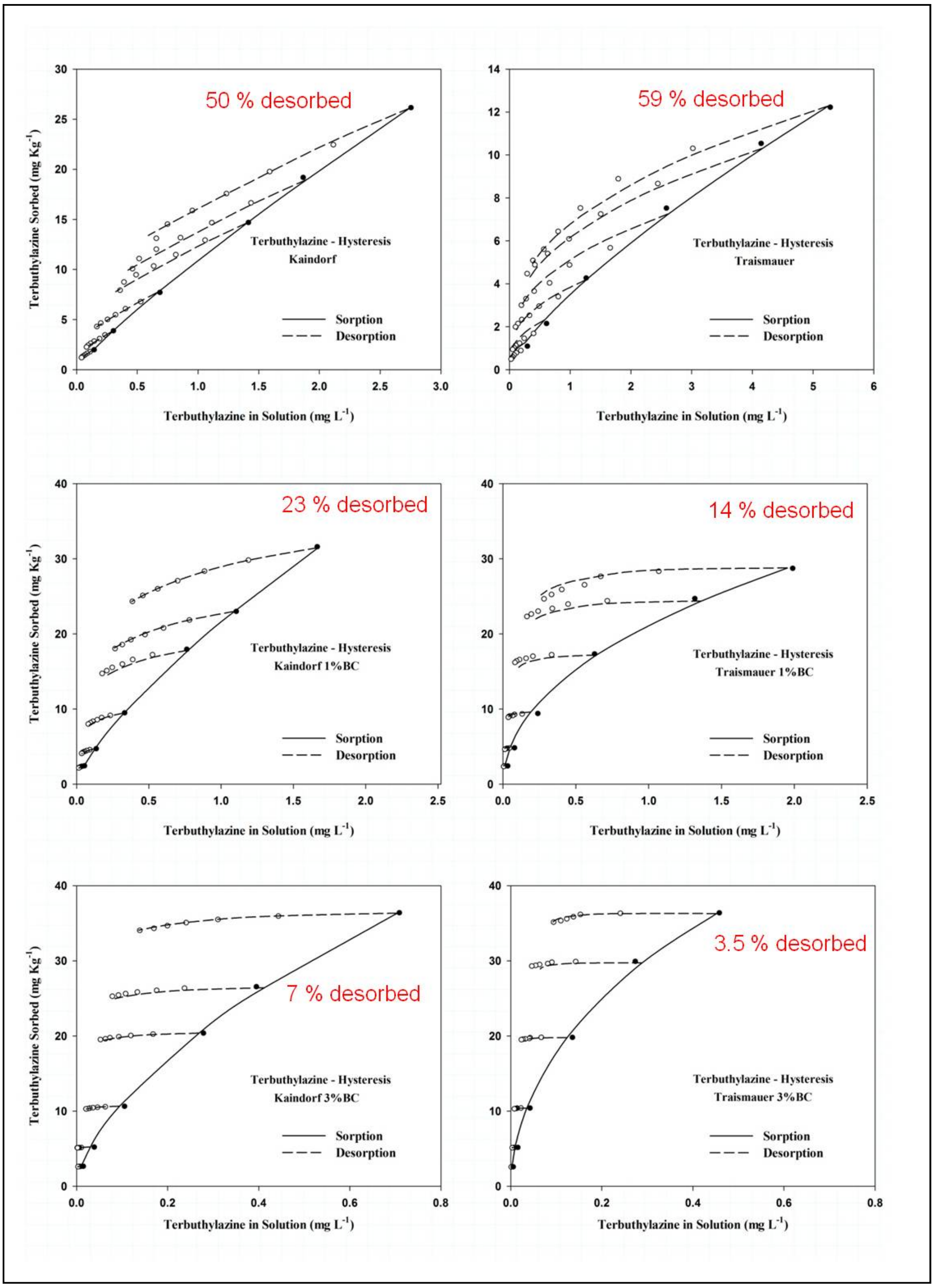

Figure 70 Terbuthylazine desorption isotherms of the soils with 0, 1 (24 t ha^{-1}) and 3 (72 t ha^{-1}) w.-% BC application for Kaindorf (left column) and Traismauer (right column).

Effects of biochar on trace metal availability

In addition to the sorption potential for HM, we also investigated the effect of BC on the availability of trace metals. At this, we carried out soil extractions using NH_4NO_3. We compared trace metal availability at t=0 and t=7 months as displayed in Figure 47; in addition we investigated trace metal contents in the leachates collected on November 25th 2010 and January 18th 2011 as well as trace metal content in the first crop mustard (0).

Following elements were subject to investigation:

B, Al, Cr, Mn, Ni, Co, Cu, Zn, As, Se, Mo, Cd and Pb.

Methodology

To determine plant-available trace elements, 1 M NH_4NO_3 solution was prepared (based on ÖNorm 1094). At this, 20 g of air-dried soil was weighed into flasks and filled with 50 mL of solution. The flasks were shaken for 2 h, let stand and filtrated. The filtrate was stabilized with 1 vol-% of HNO_3 (65%). Subsequently, the trace metals in the filtrate were measured. Elemental composition of the mustard plants was determined by digesting the dried plant material with HNO_3: $HClO_4$ (20 + 4 mL; *ÖNorm* L 1085, 2009).

Preliminary results

Figure 71 displays the results of the NH_4NO_3 extractions for Al, Cd, Co and Cr for the three investigated soils. Therein, NH_4NO_3-extractable trace elements are shown for the beginning as well as 7 months after start of the pot experiment.

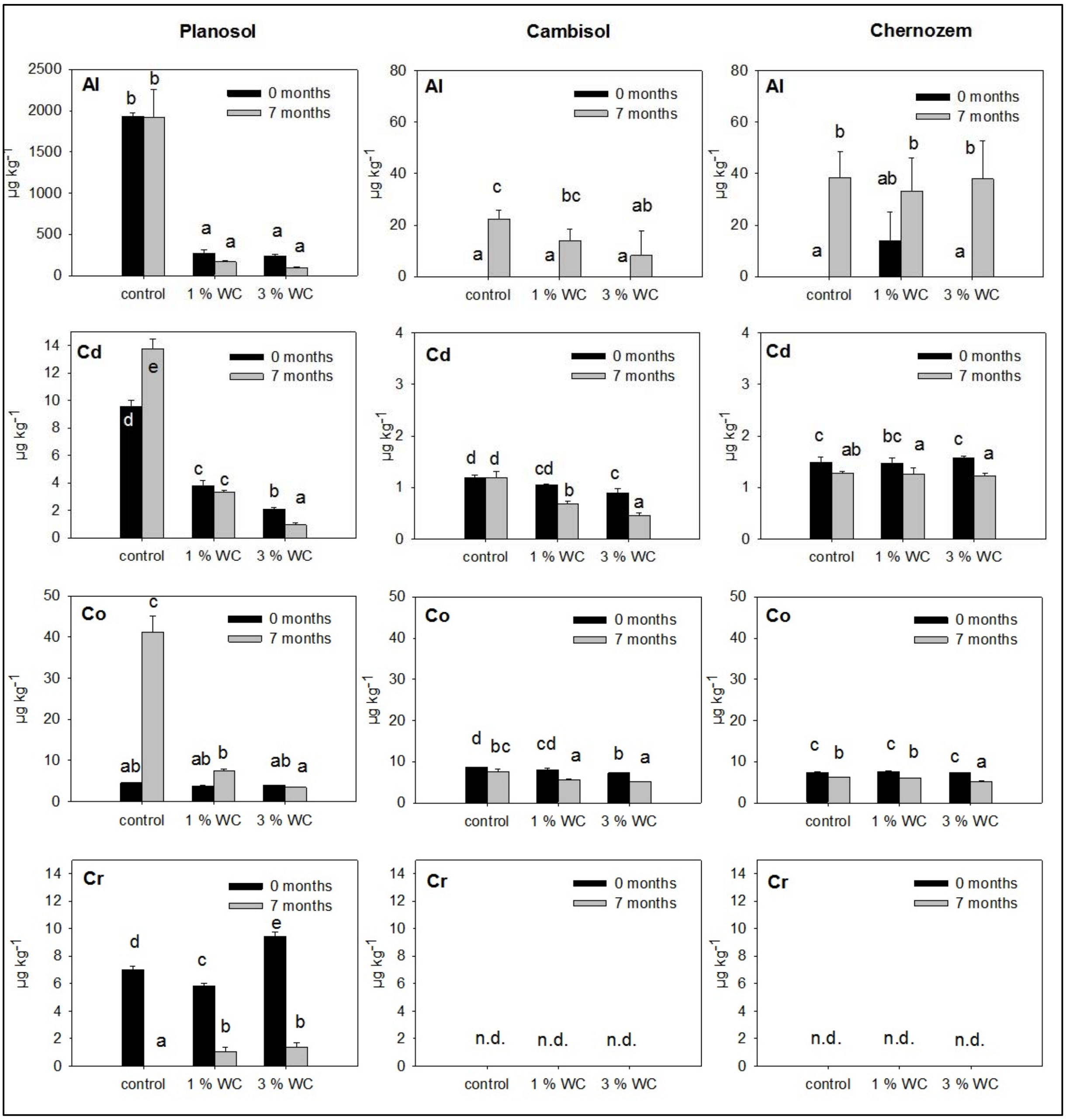

Figure 71 NH_4NO_3 extractable trace elements (Al, Cd, Co, Cr) of the three investigated soils at 0 and 7 months after start of the pot experiment (WC: woodchips-derived Biochar (BC); 1 and 3 w.-% BC application rate). Statistical evaluation included 2 way ANOVA with the factors BC application rate and sampling time; different letters indicate significant differences at $P < 0.05$; Tukey's post-hoc test; n.d.= not detectable)

Figure 71 shows that Al availability in the soil significantly decreased after BC application in the Planosol. To a lesser extent this was also found for the Cambisol. The reduction of Al availability in the soil was caused by the significant pH increase, which was most distinct in the Planosol where a pH increase of up to 1.6 units was found (Table 12). At the same time, the same pattern was found for Cd, where the most pronounced reduction was found in the Planosol after BC application. Less obvious effects were found for Co and Cr. The latter was not detectable in the Cambisol and Chernozem.

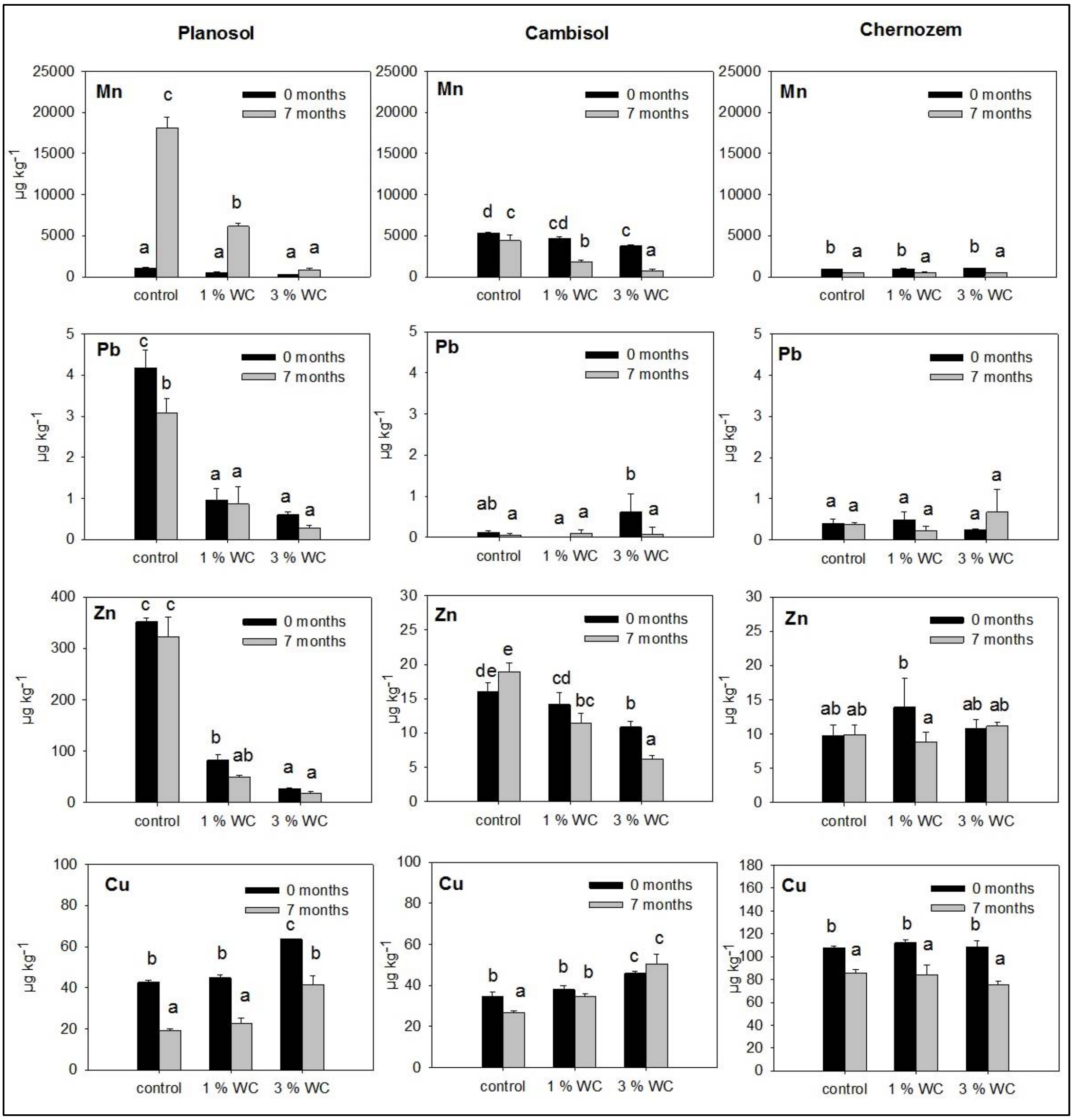

Figure 72 NH_4NO_3 extractable trace elements (Mn, Pb, Zn, Cu) of the three investigated soils at 0 and 7 months after start of the pot experiment (WC: woodchips-derived Biochar (BC); 1 and 3 w.-% BC application rate). Statistical evaluation included 2 way ANOVA with the factors BC application rate and sampling time; different letters indicate significant differences at $P < 0.05$; Tukey's post hoc test)

Figure 72 displays the availability of Mn, Zn, Pb and Cu on BC amended soils. Mn availability decreased after BC application especially in the Planosol, although for the Planosol there was initially no effect immediately after BC application, but became more remarkable after 7 months. Pb availability was not affected in the Chernozem after BC application whereas the Planosol showed a distinct reduction. Although Cu availability is also supposed to decrease with increasing pH, no distinct effect was found for any of the soils, in fact BC application partly increased NH_4NO_3-extractable Cu. Interestingly, we found much higher Cu concentrations in the Chernozem, which can be explained by the land use. The area around the sampled field is viticulturally used; the high Cu contents may be a sign of Cu applications in the surrounding vineyards. Summarizing Figure 71 and Figure 72, BC application caused reduction of the above mentioned trace elements, which were most pronounced in the Planosol, where the pH increase was highest after BC application.

In contrast, Figure 73 shows NH_4NO_3-extractable anions, i.e. As, B, Mo and Se. Here, the most distinct effect was also found in the Planosol; however, all trace metals except for Se showed a significant increase after BC application with the highest values found for the 3 w.-% BC application.

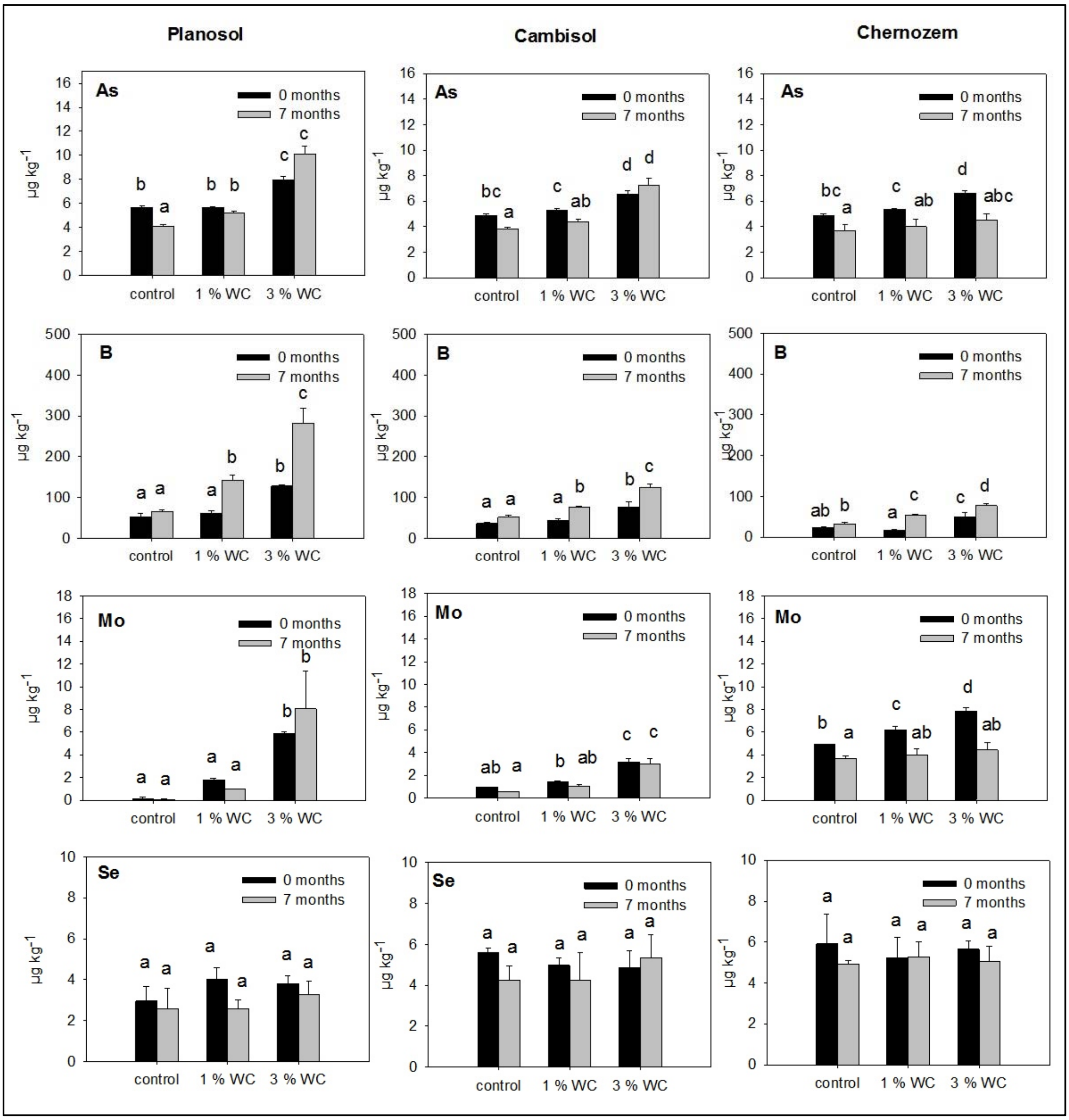

Figure 73 NH_4NO_3 extractable trace elements (As, B, Mo, Se) of the three investigated soils at 0 and 7 months after start of the pot experiment (WC: woodchips-derived Biochar (BC); 1 and 3 w.-% BC application rate). Statistical evaluation included 2 way ANOVA with the factors BC application rate and sampling time; different letters indicate significant differences at $P < 0.05$; Tukey's post hoc test).

In detail, Figure 73 shows that NH_4NO_3-extractable As significantly increased in the Planosol variants; the same was found for the Cambisol at a 3% application rate. Distinct increases in the Planosol were also present for B and Mo, both showing a further significant increase after 7 months. NH_4NO_3-extractable Se was not affected in any soil and at any application rate, respectively. The results of the leachate concentrations are presented in Figure 74 to Figure 76. In general, values for all trace elements in the leachates were fairly variable, which is seen in the high standard deviations. Despite a significant reduction of Al in the soil (Figure 71) especially for the Planosol, Al content in the leachate showed no changes after BC application.

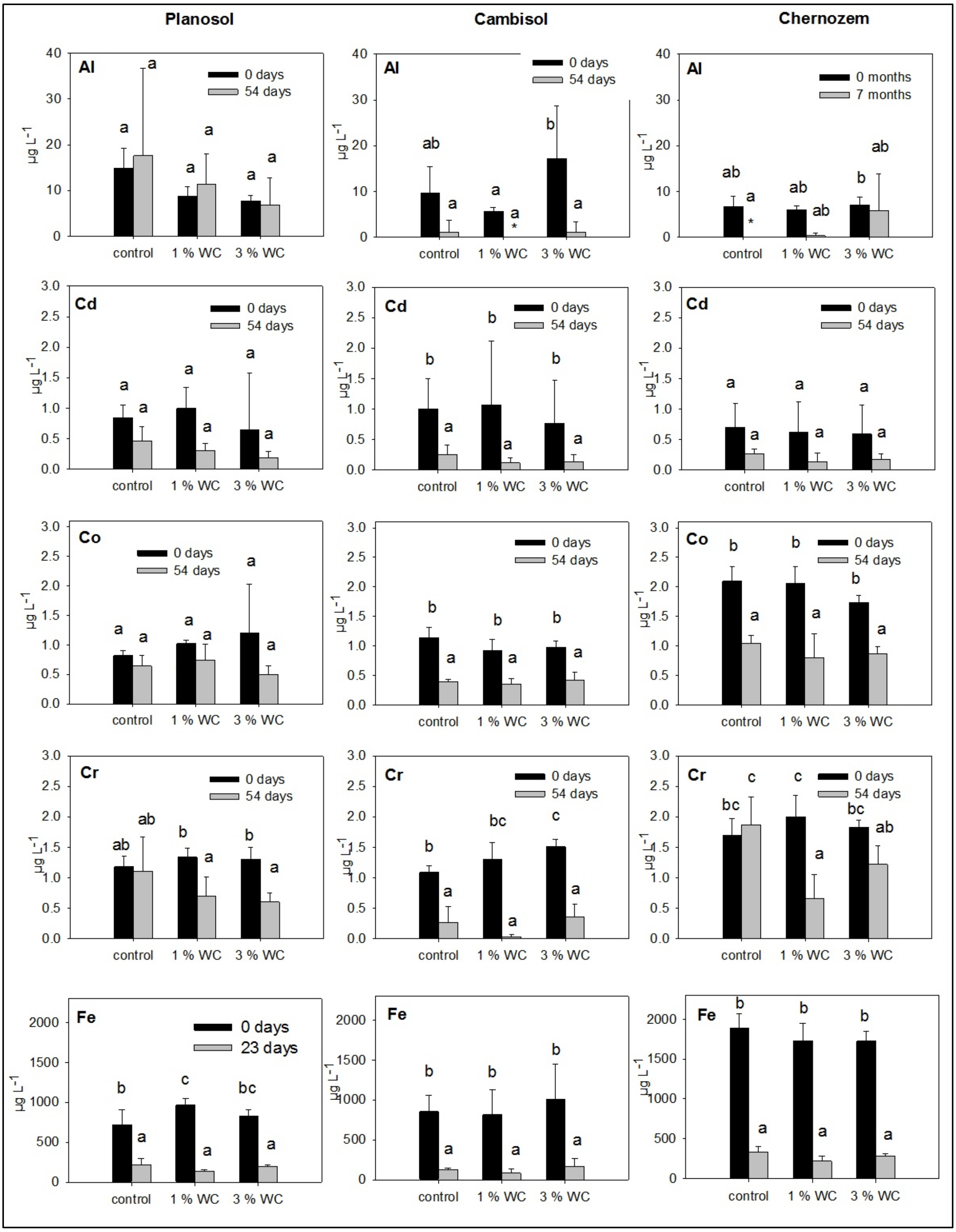

Figure 74 Leachate characteristics (Al, Cd, Co, Cr, Fe) for different soil types and BC concentrations (0 days and 54 days after the start of the pot experiment (n=5; different letters indicate significant differences at $p < 0.05$).

Cd, Co, Fe and partly Cr showed much higher contents immediately after the start of the pot experiment and then significantly decreased after 54 days, which shows that the leaching of these elements for both BC treated and untreated pots was only a short-term effect.

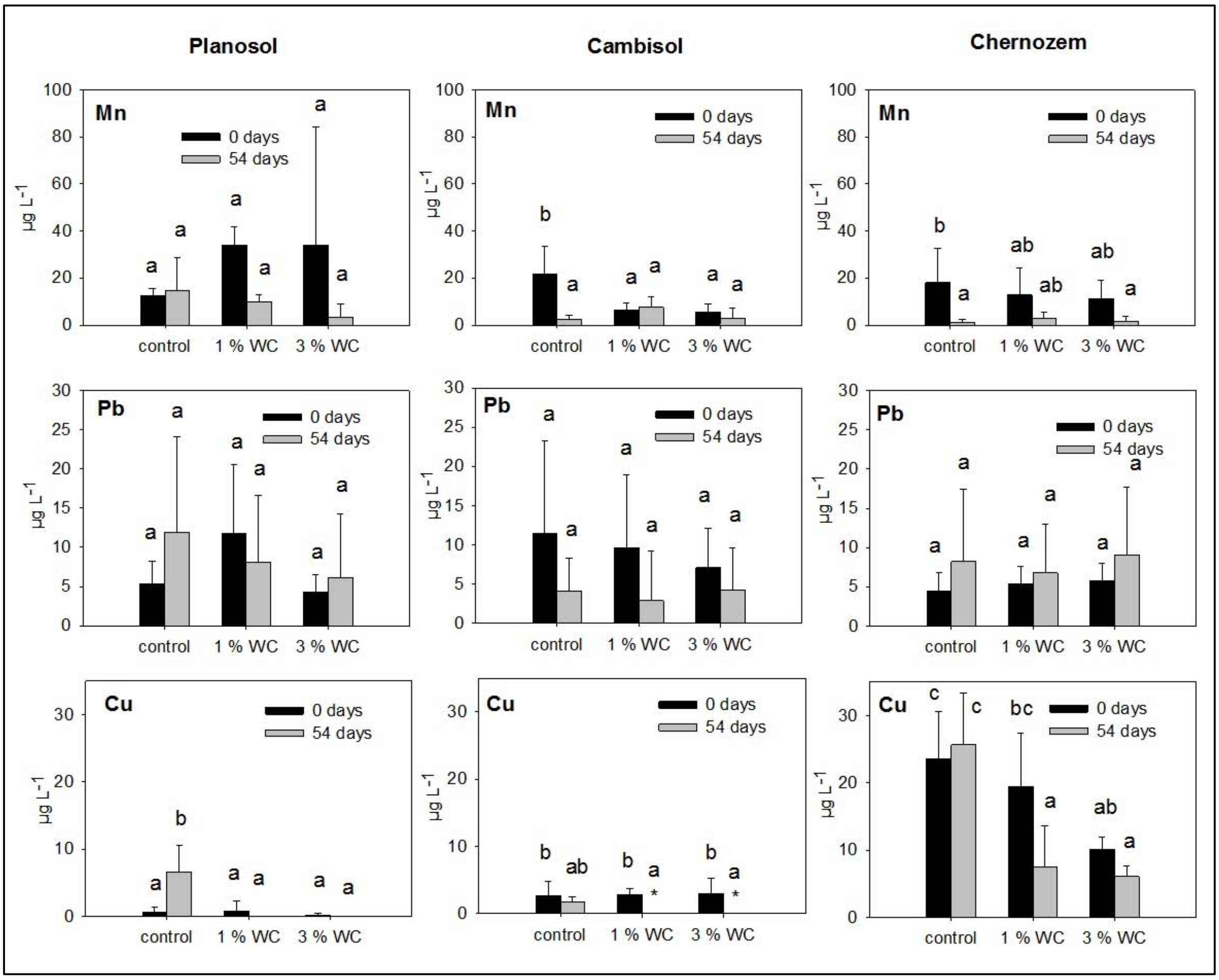

Figure 75 Leachate characteristics (Mn, Pb, Cu) for different soil types and BC concentrations (0 days and 54 days after the start of the pot experiment (n=5; different letters indicate significant differences at $p < 0.05$).

A similar picture like for Al is given for Pb (Figure 75), which, despite a significant reduction in the soil showed no difference in the leachates. Corresponding to the results of the NH_4NO_3 extractions (Figure 72) we found much higher Cu concentrations in the Chernozem compared to the Planosol and Cambisol, which is likely due to the nearby viticultural land use. However, despite the initially high Cu contents in the leachates, BC application was able to retain more Cu and therefore significantly decrease Cu leaching. Figure 76 shows the trace metal anion contents of the leachates. Here, clear pH dependence was found for B; the Planosol showed significant increases in B contents for both BC application rates up to > 500 µg L^{-1}. B concentrations also significantly increased in the Cambisol and Chernozem, but were below 200 µg L^{-1}. A similar picture is given for Mo. Se concentrations also significantly increased after BC application; however, this was only a short-term effect. After 54 days, Se concentrations were not different from the controls anymore.

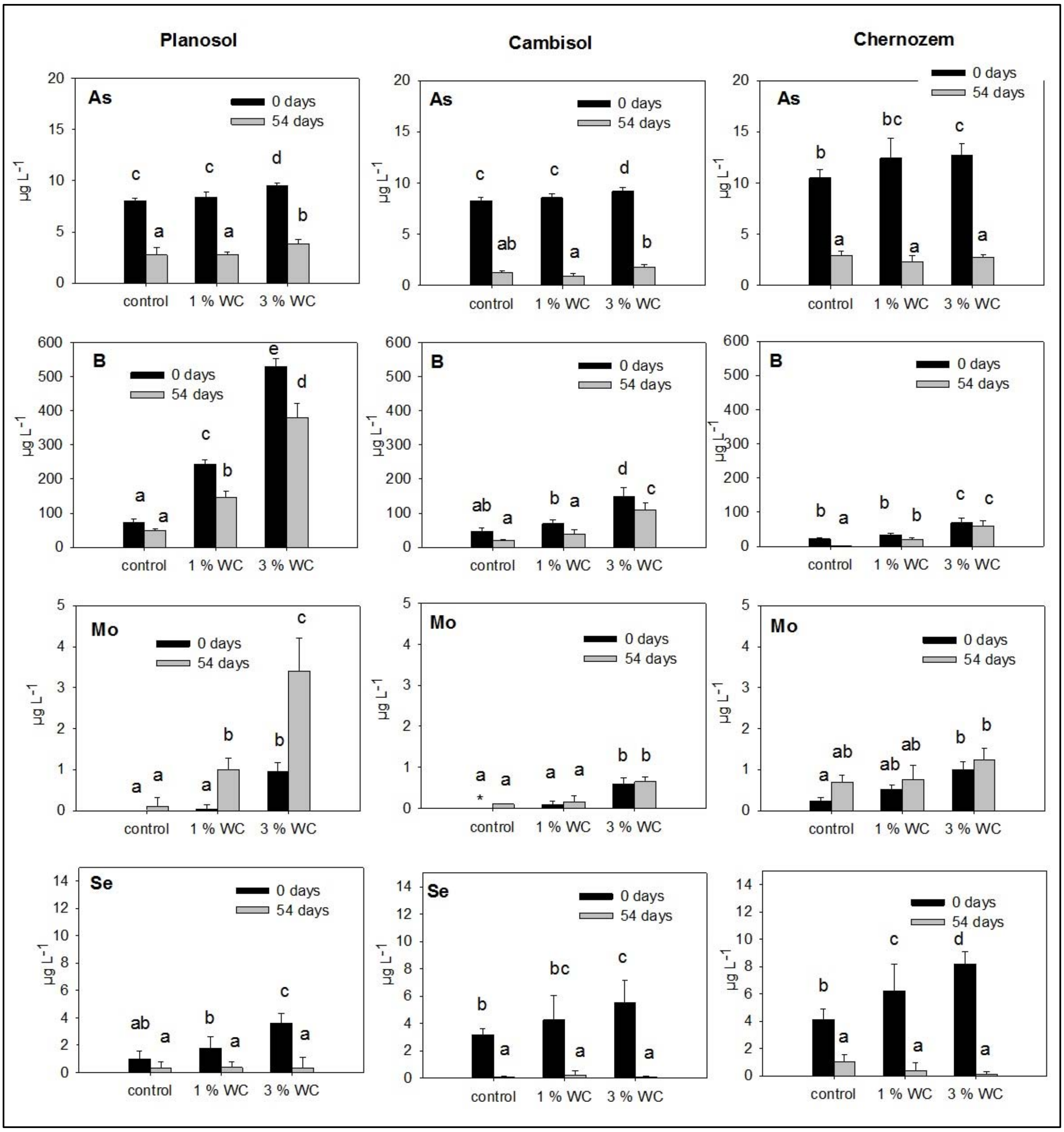

Figure 76 Leachate characteristics (As, B, Mo, Se) for different soil types and BC concentrations (0 days and 54 days after the start of the pot experiment (n=5; different letters indicate significant differences at $p < 0.05$).

The results of the trace metal contents of mustard are given in Table 15.

Table 15 Trace metal contents of mustard (WC: woodchips-derived biochar (BC); 1 and 3 w.-% BC application rate). Different letters indicate significant differences within one element and soil P< 0.05; Tukey's post hoc test).

$mg\ kg^{-1}$ DM	**Planosol**			**Cambisol**			**Chernozem**		
	control	1% WC	3% WC	control	1% WC	3% WC	control	1% WC	3% WC
Cr	5.07 a ± 1.91	3.57 a ± 1.59	3.32 a ± 0.55	2.80 a ± 1.22	2.25 a ± 0.23	2.33 a ± 0.39	2.56 a ± 0.39	2.06 a ± 0.25	2.41 a ± 1.28
Mn	49.60 b ± 9.09	23.50 a ± 3.24	22.34 a ± 0.88	24.02 b ± 3.74	21.05 ab ± 2.03	18.07 a ± 1.21	45.91 b ± 1.49	42.11 ab ± 4.24	36.35 a ± 6.52
Ni	1.59 a ± 0.64	1.03 a ± 0.50	1.22 a ± 0.44	0.83 a ± 0.44	0.57 a ± 0.12	0.63 a ± 0.15	0.71 a ± 0.27	0.53 a ± 0.07	0.66 a ± 0.49
Co	0.26 a ± 0.10	0.17 a ± 0.04	0.16 a ± 0.02	0.17 a ± 0.06	0.14 a ± 0.02	0.13 a ± 0.02	0.13 a ± 0.01	0.12 a ± 0.01	0.11 a ± 0.08
Cu	5.13 b ± 0.73	3.98 a ± 0.42	4.07 a ± 0.30	5.05 b ± 0.69	4.29 ab ± 0.35	3.76 a ± 0.22	6.17 a ± 0.09	5.60 a ± 0.38	4.55 b ± 0.49
Zn	95.07 b ± 12.91	47.19 a ± 8.18	42.49 a ± 4.74	54.28 b ± 8.23	41.35 a ± 6.03	32.97 a ± 3.61	44.46 b ± 2.29	40.44 ab ± 1.64	39.85 a ± 3.40
As	1.55 a ± 0.39	1.71 ab ± 0.06	2.07 b ± 0.14	2.10 b ± 0.14	1.94 ab ± 0.18	1.54 a ± 0.38	2.04 b ± 0.12	0.82 a ± 0.58	0.96 a ± 0.47
Se	0.79 a ± 0.47	0.81 a ± 0.42	0.92 a ± 0.39	0.76 a ± 0.58	0.94 a ± 0.14	0.35 a ± 0.41	1.18 a ± 0.28	1.15 a ± 0.63	0.57 a ± 0.55
Mo	0.73 a ± 0.10	2.22 b ± 0.18	5.39 c ± 0.30	1.53 a ± 0.06	2.03 b ± 0.17	2.57 c ± 0.22	2.50 a ± 0.25	2.48 a ± 0.33	3.24 b ± 0.60
Cd	0.84 b ± 0.09	0.63 a ± 0.09	0.76 ab ± 0.08	0.50 b ± 0.05	0.44 ab ± 0.06	0.38 a ± 0.03	0.93 c ± 0.05	0.80 b ± 0.07	0.62 a ± 0.05
Pb	0.90 a ± 0.19	0.77 a ± 0.47	0.57 a ± 0.07	0.66 a ± 0.16	0.50 a ± 0.06	0.57 a ± 0.05	0.84 a ± 0.13	0.73 a ± 0.14	0.64 a ± 0.15

Table 15 shows that there was no effect of BC on trace metal content for Cr, Ni, Co, Se and Pb, even though especially Pb availability was found to have significantly decreased after BC application (Figure 72). In contrast, element content in the mustard significantly increased for Mo for all soils, whereas Mn, Cu and Zn content in the mustard decreased, which reflects the pH dependency of plant availability of trace metals. Interestingly, As significantly increased after BC application in the mustard grown on the Planosol, whereas As content in the plant decreased in the Cambisol and Chernozem.

In order to examine the effects of soil properties and BC application on trace element content in the mustard tissue, a General Linear Model (GLM) was run. The GLM output (p values) is given in Table 16. The results show that, except for Mn and Mo, the NH_4NO_3 extractable fraction could not significantly account for the element content found in the straw, which may be a sign that soil extractions such as NH_4NO_3 may not be suitable for predicting plant uptake. Two hours of shaking may have overcome the otherwise assumed heterogeneity found in BC treated soils and may therefore not correspond to the plant content of the elements. The parameters used for the GLM showed no significant results for Co, Se and Pb and had a rather low R². Mo, As and Cd were trace elements well explained by the GLM. Mustard content of these concentration were significantly influenced by soil type, which was associated with pH. In addition, BC application rate played a role for As and Cd content in the mustard tissue as well as for Cu.

Table 16 Results of the General Linear Model (GLM) investigating the effects of soil type, biochar (BC) application rate, organic carbon (Corg), pH and NH_4NO_3 extractable fraction on trace metal content in mustard tissue. Values represent the probability value. Significant p-values are given in bold.

	Cu	Mn	Co	Zn	As	Se	Mo	Cd	Pb
soil type	0.801	**0.001** **	0.896	0.393	**0.001** **	0.113	**0.000** ***	**0.000** ***	0.194
BC application rate	**0.008** **	0.379	0.982	0.174	**0.000** ***	0.402	0.610	**0.004** **	0.087
C_{org}	0.556	0.304	0.716	0.487	0.345	0.681	0.763	0.381	0.668
pH	0.621	0.110	0.774	0.103	**0.002** **	0.229	**0.000** ***	**0.008** **	0.969
NH_4NO_3	0.198	**0.014** *	0.777	0.316	0.506	0.108	**0.035** *	0.031 *	0.708
R²	0.776	0.879	0.410	0.882	0.641	0.247	0.884	0.879	0.512

* $p < 0.05$ / ** $p < 0.01$ / *** $p < 0.001$

Milestones and Deliverables

M5-1, M5-2 and M5-3 represent the soil analyses for pot and field experiments that were supposed to be carried out within WP5. All analyses were finished successfully by the beginning of 2013. The results of the pot experiments were summarized in a publication (Kloss et al., 2013), which has been submitted in June 2012 and is currently in review. The results of the field experiments have been likewise compiled in Karer et al. (2013), which has been submitted in May 2013. M5-4 include leachate analyses. The results were obtained within the scope of a Master thesis and are currently brought together for two publications. One publication deals with general leachate characteristics, i.e. pH, EC, N, P, K and DOC (Buecker et al., 2013), whereas another publication is currently prepared on trace metal contents of the leachates (Kloss et al., 2013). D5-1, D5-2 and D5-3 have been successfully delivered within the course of these publications. The overall output of WP 5, which also includes additional analyses not originally comprised in the milestones and deliverables, is given in Table 17.

Table 17 Overall output of work package 5.

Authors	Publication title	Status	Coverage
Kloss, S., F. Zehetner, B. Wimmer, J. Buecker, F. Rempt, G. Soja	Biochar application to temperate soils: Effects on soil fertility and crop growth under greenhouse conditions	in review	M5-1, M5-3, D5-1, D5-3
Karer, J., B. Wimmer, F. Zehetner, S. Kloss, G.Soja	Biochar application to temperate soils: effects on soil fertility and crop growth under field conditions	submitted	M5-2, M5-3, D5-2, D5-3
Buecker, J., B. Wimmer, A. Watzinger, S. Kloss, F. Rempt, F. Zehetner, and G. Soja	Leachate characteristics of three biochar-amended soils	in preparation	M5-4, D5-1, D5-3
Kloss, S., F. Zehetner, Wang, S.-L., J. Lehmann, G. Soja	Influence of different biochar types and biochar aging in the soil on Cd and Cu adsorption potential.	in preparation	supplementary work
Kloss, S., F. Zehetner, E. Oburger, G. Soja	Effects of different biochar-amended soil types on heavy metal availability and plant uptake.	in preparation	supplementary work

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2.6 WP 6: Effects on non-CO_2 greenhouse gas emissions

WP leader: Sophie Zechmeister-Boltenstern, University for Natural Resources and Life Sciences, Institute for Soil Science, Vienna, and Barbara Kitzler, BFW - Federal Research and Training Centre for Forests, Natural Hazards and Landscape

Work package content:

Analyses of greenhouse gas emissions from soils with different biochar and nitrogen supplies

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Workpackage 6 deals with soil mediated greenhouse gas fluxes (N_2O, NO, CH_4, CO_2) from the pot experiment and the field experiment in Traismauer that were established in workpackage 2.

Soil respiration was reduced in biochar amended plots which is mainly attributed to lower plant growth. No direct effect of biochar on CO_2 and CH_4 fluxes could be observed. Biochar reduces NO and also N_2O emissions which is significantly reduced after rewetting the soil and after NPK fertilization. A long term reduction of N_2O emissions could be observed at the field site Traismauer but not in the pot experiement. A 3% application rate has the highest potential to reduced N_2O emissions (measured in the field and the pot experiment).

Objectives

To evaluate the positive effects of biochar regarding long-term soil carbon sequestration, the soil-atmosphere flux of CO_2 but also of potent non-CO_2 greenhouse gases such as methane (CH_4) and nitrous oxide (N_2O) have to be considered. WP6 aims to evaluate soil GHG fluxes from different biochar qualities, different soil types, biochar treated versus non-treated soils and different crops. Our hypothesis is that biochar-treated and non-treated soils will show significant differences in soil GHG fluxes.

Methods

The gas sampling from the pot experiment was accomplished from November 2010 June 2011 (period 1) and from July 2011 until April 2012 (Period 2). The closed chamber method was used to measure GHG fluxes. Different gas measurement chambers were used for gas sampling depending on the height of the vegetation. A chamber was placed upside down on top of each pot in order to evacuate the atmosphere over the soil from the surrounding air. A sealing on the top of the bucket ensured a gas-tight closure. The inside net volume of the chamber was 1.7l; 8.5l or 17.3l, depending on the height of the vegetation. In addition, each bucket had a rubber septum where a syringe could penetrate and gas samples could be drawn. At the beginning of each sampling the gas inside the chambers were mixed by flushing three times with a 20 ml gas-tight syringe. Gas samples of 15 ml were then taken with the syringe and injected into 10 ml pre-evacuated glass vials. These samples were taken four times of each chamber – 0, 5, 10 and 30 minutes. Until GHG measurement was carried out, gas samples were stored at 4°C for no longer than 14 days. The analysis of the gas samples took place at the BFW with a HP 6890 Series gas chromatograph (GC) instrument equipped with a 7683 Series injector and auto sampler on a HP - 5 capillary column (50.0 m, 0.20 mm, 0.33 µm). Temperatures of the injector and the detector were 280°C and 350°C, respectively. The injected sample volume was 1 ml (splitless mode injection). CO_2 and CH_4 concentrations were detected with FID (flame ionization detector) using Helium as carrier gas (Hewlett Packard, Wilmington, Delaware, USA). N_2O concentrations were measured using a 63Ni-electron-capture detector (ECD).

All GC measurements included internal standards for CO_2, CH_4 and N_2O to quantify GHG concentrations via recorded peak areas. Thus, GHG concentrations were measured at four different times for each chamber. The flux rates of CH_4 (µg C m^{-2} h^{-1}), CO_2 (mg C m^{-2} h^{-1}) and N_2O (µg N m^{-2} h^{-1}) were then determined via linear regression of the four data points. Outliers were not considered in the calculation. Soil temperatures in the upper 5cm was also measured when gas sampling took place and used to standardize GHG fluxes at different soil temperatures. Furthermore a correction of the camber volumes was done by subtracting vegetation volumes and addition of the formed air volume after soil compaction.

A laboratory incubation experiment was conducted in March/April 2011. Control and biochar treated intact soil cores from Traismauer and Kaindorf were used. GHG fluxes were measured under 5 different soil temperatures and 4 different soil moisture states to estimate potential GHG fluxes. The two-factorial incubation design provides the opportunity for temperature and moisture effects to be assessed independently and by excluding other factors that influences soil GHG fluxes. Moreover, the incubation scheme enabled us to compare GHG emission potentials of different treatments under similar temperature and moisture conditions.

To study the effect of biochar on soil GHG fluxes under natural climatic conditions a field experiment was started in Traismauer in spring 2011. Gas fluxes in the field was measured monthly until July 2012. For each treatment 4 replicated plots were installed (WP2). Three manual gas chambers (Vol: 2-3l) were installed at each plot. Gas samples were taken at time 0, 5, 10, 20 minutes. Gas samples were analyzed by gas chromatography (method see above). Additionally, soil cores were collected monthly to determine nitric oxide (NO) emissions. For the incubation experiment NO fluxes were detected with a chemiluminescence analyser (HORIBA, APNA 360), CO_2 was measured continuously with a IR analyzer (PP-sytems).

Results

Pot experiment: Carbon dioxide fluxes

The 3 soil types showed different soil respiration rates with highest rates at the sandy soil at Eschenau followed by Kaindorf and the loamy soil at Traismauer. Highest soil respiration was found at planted soil with maximum fluxes of 500 mg CO_2-C m^{-2} h^{-1}. Shortly after BC application we observed significantly reduced soil respiration rates compared to non-biochar treated plots. We assume that BC has toxic effects on microorganisms, but they seem to recover afterwards or microbial community gets adopted.

CO_2 fluxes are significantly lower in non vegetated pots where autotrophic respiration is missing. Depending on the stage of plant development autotrophic respiration accounts for 26 to 82% of total CO_2 fluxes. Biochar amendment generally decreased soil respiration rates (**Fig. 1**), which is possibly related to the lower plant growth and the lower root respiration, but no direct effect of biochar on CO_2 fluxes could be observed.

At unplanted pots no significant differences could be observed between biochar and control plots. Fertilization rates increased CO_2 fluxes. Here enhanced plant growth at fertilized plots which leads to increased root respiration is possibly the most important factor.

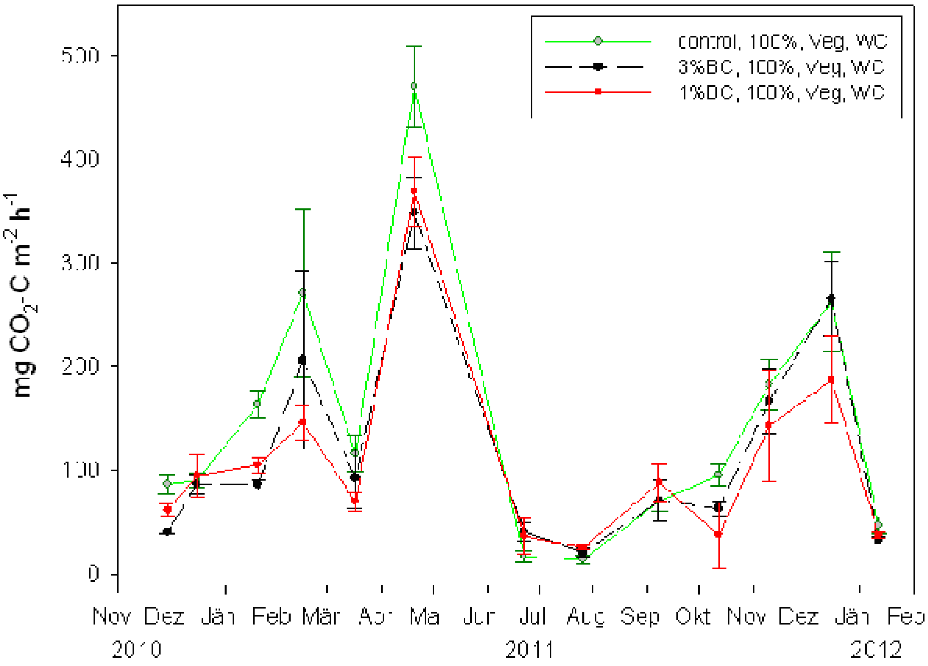

Fig. 1 CO_2 emissions of pots with different biochar treatment (black = 3% biochar, red = 1% biochar, green: no biochar); biochar from wood chips, sandy soil, with vegetation, fertilization rate 100%.

Pot experiment: Nitrous oxide fluxes

Highest N_2O flux rates were measured from the Cambisol at Kaindorf, followed by the Planosol at Eschenau and lowest fluxes were measured from the Chernozem at Traismauer (**Fig. 2**).

Nitrous oxide was highest at the beginning of the experiment, shortly after BC was added to the soil. Afterwards fluxes decreased significantly and increased again after fertilization (Mar 11) (**Fig. 2**). Biochar shows a high potential to reduce N_2O emissions after rewetting (Nov. 10) and/or fertilization (Mar. 11) (**Fig. 2**). A biochar application rate of 3% reduced soil N_2O emissions significantly by 70, 70 and 40%, respectively at the Planosol in E, K and T (**Fig. 2**), whereas a 1% BC application rates reduced N_2O fluxes significantly only at sites K and E (60% each) where soil pH is lower. Soil N_2O emissions were decreased significantly (up to -95%) in the 1st measurement period after BC application under clover however, no significant differences could be found. In the second period, when clover was grown we did not observe these high reduction rates of N_2O emissions as reported before. Nevertheless, in period 2 we observed a 40 % reduction of N_2O emissions at the Planosol in Eschenau (E).

In March 2012 soil samples were taken from the uppermost soil layer (5cm) for analysing NO_3' , NH_4 and N in the microbial biomass in order to see whether NO_3- is the limiting factor for N_2O production under clover. It is expected that this might help to explain differences in the N-pools which could not be explained by considering N_2O gas fluxes so far. NPK-fertilizer was applied in April 2012 to biochar and control pots. We expected to see higher N_2O flux rates after fertilization. However, in the second period microorganisms did not respond to N-fertilization by elevated N_2O emissions as we supposed. It seems that in this period carbon is the limiting factor for denitrification.

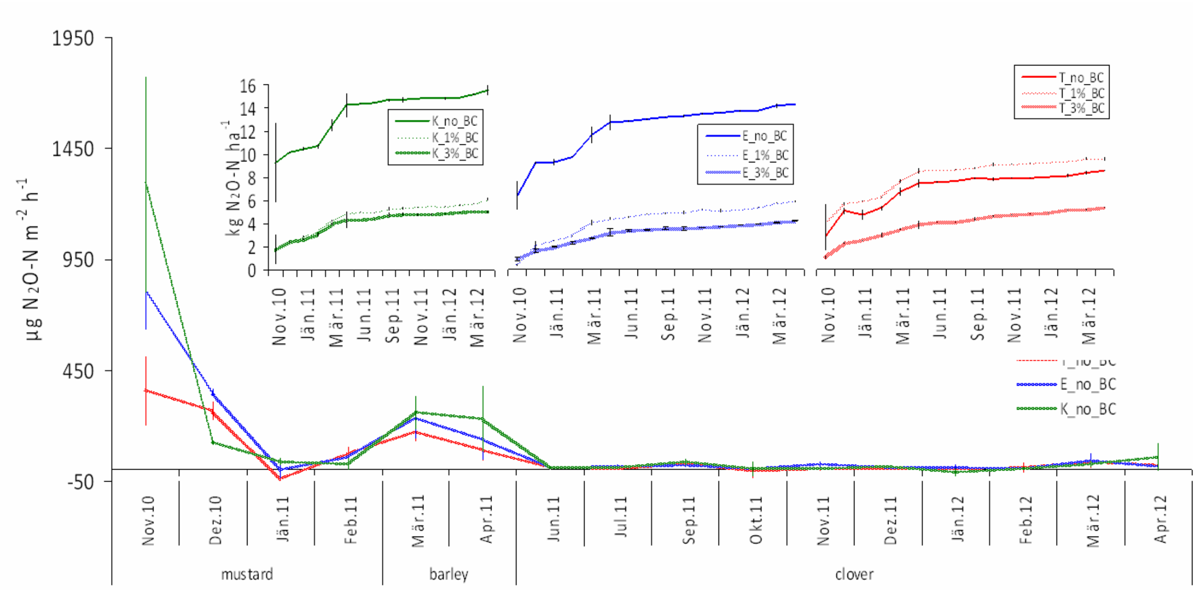

Fig. 2 Pot experiment: Cumulative N_2O fluxes from control plots and biochar (1% and 3%) treated plots measured at T, E, K and N_2O emissions of control plots from soils of T, E and K over time.

Different biochar types have different mitigation potentials. Biochar made from vineyard pruning and wood chips have a high potential to reduce N_2O by around 70%. The N_2O reduction potential when applying straw is lowest (30%) (Fig. 3) compared to the other BC materials.

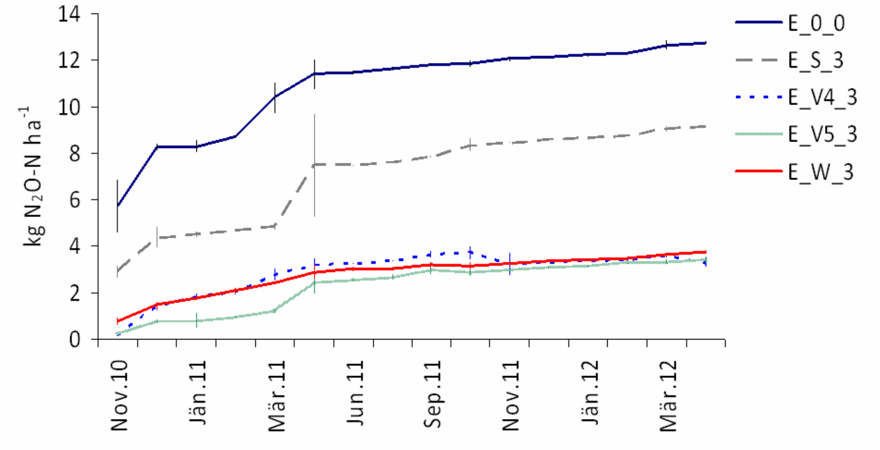

Fig. 3 Pot experiment: Sum of N_2O fluxes from different BC feedstock treated plots over time. (O=control, S=straw, V4= vineyard pruning 400°C, V5= vineyard pruning 525°C, W=wood chips).

N_2O emissions were decreased in fertilized BC amended plots by almost 80% compared to fertilized control plots (data not shown). We assume that the added N was fixed to the BC surface and is thus not accessible for microbes.

With an application rate of 1% N_2O emissions were only reduced at the beginning of the experiment (Fig. 4). One of the factors responsible for the decrease in N_2O emissions is the increases of soil pH that is leading to an increased activity of the N_2 producing enzyme. Furthermore soil aeration improves due to the porous nature of biochar, thus providing unfavourable conditions for N_2O production.

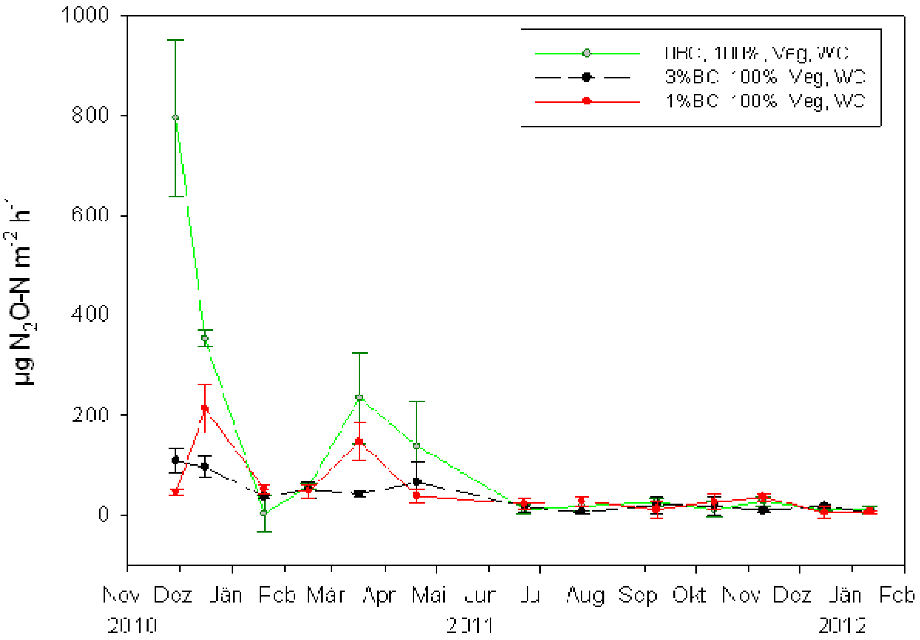

Fig. 4 N_2O fluxes of different biochar application rates (black = 3%, red = 1%) and control without biochar (green); biochar from wood chips, fertilization rate 100%, sandy soil, with vegetation.

We found a high potential to reduce N_2O production with most of the biochar types when growing mustard and barley. Considering the different origins and pyrolysis temperatures, however, biochar from straw seemed to decrease N_2O less compared to the other types and even has the potential to increase N_2O production (Fig. 5).

Considering different pyrolysis temperatures biochar produced at 400°C reduced N_2O fluxes significantly more than biochar produced at 525°C until clover was planted.

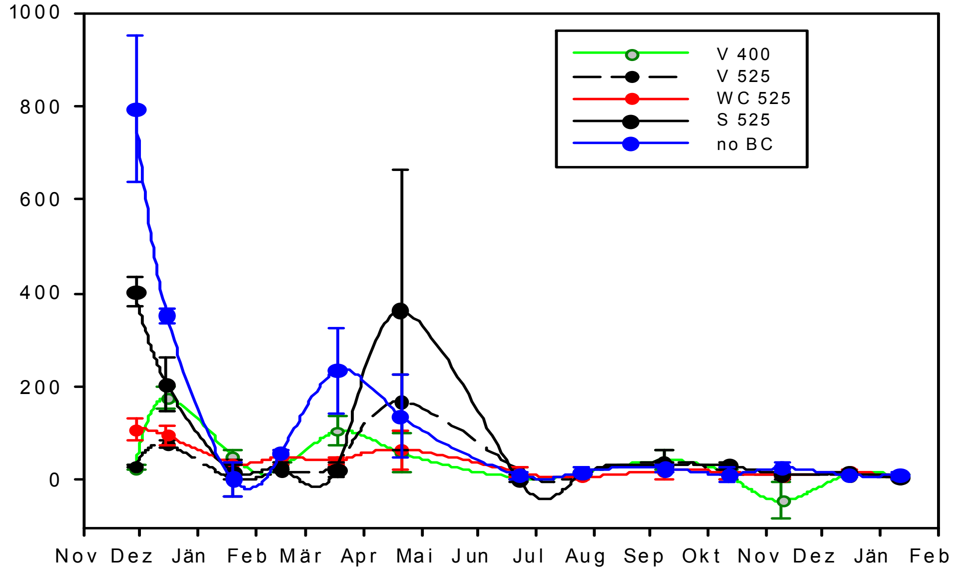

Fig. 5 N_2O fluxes of different types of biochar (BC) (green = BC from vineyard pruning, pyrolysis temperature 400°C; black, dotted line = BC from vineyard pruning, pyrolysis temperature 525°C; red = BC from wood chips, pyrolysis temperature 525°C; black, full line = BC from straw, pyrolysis temperature 525°C; blue = control without biochar application), sandy soil, with vegetation, fertilization rate 100%.

Pot experiment: Methane fluxes

No significant differences could be found between biochar treated vs. control plots. Methane fluxes showed a high variability. As CH_4 can be produced and oxidized simultaneously within a soil column it seemed that soil moisture and oxygen availability in the soil profile influence CH_4 fluxes in our experiment. Furthermore, vegetation seems to influence CH_4 fluxes which could be proved statistically. At the beginning of the experiment pots with vegetation showed significantly lower CH_4 fluxes compared to pots without vegetation. First, plants decrease the water content in the soil and second, plant roots aerate the soil and assure an improved oxygen supply for methanotrophs.

Incubation experiment in the laboratory

In March/April 2011 we conducted an incubation experiment to gain information about potential soil GHG fluxes. Nitric oxide emissions were significantly higher from the Cambisol at the site Kaindorf compared to the Chernozem from Traismauer. The pH at Kaindorf is lower pH compared to the site Traismauer, which favours NO production. Biochar application reduces the emission of nitric oxide in Kaindorf (Fig. 6) and Traismauer significantly. Nitric oxide is an indirect GHG by catalyzing tropospheric ozone. We assume that the increase in pH after the application of biochar is the most dominant factor as NO production is reduced in soils with high pH.

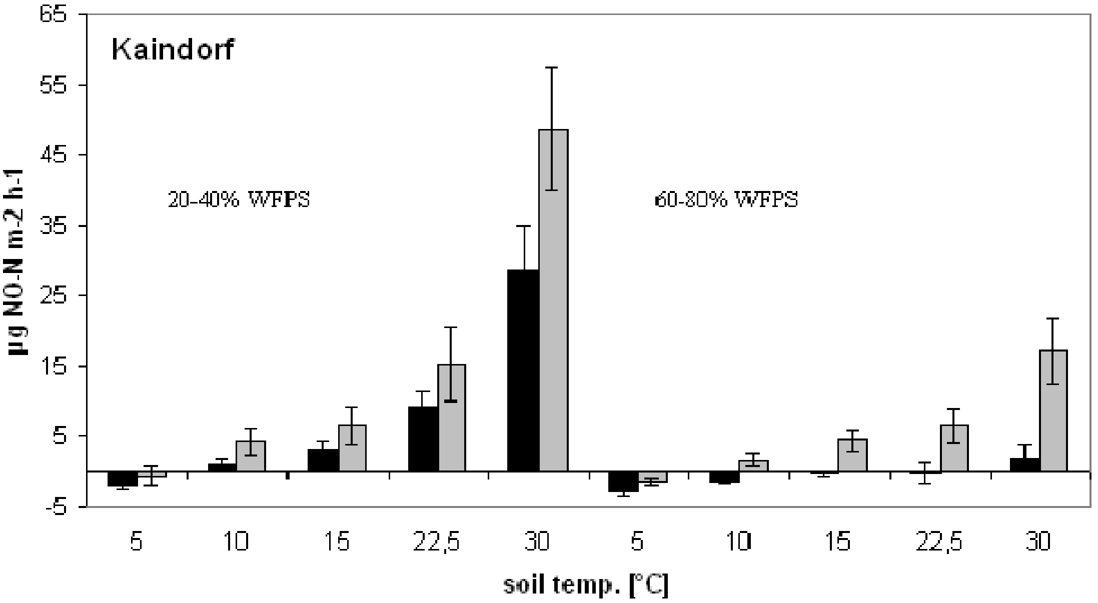

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Fig. 6 Nitric oxide fluxes at dry (20-40% WFPS) and wet soil (60-80% WFPS) under different soil temperatures at the site Kaindorf. Black bars=biochar treated, grey bars=control.

1.2.1. Field experiment in Traismauer

Gas flux measurements and accompanying soil analysis (NO_3, NH_4, Nmic) was continued until September 2012 to calculate an annual GHG balance that is furthermore used as a basis for economical cost-benefit analysis of the application of biochar (WP7). Air and soil temperature, soil moisture, NO_3^- and NH_4^+ concentration, N in the microbial biomass and the soil fluxes of CO_2, CH_4 and N_2O were measured at the site Traismauer from June 2011 until September 2012.

Soil moisture was significantly higher at plots with 3% BC and similar, but somewhat higher at 1% BC plots (Fig. 7) compared to non BC amended plots. Soil temperature was not significantly different in the different treatments.

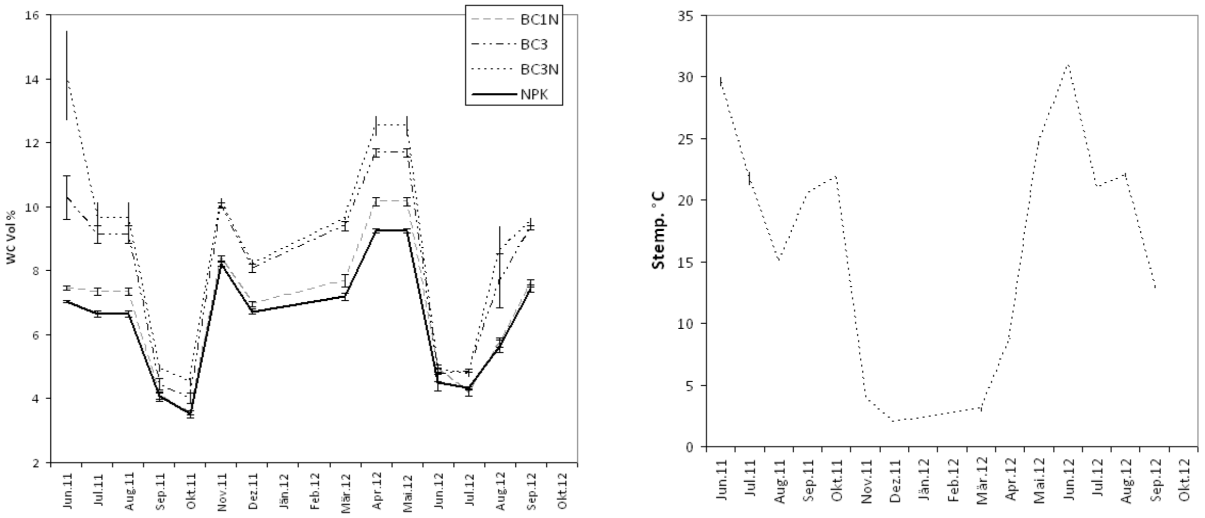


Fig. 7 Water content (Vol%) and soil temperature of soil samples taken from the field experiment in Traismauer. BC1N= 1%BC + NPK fertilizer, BC3N= 3%BC + NPK fertilizer, BC3=3%BC no fertilizer, NPK=no BC + NPK fertilizer. Soil temperature from NPK treated soil.

In the field a long term reduction of N_2O could be observed. Highest N_2O fluxes were measured in June 2011 1 month after fertilization (Fig. 8) and follows mainly the course of soil moisture ($p<0.05$). Biochar decreases N_2O emissions significantly under field conditions. An application rate of 3% has the highest potential to reduce N_2O. In dry periods (Oct. 11) even an uptake of N_2O was found at treatment BC3. Nitrogen in the microbial biomass is lower (up to 10%) in BC (1%, 3%) treated plots, but is higher after plant harvest (up to 25%) (Fig. 10). NO production was significantly reduced in BC treated plots (data not shown), but is generally low at this site. Methane fluxes were mainly taken up but showed a high variability and no clear pattern. Biochar amendment had no influence on the CH_4 uptake rates.

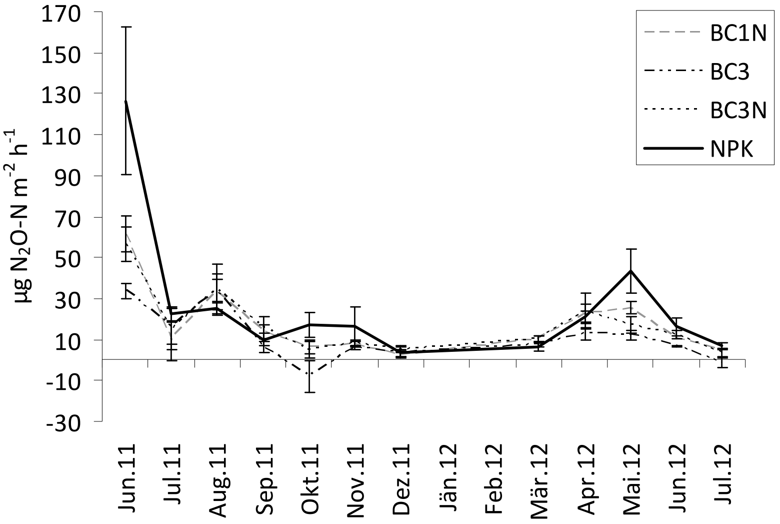


Fig. 8 N_2O fluxes from biochar treated and control plots measured at Traismauer from June 2011-July 2012. n=48. BC 1N and BC 3N= 1% and 3% biochar, respectively and NPK, BC 3= 3% biochar, NPK= no biochar and NPK fertilization.

From NPK fertilized plots (control) a cumulative flux of 2.3 kg N ha-1 yr-1 were emitted in form of N_2O-N (Fig. 9). At biochar and fertilized plots (BC1N and BC3N) N_2O fluxes were reduced by 30 and 35% and were hence not significantly different from each other. From BC treated and not fertilized plots a reduction of N_2O of around 60% was observed. Compared to the high amount of N-fertilizer that was applied during the investigation period, annual N_2O emissions can be neglected and the reductio potential of N_2O at this soil type is low.

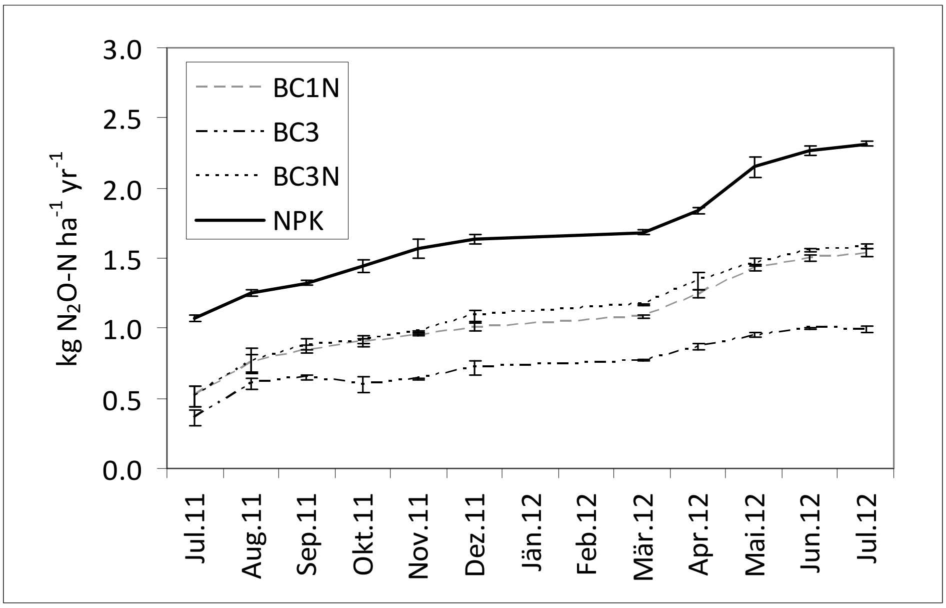


Fig. 9 Cumulative N_2O flux from BC treated and control plots at the field site Traismauer.

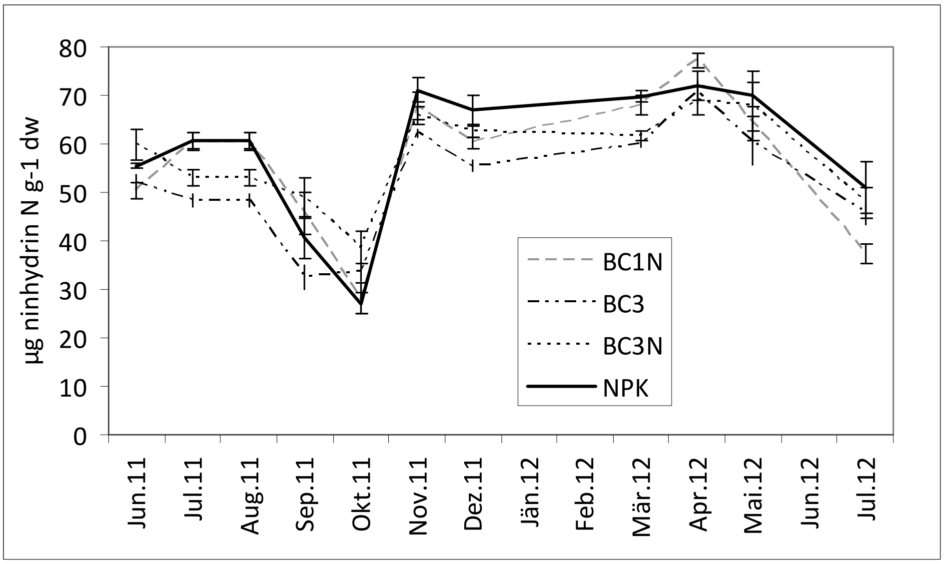


Fig. 10 Nmic from BC treated and control plots at the field site Traismauer over time.

Discussion

Biochar amendment shows a high potential to reduce soil N_2O, NO fluxes and N-leaching. Microbial biomass N and inorganic N was lower in BC amended plots. We assume that N_2 is the main end product as pH increases after BC application.

Biochar from wood chips and vineyard pruning is in contrast to straw more effective in the reduction of N_2O emissions.

In the field experiment, in contrast to the pot experiment, a long term (1 year) reduction of N_2O could be observed but compared to the high amount of N-fertilizer that was applied during the investigation period, annual N_2O emissions can be neglected and the reduction potential of N_2O at this soil type is low.

Long term gas measurements are needed to evaluate if BC application can be used as a sustainable, future mitigation strategy for soil GHG emissions.

Based on the results of this study a biochar application for mitigating soil N_2O emissions can only be recommended for poor agricultural soils, such as sandy soils. In both measurement periods GHG emission reductions were higher the poorer the soil was (Planosol at Eschenau). If a soil site displays better physical and chemical properties, biochar application rate has to be elevated to 3 % to receive better results regarding GHG emissions. For example, CO_2 emissions were decreased with both a 1 and a 3 % biochar application rate at the sandy Planosol whereas at the loamy Cambisol only a 3 % biochar application rate reduced CO_2 emissions.

In both periods and in the field trial CH_4 fluxes were not remarkably changed by a biochar application. When we considered CH_4 fluxes, we observed great variation within the five replications.

We suppose that a high proportion of N-losses were emitted in form of N_2. This leads to the following assumptions:

- The measured high NO_3- contents promoted denitrification and hence N_2 production; → N_2 emissions were probably increased at unplanted pots.
- The liming effect of biochars may lead to N_2 instead of N_2O production; → N_2/ N_2O rate was probably elevated at biochar-treated soils.

Thus, we recommend also a N_2 measurement for future studies.

In conclusion, we observed the best results of biochar application considering GHG emissions and soil N compounds if wood chips are used as biochar feedstock material, the pyrolysis temperature at biochar production is at 525 °C, biochar is applied on a rather poor soil with a high sand content and the biochar application rate is 3 %.

2.7 WP 7: Economic evaluation of Biochar Production and application

WP leader: Maximilian Lauer / Stefan Gunczy, Joanneum Research, Graz

Work package content:

Cost assessment on the total cost of biochar production in rural settings (including biomass procurement, preparation, C sequestration, biological effects)

This chapter has been produced during the year 2010 in order to complete Deliverable D7-1 “Report on possibilities of AGRICHAR production and the related cost” (6/2010) corresponding with Milestone M7-1 “Techno-economic evaluation of char production process” (12/2010).

In the deliverable the expression Biochar is used for any carbonized biomass, the expression AGRICHAR can be used for biochar, if dedicated for the use as soil enhancement agent.

Introduction

Biomass can be decomposed in a number of ways. The two basic pathways relevant to production of biochar are thermo-chemical and hydrothermal conversion.

Thermo-chemical conversion processes use heat to break down the molecular structure of the biomass and use chemical reactions to obtain the desired products. Combustion, gasification and pyrolysis are the primary thermo-chemical processes. Hydrothermal processes follow a different principal approach. Subjecting biomass in water to pressure and temperature results in its decomposition into a variety of substances, with the resulting mix depending on the temperature and pressure applied as well as the catalysts used. Thus at least in principle, different products can be achieved by adapting the process parameters. Possible products via gasification include CH_4 and H_2, while pyrolysis and hydrothermal processes can generate liquids similar to crude petrol and char.

From the point of view of practicality, biomass used for biochar production needs to include not only wood (e.g., the firewood used in classical wood char production), but all biomass sources, particularly components not having high-value uses, such as straw and herbaceous biomass (e.g., leaves, stems, and roots). This plays an important role in the discussions of specific processes found in various chapters in this report.

The following chapters review information relevant to biochar production. An overview of decomposition processes for biomass is given in chapter 0, details of different conversion processes are discussed in chapter 0, and costs of biomass carbonisation technologies are investigated in chapter 0.

Overview of conversion processes

Biomass chemically consists of a variety of complex molecules, for example in the case of wood mainly lignin, cellulose and hemi-cellulose. In order to make use of the chemical composition of biomass feed stocks to produce specific preferred products like biochar, several process pathways are available.

Two pathways to break down biomass' large molecules are well known.

- Thermo-chemical processes (chapter 0Thermo-chemical processes) and
- Hydrothermal processes (chapter 0)

Thermo-chemical processes

Thermo-chemical processes use heat to break down the structure of the large molecules. There are in principal three processes that use heat to start decomposition and facilitate the various chemical reactions that lead to the desired products:

- Combustion: The well-known process is e.g. used in stoves and boilers. It results in total conversion of biomass to oxygenated flue gases and the product heat (enthalpy of flue gases)
- Gasification: This process converts biomass completely to a combustible gas ("Wood gas"). The mix of components of the gas can be used for further products or the chemical enthalpy of the gases can be used for heat.
- Pyrolysis: This process converts biomass into a set of products including solids (char), liquids (condensates, bio-oil), and non-condensable gases.

In Figure 77 a schematic illustration of the pyrolysis process is shown [Knoef2005]

The pyrolysis process is the only thermo chemical process able to produce a solid product, i.e., a char. Gasification will also produce some char, but this basically occurs only because gasification is generally technically incomplete. Details on char production via the pyrolysis process will be discussed in chapter 0.

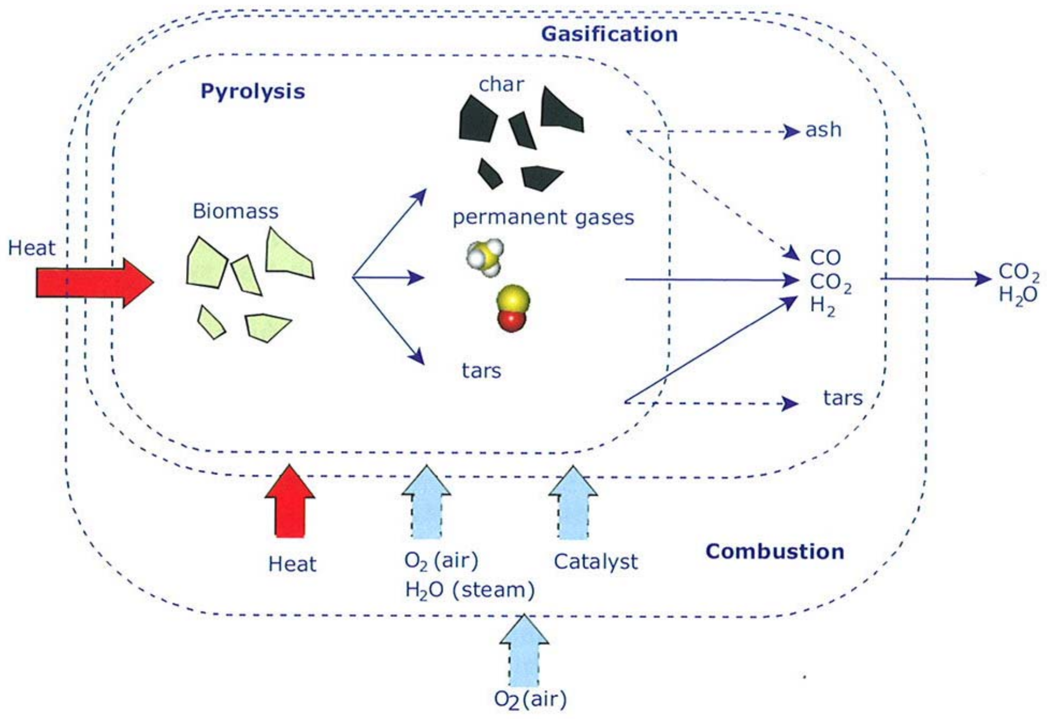


Figure 77: Schematic description of biomass decomposition [Knoef 2005]

Hydrothermal degradation

Hydrothermal is a technology used to break up large molecules in water under elevated pressure and temperature, often using catalysts to enhance the reactions.

Hydrothermal conversion has been known since 1932, when Friedrich Bergius was awarded the Nobel Prize for his research [Bergius 1932]. In the last two decades hydrothermal conversion became the focus of biomass for energy research in several research efforts (e.g. the HTU-process by Shell, NL and at the "VERENA" research facility of FZK-Forschungszentrum Karlsruhe, GER). Most of the research focused on finding new ways to utilize the energetic content of biomass, either in liquid bio fuels (e.g., HTU) or in gases such as CH_4 and H_2 (e.g., VERENA). In the last few years the possibility of producing biomass char has emerged as an additional focus of research with the objective of reducing greenhouse gas emissions by using the char as means of carbon storage and as a soil productivity improvement agent or also as a fuel.

Several processes have been developed for hydrothermal carbonisation (HTC) using hydrothermal processes. These processes all work at elevated temperatures (>180°C) and elevated pressures (>200.000 pa) in the presence of water and catalysts (acids etc.). Most of these processes need quite long residence times (> 4 h). Many of the processes are slightly exothermic, so there is no need for an external source of heat except for starting the process. Most of the recent research work and technical development on these processes seems to have be done in Germany. An internet research resulted in virtually no hits for activities in other countries.

Prof. Antonietti (Planck Institute Potsdam) issued one of the early serious publications on HTC [Antonietti 2006], in which he provides a vision of the importance of HTC for climate issues, energy production and soil-quality enhancement. At the moment two companies could be identified offering HTC-technology (i.e., not only plans for RTD work) for producing biomass char.

- The Swiss company AVA-CO2 [Schmidt 2010] is running a demonstration plant in Karlsruhe with a capacity of 8.400 t of biomass per year as a batch process.

- The German company "Terra Nova Energy GmbH" has announced a demonstration plant to be built in Kaiserslautern (GER) (www.terranova-energy.com, 15.2.2011).

Schmidt [Schmidt 2010] compares the quality of chars produced by hydrothermal carbonisation with the quality of pyrolytic chars (i.e., chars produced by thermo-chemical processes). He discusses the chars from HTC- processes as "hydochars" and those from form thermo-chemical processes as "pyrochars". He states that the products are not comparable for use as soil additives. They apparently are quite different in porosity (hydrochar very low, pyrochar high), content of volatiles (hydrochar very high, pyrochar rather low) and other qualities. According to Schmidt there are indicators showing that hydrochars could be good fuels although probably poor for soil-quality improvement.

Hydrothermal carbonisation is in a very active research phase with, up to now, few results and applications. There seem to be uncertainty regarding the suitability of chars derived from hydrothermal carbonisation as soil additives, if the goal is soil-quality improvement. The results of this active research should be evaluated again in a few years.

Due to the above considerations, char production using hydrothermal processes will not be considered further in this report.

Thermo-chemical Carbonisation of biomass

Wood char created through thermo-chemical carbonisation has a history of several thousand years of uninterrupted use (chapter 0). Wood char production is still important for some countries in Asia, Africa and Latin America both for cooking and heating and for production processes. In section 0 technical processes able to meet the specifications of biochar production are discussed and promising ones identified.

History of wood char production

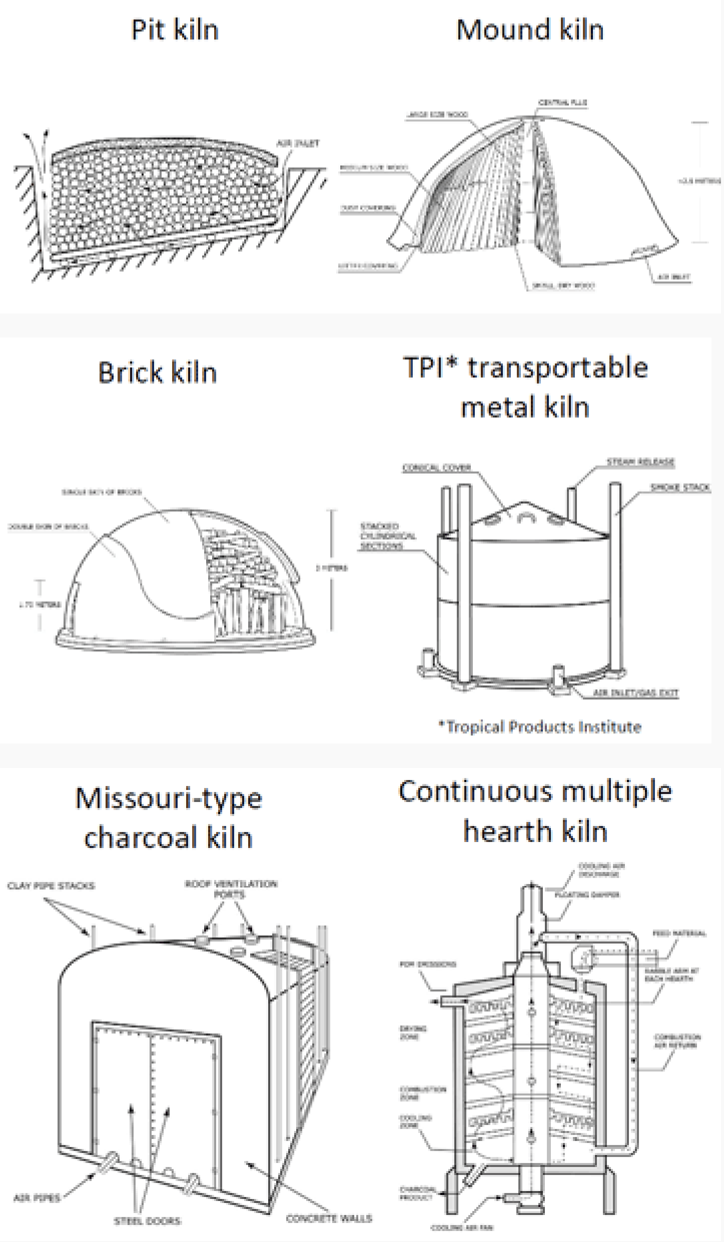
In the past wood more or less the only material used to make charcoal. A few other substances with qualities similar to wood such as coconut shells have also been used. Typically wood char has been produced in kilns of different types, including earth covered, and in holes or stone structures and metal structures. All these kilns operate in a batch-process manner. In the case of wood, only solid wood of particular sizes -- from chunks to logs -- can be used for charcoal making in kilns. A comprehensive description of wood char technologies and history is provided in [Gronli 2005]. Some important effects of temperature, heating rate and pressure on charcoal productivity are also reported as the result of a literature review [Gronli 2005]. Figure 78 shows examples of simple kilns for wood char production.

The first “industrial” process seems to be the “Reichert” process using retorts with external heating. This was also a batch process, however by using seven retorts working sequentially, so a “semi continuous” operation could be achieved. This process was until recently in operation at Bodenfeld (GER) operated by Chemviron Carbon. [personal communication with Chemviron Carbon 2003].

Continuous charcoal production processes were developed by Lambiotte and Lurgi starting at the 1940s. The applications were of industrial size (20.000 to 30.000 t/a) and used a process in principle similar to an so called “inversed updraft gasification” but focussed on char instead of gas production. Very few of these installations are still in operation today.

No information could be found on substantial char production using powdered or small-sized biomass particles (e.g. sawdust) of any kind. There is one source of information on experiments on straw gasification for char production using an updraft wood gasifier at the Munich Technical University in the 1980s. The experiments were not successful and stopped because of excessive slagging [personal communication with TU-Munich 1985].

Today there is a small amount of charcoal production in several European countries, with the European imports exceeding exports by far.



Pit kiln

Mound kiln

Brick kiln

TPI* transportable metal kiln

*Tropical Products Institute

Missouri-type charcoal kiln

Continuous multiple hearth kiln

Source: From Biochar for Environmental Management, Chapter 8, adapted from: FAO (1983); Whitehead (1980); Maxwell (1976); and Radian Corporation (1988)

Figure 78: Examples of simple wood-char production kilns and processes

Thermochemical processes for the production of biochar

As reviewed in section 0, pyrolysis is the only thermo-chemical char production suitable to producing significant amounts of char and hydrothermal processes are not further discussed due to the considerations stated in section 0.

The outcome of the pyrolysis process is influenced by several parameters as:

- Heating rate
- Carbonisation temperature
- Residence time

For maximizing the yield of liquid output fast pyrolysis is most suitable. Fast pyrolysis is characterized by a very high heating rate, a relatively high temperature (>450°C) and a very low residence time. On the other hand, for maximizing the solid (char) output slow pyrolysis, characterized by a very low heating rate, moderate carbonisation temperatures (about 350 to 450 °C) and a very long residence time is preferred [Piskorz 2002], [Bridgwater 2002].

As a practical consideration, a process for biochar production should be able to process all kinds of biomass available, e.g., wood, straw, leaves, etc. Consequently the technology should be able to use powdery or very small sized biomass. In order to meet the principal requirements of a thermo-chemical process, the water content of the biomass feed should be as low as possible. The classic wood-char production processes are not viable because of their requirements for large-size feedstock and classical fast pyrolysis processes are not viable because of the process parameters, especially the very short residence times. Processes are thus needed that produce biochar from powdery biomass and have long reactor residence times.

Two processes can be considered as viable at the moment, the entrained flow and fluidized bed processes. These are discussed in sections 0and 0 respectively.

Entrained flow process

Both rotating kilns and screw reactors are used in current entrained flow technologies. Biomass pyrolysis using rotating kilns or screw reactors has the advantage that the residence time can be adjusted over a wide range as needed to obtain the best results for the specific feedstock.

A number of entrained flow biochar production processes can be identified in the literature or through internet research. Two of them seem to be operational with some experience at an advanced stage of development. Below the technology developed and tested by EVN in Austria and the technology offered by PYREG GmbH. in Germany are described.

EVN biochar technology, Austria

In Lower Austria the utility company EVN has constructed and runs a test unit for slow pyrolysis of straw. The objectives are to produce a pyrolysis gas intended for combustion in a nearby coal power plant while using the char for energy production either at a different location or as a commodity, if practicable. (personal communication with EVN, July 2010).

The process consists, in principle, of a:

- Fuel handling system: a straw bale handling system, a straw chopper, a fuel hopper and a conveying system;
- Plug screw feeder ensuring both transport and avoiding air intake to the pyrolysis reactor which is rendered airtight by plugging the feeding hole;
- Pyrolysis reactor in the form of an externally heated rotating kiln (Figure 79); and
- Char discharging and handling unit.

The testing facility is capable of processing 6.000 t/a of biomass (mostly straw) and producing 2.000 t/a of biochar. The operator reports smooth operation with very high availability over several thousand hours during a successful test phase. The plant design uses only well-tried industrial components available for chemical engineering plants. [personal communication with EVN, July 2010]

For practical operation in an agricultural context, which would take place after the testing phase is completed, some additional equipment will be needed. Additional equipment includes a pyrolysis gas burner for kiln heating, flare, and flue gas piping. The test runs of the plant are still ongoing and there are no final data available on either investment or operating costs. A conversion rate of 35% was stated as having been achieved in July 2010.

The specific advantage of the EVN technology seems to be the plug screw feeder in the biomass feeding system. It is airtight in operation and compresses the biomass, so most of the air in the structure the biomass (straw) remains outside the reactor.

Figure 79*: **EVN Pyrolysis plant, detail of the rotating kiln reactor (photo: Lauer)***

PYREG biochar technology Germany

The technology developed by PYREG is in principal similar to the EVN technology. It uses gas tight rotating lock for the feeding system and a twin screw-type reactor instead of a rotating kiln. Fuel input is rated at max. 500 kW (40 to 180 kg/hr). The entire plant is mounted in a 20’’ transport container.

An interesting detail is that a FLOX burner (flameless oxidation) is used to burn the pyrolysis gases, aiming at high efficiency and low emissions in NO_x and particles. If proven by tests, this could be an interesting option for other biochar production technologies. Reliable data on cost, performance and availability are not available at the moment. In Figure 80_an illustration of the PYREG plant is shown.

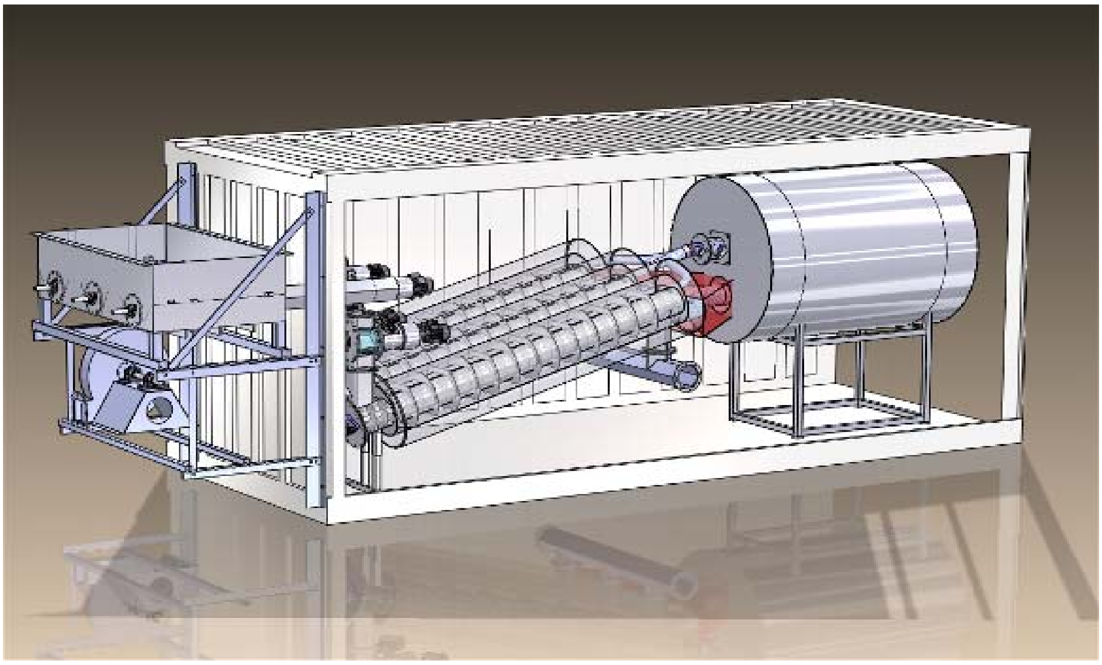


Figure 80: ***Illustration of the design of the PYREG biochar production plant [PYREG]***

Other producers also are offering pyrolysis plants for biochar production. In Figure 81 another example of a rotating kiln reactor is shown (3R Agrocarbon, Sweden/Hungary) Agrocarbon is offering a technology for producing bone char. There is no indication that this technology should not be able also to process other biomass types as straw and wood (as also 3R Agrocarbon claims).

Figure 81***: Rotating kiln char process of 3R Agrocarbon (Photo 3R Agrocarbon)***

Fluidized bed Processes.

Fluidised bed processes are commonly in use for biomass gasification and fast pyrolysis at medium and large scales. Current fast pyrolysis processes produce biochar as a by-product (~ 15-20% of the biomass input). By adapting the process parameters, e.g., temperature, residence time, and reactor geometry, the yield of biochar should be increased significantly (not proven up to now).

If the temperature in the fluidised bed is reduced to temperatures optimal for the carbonisation process, the freeboard (above the fluidised bed) is high enough and the gas flow rate in the bed is kept as low as possible, the conditions for slow carbonisation should obtain. However, instances of fluidised bed pyrolysis dedicated to biochar production did not turn up in either the literature, personal communication or internet searches.

Fluidised bed pyrolysis is a well known technology producing relatively few problems. Feeding systems, ash and carbon separation systems etc. are state–of-the-art. If the production of biochar for use in agriculture is accepted as a useful strategy, fluidised bed systems will be a very interesting option to explore.

Cost of Biomass Carbonisation

No cost information from actual biomass carbonization projects is available for either hydrothermal or thermo-chemical processes. Some experimental experience is reported from several companies in testing/demonstration with thermo-chemical carbonisation. No demonstration plant experience was found using continuous processes for hydrothermal carbonisation.

The cost data presented in this chapter are primarily derived from a project being promoted by the company “Sonnenerde” in Riedlingsdorf, Burgenland, Austria [Dunst, 2011]. The company produces a variety of soil mixtures for different uses. It has the intention of also producing some kind of “terra preta” in the form of a biochar enriched soil. A project of a biochar based on the PYREG process has been proposed, which is now in the process of getting the legal permits. The project foresees biochar production using various types of biomass including dried sewage sludge, straw, woody biomass from vineyards, etc.

Relevant information given by [Dunst, 2011] on this proposed project is:

- Investment including engineering, founding etc.: 400.000,-- €
- Useful lifetime: 10 years
- Production: ca. 300 t / a biochar (including ashes) over 7.500 to 8.000 hrs annual operation, corresponding to a production rate of ca. 40 kg / h
- Operation costs:
    - Electricity consumption: 10 kW
    - Personal cost: 2 hrs per day
    - Repair and maintenance cost: 8 % of investment cost per year
    - Cost of straw: 73 € / t
- Cost of wood char grit as a commodity: 300 € / t at next railway station

Annual investment related costs calculated at 5 % interest rate over 10 years, (annuity factor 0,1295) 51.800,-- € / a

Operation related costs (without biomass cost):

Electricity consumption (10 KW, 8.000h / a, 0,20 € / kWh): 16.000,-- € / a

Personal cost: (2 hrs / d; 340 d / a; 35 € / h): 23.800,-- € / a

Repair and maintenance cost (8 % / a of 400.000 €) 32.000,-- € / a

Total operation related costs (without biomass cost) 71.800,-- € / a

Total annual cost (without biomass cost) for 300 t / a of biochar 123.600,-- € / a

Cost of carbonisation of biomass (without biomass cost) 412,-- € / t

Adding biomass acquisition costs to the carbonisation cost of 412,-- €/t biochar and other boundary conditions results in:

- If straw is used, about three tons of straw have to be provided raising the cost by 219 € per ton of biochar produced (about 3 tons of straw for 1 ton of biochar), resulting in total biochar cost of 631, -- €/t biochar.
- Current costs for industrial waste wood are the same as for straw (60 to 90,-- €/t dry wood), so the resulting biochar cost would also be in the range of 631,-- €/t biochar
- Forestry wood chips actually cost 120 to 150, -- €/t dry wood, resulting in total costs of 770 to 860,-- €/t biochar.

To put these costs in a perspective, bulk prices for imported low quality biochar, i.e., wood char grit, are about 300 €/t. Thus based on available, currently immature technology, the cost of biochar production using straw, wood chips or agricultural residues will be roughly double the cost of imported bulk biochar, i.e., in the range of 600 to 650 €/t. Nearly one third of these costs are investment related and about one third due to biomass acquisition costs.

Three factors should be taken into consideration in evaluating these results: the cost of the biomass feedstock, particularly the option of using waste materials; plant size; and stage of technology development.

The cost situation can be dramatically changed if, instead of virgin biomass, wastes are used as a feedstock for carbonisation. In some cases, rather than needed to pay for a feedstock, if the feedstock is a waste, a disposal fee may be received. By using wastes such as sewage sludge or recycled wood, which would have no, or even a negative feedstock cost, the production cost of biochar would be at about the same level as imported biochar grit. However, strict legal restrictions and conditions imposed by a range of authorities have to be adhered to in processing waste materials.

The investment costs as well as plant size used for the cost assessment are based on a very early stage of technology development and on a very small plant. Plants in a mature state of technology and of a reasonable size (several 100 kg/h) will be able to produce biochar more cost effectively, but will not produce it at the level of biochar grit import costs as of 2010.

Economic assessment of AGRICHAR production and use

Introduction

A comprehensive economic assessment of agrichar production and use includes both a techno-economic assessment as well as a socio-economic assessment.

The techno-economic assessment is based on a technical analysis about the effects of agrichar on corn yield and a subsequent business economic assessment whether extra corn yield of this new technology exceeds additional costs.

The socio-economic assessment belongs to the question how the application of agrichar affects the society in general. Often this assessment includes calculations about the effects on "market based" economic indicators as employment, GDP (Gross Domestic Product), tax yields, avoided unemployment benefits, etc. [1]. However, the new technology agrichar was tested so far under "laboratory conditions" (field tests in Eschenau, Kaindorf and Traismauer/ Austria) to generate first basic insight about this technology. Thus, it is not sufficiently clear yet for how much of the Austrian agricultural crop land it would be reasonable to be treated with agrichar. As the extent of application is not sufficiently clear also the effects on these "market based" economic indicators cannot seriously be estimated. Nevertheless, the socio-economic assessment does not include only "market-based" economic indicators but also those effects which are not displayed on markets[2] but also affect the welfare of the society. Literature often refers to these effects as "external effects" or "externalities". Estimating comprehensively socio-economic effects of the agrichar technology have to take into consideration these external effects as conclusions about agrichar might not be optimal from an overall society point of view.

Many efforts have been made in the past to understand different types of external effects and to quantify them. Studies such as ExternE[3], CAFE[4], NewExt[5] or RECaBs[6] are only a few examples.[7] Corresponding literature distinguishes between the following types of external effects from energy use:[8]

- Damages from climate change caused by greenhouse gas emissions: the anticipated increase of extreme weather events (floods, draughts, etc.) may not only lead to damages on infrastructure and environment (e.g. crop yields), but also to impacts on human health, e.g. caused by extreme and long-lasting heat waves.
- Damages from air pollutants on human health, materials and crops: besides particulate matter (PM_{10}, $PM_{2.5}$) also SO_2, NO_x and VOC emissions affect human health through the formation of secondary pollutants. Furthermore, emissions of NO_x and VOC affect human health through the formation of ozone. Buildings-related damages are mainly caused by SO_2 (acidification), but also by ozone. Emissions from

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[1] Market based economic indicators result from impacts on the labor, goods, capital and foreign trade markets.

[2] Compare Tuerk et al. (2011), p. 96

[3] Externalities of Energy; Bickel & Friedrich (2005)

[4] "Clean Air for Europe"; Watkiss et al. (2005b)

[5] "New Elements for the Assessment of External Costs from Energy Technologies"; Friedrich et al. (2004)

[6] Renewable Energy – Costs and Benefits for Society; EA Energy Analyses (2007)

[7] For a comprehensive compendium see e.g. Maibach et al. (2007), p. 128 et seq

[8] For a comprehensive compendium see e.g. Steiner (2006) or EA Energy Analyses (2007)

SO_2, NO_x and VOC also adversely affect crops and ecosystems through the formation of secondary pollutants.[9]

- Potential costs from nuclear damages based on historic records. Moreover, this component includes long-term health costs of radioactive emissions from abandoned uranium mill tailings.[10]
- Costs of fuel supply security (if not internalized)
- Noise
- Some other external effects like reduced biodiversity, damages on the overall appearance of the landscape or usage of exhausting energy sources[11]are also mentioned in literature.

Not all of these effects are applicable for the underlying assessment. External effects belonging to agrichar use are rather avoided external effects due to the sequestration of carbon or avoided greenhouse gas emissions (N_2O). As external effects are not displayed on markets, their quantification is not straight forward and therefore subject to many uncertainties.[12] Nevertheless it is necessary to take external effects into consideration because otherwise this may result in making wrong decisions as stated by Bickel & Friedrich et al. (2005): "… the uncertainties should not purely be looked at by themselves; rather one should ask what effect the uncertainties have on the choice of policy options. The key question to be asked is *how large is the cost penalty if one makes the wrong choice because of errors or uncertainties in the cost or benefit estimates?* "[13] The authors came to the conclusion for numbers provided in ExternE that "the risk of cost penalties is surprisingly small even with a very large range of uncertainties."[14]

Economic effects of agrichar use additionally to business as usual

For assessing the impacts of agrichar on the fertility of the agricultural crop land a field experiment with spring barley has been conducted in Traismauer, Austria. For this 90 t of agrichar per hectare have been dispersed additionally to 120 kg nitrate per hectare already used for fertilization purposes. This has resulted in more than 10 % increase in crop yield (Figure 82).

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[9] Compare with European Environmental Agency (EN35)

[10] Compare EA Energy Agency (2007), p. 77

[11] See Kaltschmitt et al. (2000)

[12] For more detailled information see Tuerk et al. (2011)

[13] Bickel & Friedrich et al. (2005), p. 264

[14] Ibid

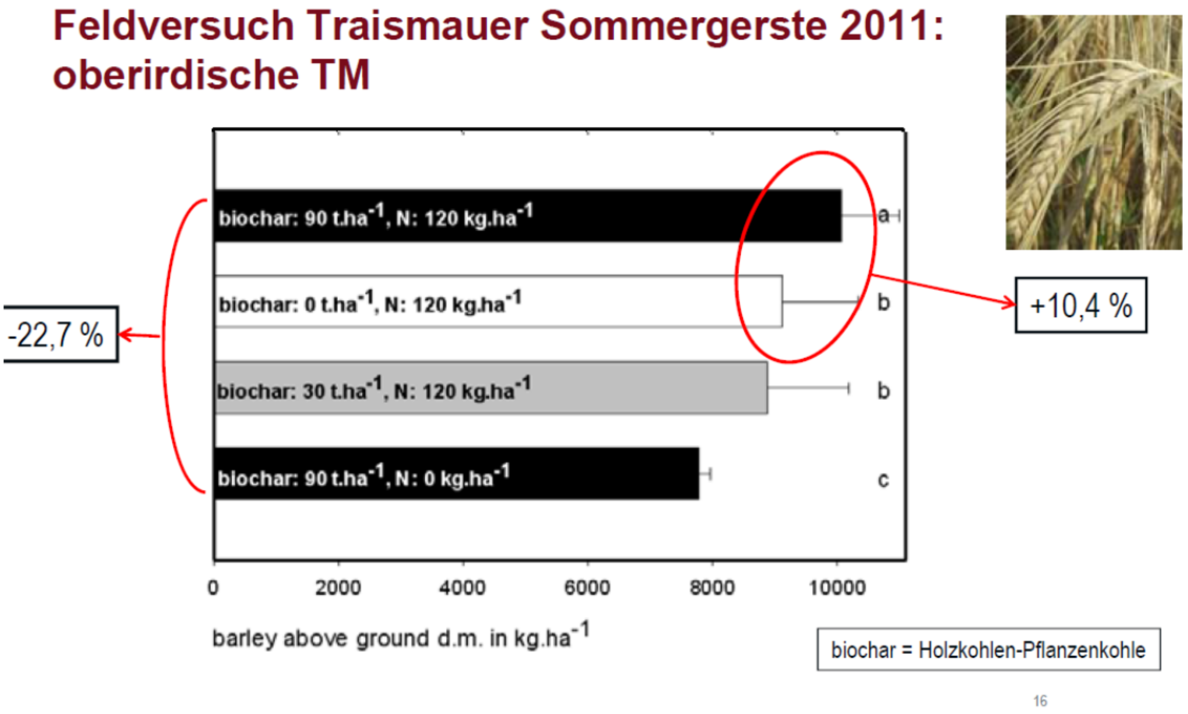

Figure 82: Chances in crop yields due to different dispersion of agrichar and nitrate

This effect resulted mainly from increased water retention of soil rather than an increased fertilization effect from agrichar. This increased water retention of soil impacts the fertility of especially dry soils, therefore increased fertility due to agrichar cannot be assumed for the entire Austrian agricultural crop land.

In 2011 spring barley was grown in Austria on 74,810 ha with a crop yield of 371,940 tons (Statistik Austria, Feldfruchternte 2012). This implies per hectare yields of approx. 5 tons of spring barley. Increasing the crop yield due to agrichar by 10 % implies additional 0.5 tons/ha. At an assumed price for spring barley of 200 €/t rounded value based on “Grüner Bericht”, Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft this additional crop yield results in additional revenues of 100 €/ha/year. On the costs side the following expenses have to be included: Per hectare 90 tons of biochar were dispersed in the field experiment - Traismauer. Costs for wood char grit have been determined at € 300,- /t in chapter 0. Using 90 tons of agrichar per hectare costs of € 27,000 per hectare accrue (costs of dispersion not included). This relationship leads to a period of amortisation of approx. 270 years even when assuming that applying agrichar once would keep up fertility for this entire time period.

However, improved water retention due to agrichar might protect certain dry soils/regions from being completely unusable for cultivation of grains. This issue might become especially relevant with proceeding global warming and potentially more frequent extreme weather events like droughts. Assuming for dry soil that droughts might lead to total failures of crop yield, this would result in revenue losses of € 1,000 /ha/year[15], which might be avoided

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[15] € 200/t times 5 t/ha

through the improved water retention of agrichar. If we consider – once agrichar is applied – that improved ability for water retention remains for the next 10 years, in the worst case of total crop failure each year if agrichar would not be applied, revenue losses of € 10,000 /ha/ within 10 years could be avoided.In contrast to that cost of € 27,000 per hectare for agrichar treatment have to beard. This implies that from a pure business economic viewpoint it might not – at current agrichar costs and grain prices – profitable to use agrichar even as adaptation measure at least in the Austrian regions. However, taking into consideration overall economic benefits e.g. from avoided migration from rural to urban regions if farmers do not face higher risks of bad harvest, additional research might show that agrichar could be an useful climate change adaptation measure also in Austria.

Nevertheless, it is pointed out at this stage once again that these results specifically correspond to spring barley at dry soils in Austria. As Klinglmüller (2013) states the impact on fertility rate highly depends on different agrichar characteristics, application rate, soil properties and type of crop used.

A similar picture compared to the business economic viewpoint appears when including also the monetized social benefits from carbon sequestration due to agrichar and its therefore resulting positive impacts on climate protection. Benefits from sequestered carbon are not easy to quantify as damages resulting from climate change may appear just in several decades and their magnitude is still unclear. Also the valuation of future damages in current values are a matter of intergenerational discounting and therefore also a rather philosophical issue.[16] Beside that its valuation – and therefore the society's willingness to pay to avoid such damages – is a matter of the potential vulnerability of a certain region. However, several studies have monetized benefits from carbon sequestration, although they are varying. Including the social value of carbon sequestration in economically assessing agrichar has therefore to take into account a certain range of monetized benefits from carbon sequestration. Respective literature corresponds to marginal damage costs of CO_2 of € 15 / t_{CO2} as a lower value, € 25 / t_{CO2} as a central estimate and € 80 / t_{CO2} as a high estimate[17]. The social (societal) value of carbon sequestration is given by:

$$\textit{Social value of carbon sequestration per hectare} = Q_{AC} * C_{AC} * \beta_c * \Omega_{C \rightarrow CO2} * SV_{CO2} \qquad [1]$$

Whereas:

Q_{AC}	*Quantity of agrichar dispersed per hectare (t_{AC}/ha)*
C_{AC}	*Carbon content of agrichar (t C/ t agrichar)*
β_c	*Stability factor of agrichar C in soil*
$\Omega_{C \rightarrow CO2}$	*Conversion factor between weight of Carbon (C) and weight of CO2 (44 t CO_2 = 12 t C ➔ 1 t C = 3.67 t CO_2/t C sequestered)*
SV_{CO2}	*Social value of avoided CO_2-emissions per ton of CO_2 (€ / t_{CO2})*

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[16] See Tuerk et al. (2011) or Schelling (1995)

[17] Compare European Environmental Agency: EN35 or Watkiss et al. (2005b)

In the field experiment 90 tons of agrichar per hectare cropland was dispersed. The carbon content of agrichar varies considerably depending on used feedstock and kind of pyrolysis (slow/fast). The used feedstock for the pyrolysis in the field experiment has been wood and agrichar has been produced by slow pyrolysis. Brown et al. (2011) propose a carbon content of wood chips based agrichar made by slow pyrolysis of 73 %. A crucial question now for determining the climate protection effect of agrichar is how long sequestered carbon remains in the soil and is therefore withdrawn from the atmosphere. Scientific results in this area is still uncertain, therefore respective literature proposes conservative estimates of 68 to 80 % of carbon content to be stable in soil for more than 100 years.[18] An assumed carbon stability factor of 0.75 (= 75 %) sounds therefore reasonable for subsequent calculations. Another aspect to be considered is a conversion factor from C to CO_2. Chemistry teaches that for each ton of C sequestered 3.67 tons of CO_2 are withdrawn from the atmosphere. The last factor in determining the external benefits of agrichar use is the abovementioned social value of avoided CO_2-emissions, which varies between € 15 / t to € 80 / t of withdrawn CO_2. In the table below all factors used are displayed:

Factor	**Value**
Q_{AC}	90 *[t / ha]*
C_{AC}	0.73 *[t C / t agrichar]*
β_c	0.75
$\Omega_{C \rightarrow CO2}$	3.67 *[t CO_2 / t C]*
SV_{CO2}	80/25/15 *[€ / t_{CO2}]*

Applying all these factors following avoided social costs from carbon sequestration arise per hectare:

Social value of CO_2	**Avoided Damage Costs** (due to carbon sequestration)
80 [€ / tCO_2]	14,500 [€ / ha]
25 [€ / tCO_2]	4,500 [€ / ha]
15 [€ / tCO_2]	2,700 [€ / ha]

Additionally to carbon sequestration, dispersing agrichar might influence fluxes in CO_2, CH_4 and N_2O from soil. However, Klinglmüller (2013) state that "the influence of biochar on GHG emissions from agricultural soils was difficult to quantify as results vary considerably for different biochar types, soil types and stages of plant growth. Furthermore, the impact of

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[18] Compare Klinglmüller (2013)

other parameters such as soil temperature, soil water content etc. could not be ruled out."[19] These uncertainties specifically apply for CH_4 fluxes, where Klinglmüller (2013) states that "statistical analysis revealed no clear trend concerning the effect of biochar."[20] Similar uncertainties arise for CO_2 fluxes.[21] Only for N_2O "statistical analysis showed about 50% lower fluxes for biochar-treated varieties compared to untreated varieties."[22] Klinglmüller (2013) states that agrichar could halven N_2O fluxes (which are again estimated as a result of N input to soil)[23] to 1.44 kg N_2O /ha/year, or differently expressed, to 429 kg $CO_{2eq.}$ /ha/year. Assuming a constant suppression effect over ten years, this leads to 4.3 tons $CO_{2eq.}$ /ha mitigated within this 10-years period due to reduced N_2O fluxes, which is a rather insignificant amount compared to carbon sequestration.

Other factors are reversing the positive effects of carbon sequestration and reduction of N_2O fluxes. For instance biomass as raw material for agrichar could also have been used for heating purposes, thereby substituting fossil fuels in heating systems. Also, transporting agrichar to the fields results in certain emissions, which insignificantly reduce the greenhouse gas mitigation potential of agrichar according to Klinglmüller (2013). Due to the assumed minor importance or minor impacts of these effects, those as well as effects from possibly reduced CH_4 fluxes and CO_2 fluxes are not taken into consideration in subsequent calculations.

It can be observed that combined avoided damage costs due to sequestered carbon and reduced N_2O fluxes are much above increased revenues due to increased crop yields. Remembering that the ability of water retention of agrichar is assumed to remain for the first 10 years after applying agrichar, increased revenues amount to € 1,000/ha at current crop prices (without discounting future revenues).[24] The combination of both "revenue terms", i.e. internal effects (extra revenues for farmers) and external effects (extra benefit for society) can thus be compared with the costs of agrichar.

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[19] Klinglmüller (2013), p. 50

[20] Klinglmüller (2013), p. 51

[21] Compare Klinglmüller (2013), pp. 52/53

[22] Klinglmüller (2013), p. 53

[23] Klinglmüller (2013), p. 58/59

[24] 10 years times additional 0.5 t crop yields/ha/year times revenues € 200.-/t crop

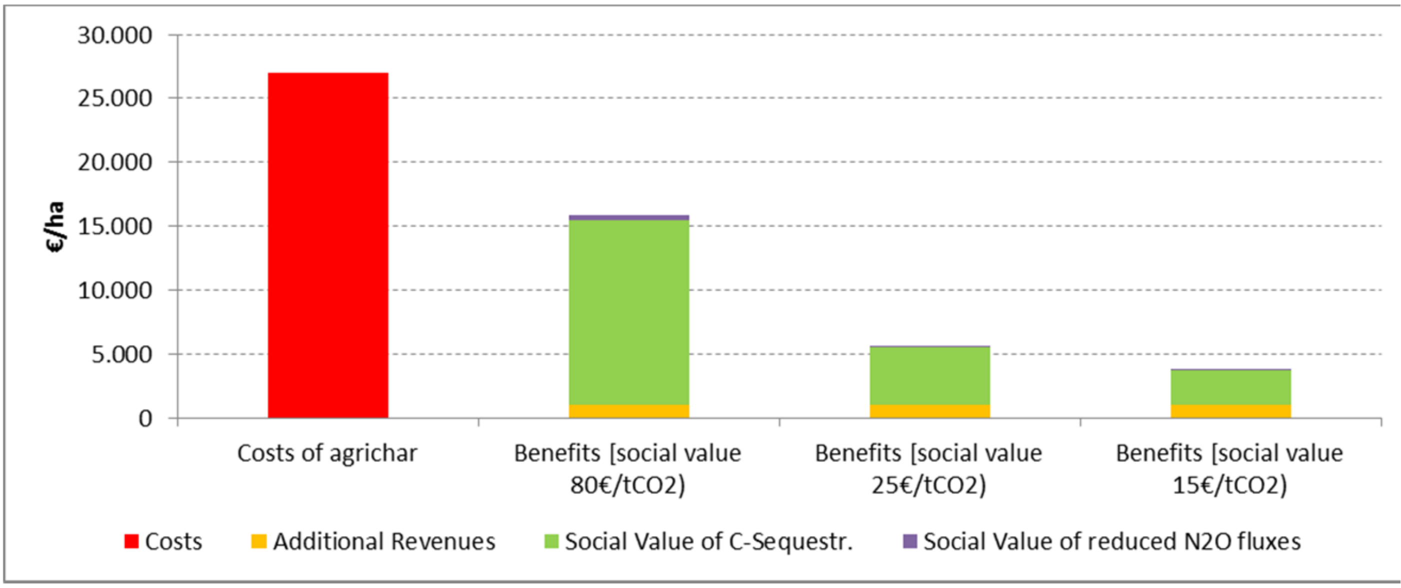

Figure 83: Comparison of costs and benefits of agrichar

Calculations above show that even including the social value of carbon sequestration and reduced N_2O fluxes beside additional revenues from increased crop yield cannot balance costs for agrichar, which are assumed to be € 300 / t of agrichar or € 27,000 / ha.

It thus turns out that costs for agrichar need to be decreased by nearly 40 % at high assumptions about the social value of sequestered CO_2 and by more than 80 % at low assumptions about the social value respectively. Or the other way around, society must be willing to pay for sequestered CO2 around € 138 / t_{CO2} that costs for agrichar of € 300 / t could be justified.

Our calculations about the social value of carbon sequestration and reduced N_2O fluxes compared to the costs of agrichar are quite conservative. Other studies like Woolf et al. (2010) have been more optimistic and included also assumptions about fluxes of CH_4 and CO_2 and other aforementioned effects (e.g. from transportation). Whereas in our analysis around two tons of sequested CO_2 per ton of agrichar was assumed[25] Woolf et al. (2010) assumes for that a factorof 2.6 to 4.7 .

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[25] $C_{AC} * \beta c * \Omega_{C \rightarrow CO2}$; 0.73 [t C / t agrichar] * 0.75 * 3.67 [t CO2 / t C]

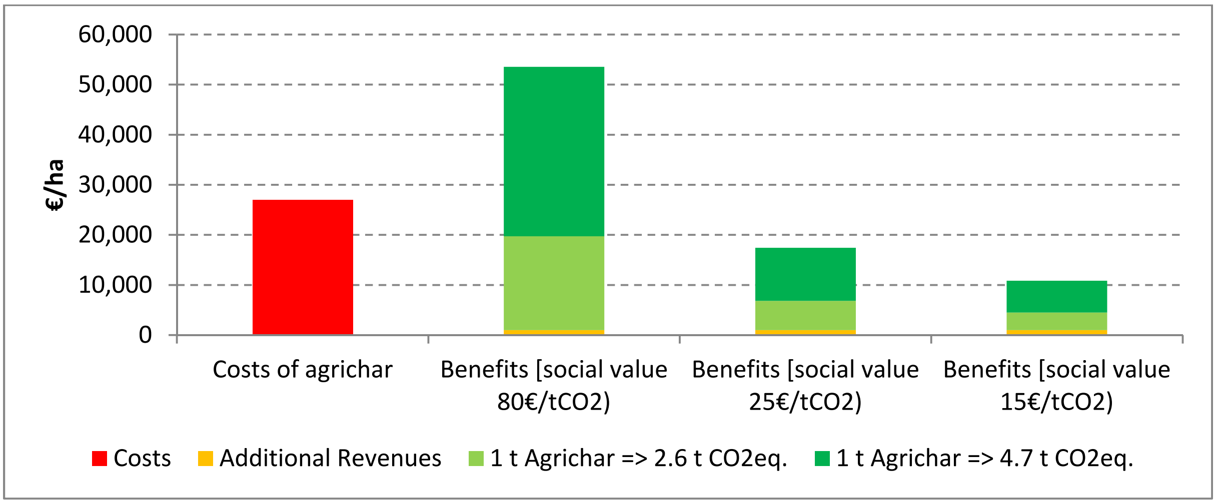
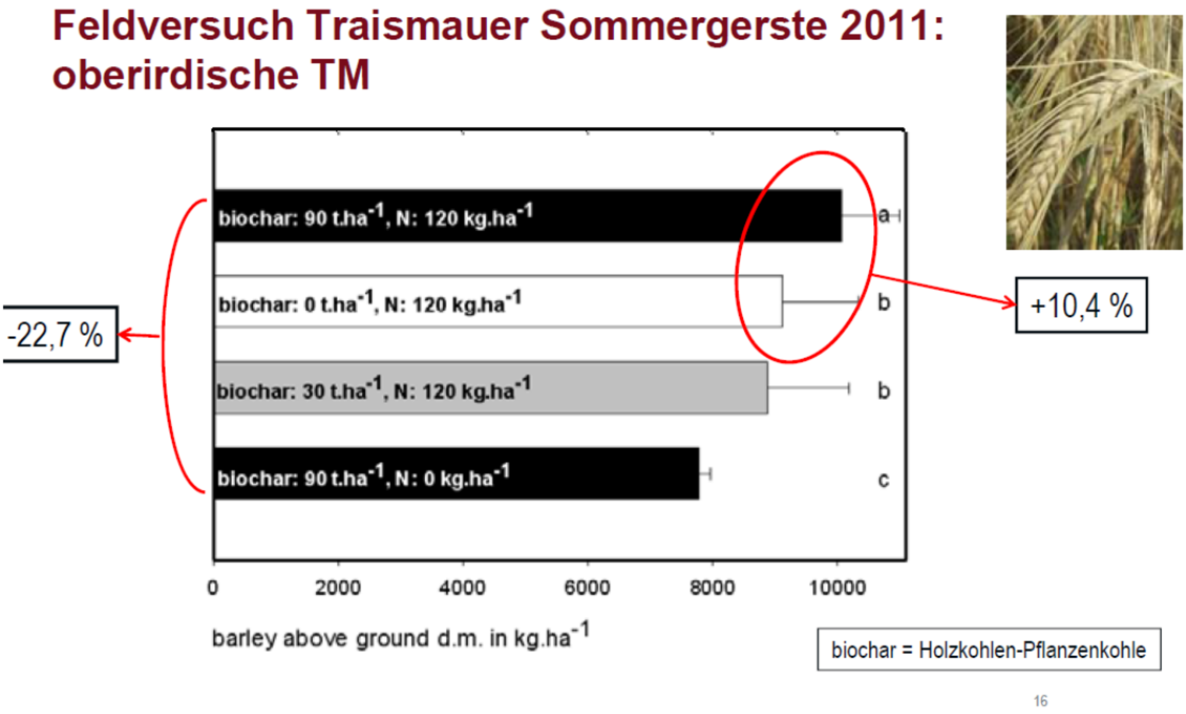


Figure 84: Comparison of costs and benefits of agrichar (optimistic assumptions about benefits)

Even the more optimistic assumption of Woolf et al. (2011) shows that benefits exceed costs of agrichar only in the case where one ton of carbon from agrichar is assumed to finally leading to an overall reduction of 4.7 tons CO_2eq. and where a social value of greenhouse gas reduction of € 80/tCO_2eq. is assumed. In all other cases, either where a lower social value of greenhouse gas reduction or a more conservative estimate of saved greenhouse gases per ton of agrichar (value 2.6 instead of 4.7) was assumed, costs exceed benefits.

Economic effects of agrichar use instead of nitrate fertilization

An alternative option at tillage operation is the substitution of nitrate as fertilizer by agrichar, i.e. dispersing agrichar but forgoing of nitrate fertilization. The field experiment showed that the positive effects on crop yield due to agrichar could not balance crop yield reductions due to the lack of nitrate fertilization (Figure 85).



Feldversuch Traismauer Sommergerste 2011: oberirdische TM

Figure 85: Chances in crop yields due to different dispersion of agrichar and nitrate

It turns out that abandoning nitrate fertilization but keeping up biochar use leads to a reduction in crop yields by 12.3 %[26] compared to the reference case without use of agrichar but with nitrate fertilization. This – in sum – reduced fertility results annually in decreased crop yields per hectare by 0.6 tons. At an assumed price for spring barley of 200 €/t (rounded value based on “Grüner Bericht”, Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft) this reduced crop yield results in an annual decrease of revenues by 120 €/ha.

However, at the asset side, firstly carbon is sequestered to the same extent than calculated above (if 90 tons of agrichar per hectare are dispersed), and secondly, emissions of the greenhouse gas N_2O normally caused by nitrate fertilization are avoided. The social (societal) value of avoiding N_2O emissions is given by:

$$\textit{Social value of avoiding } N_2O \textit{ emissions per ha} = Q_N * \Omega_{N \rightarrow CO2eq.} * SV_{CO2} \qquad [2]$$

Whereas:

Q_N	*Quantity of mineral fertilizer avoided per hectare* (t_N/ha)
$\Omega_{N \rightarrow CO2eq.}$	*Emission factor from nitrate fertilizers* ($t_{CO2eq.}/t_N$)
SV_{CO2}	*Social value of avoided* CO_2*-emissions per ton of* CO_2 (€ / tCO_2)

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[26] 10.4 % - 22.7 %

In the field experiment, avoided nitrate fertilization has been 0.12 ton fertilizer (N) per hectare. The question now arises, how much of the climate-damaging gas N_2O are avoided by avoiding the use of 0.12 ton fertilizer (N) per hectare. Yara, a Norwegian supplier of mineral fertilizers quantifies emissions per kilogramme (kg) of nitrate to 8.8 kg of $CO_{2eq.}$ (CO_2-equivalent)[27] – the expression in "CO_2-equivalent" is a translation to make emitted N_2O comparable with CO_2-emissions by taking into consideration the much higher global warming potential (GWP) of N_2O, which is 296. In other words one kg of N results in N_2O emissions of 0.03 kg which is equivalent – regarding its impact on global warming – to 8.8 kg of CO_2. This figure includes emissions of the entire life cycle of nitrate fertilizers, which includes production (3.6 kg of $CO_{2eq.}$), transport (0.1 kg of $CO_{2eq.}$) and application on the field (5.1 kg of $CO_{2eq.}$). These emissions are an upper limit as climate-damaging effects from land use change (e.g. converting tropics to arable land) could potentially be avoided by N-fertilizers due to enabling increased yield on existing agricultural land. For the social value of CO_2 the range used above is applied. In the table below all factors used are displayed:

Factor	**Value**
Q_N	0.12 $[t_N / ha]$
$\Omega_{N \rightarrow CO2eq.}$	8.8 $[t_{CO2eq.} / t_N]$
SV_{CO2}	80/25/15 $[€ / t_{CO2}]$

Applying formula [1] for calculating avoided social costs from carbon sequestration and formula [2] for calculating social benefits from avoided use of nitrate fertilizers following information arise at different assumptions about social values:

Social value of CO_2	**Avoided Damage Costs** (due to carbon sequestration)	**Social Benefits** (due to avoided N-fertilization)
80 [€/tCO_2]	14,500 [€/ha]	84 [€/ha]
25 [€/tCO_2]	4,500 [€/ha]	26 [€/ha]
15 [€/tCO_2]	2,700 [€/ha]	16 [€/ha]

These figures show already that social benefits from avoiding N-fertilization are much lower than lost revenues from lower crop yield – even at high assumptions about the social value of nitrate reduction. Furthermore it can be observed that avoided damage costs due to sequestered carbon are much higher than social benefits on avoided N-fertilization. In other words the social benefits from avoided N-fertilization could be neglected compared to the social benefits of avoided damage costs from carbon sequestration. Furthermore, reduced N_2O fluxes are neglected in this case as on the one hand the value of reduced N_2O fluxes over a 10 years period is only of minor significance (see above), and on the other hand it can

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[27] Compare Yara http://www.yara.de/doc/36294_Carbon%20Footprint%20pdf.pdf ; August 2, 2013

be assumed that N_2O fluxes are lower than in the case above as N_2O fluxes also depend on N_2O fertilization[28], which is zero in this case.

Avoiding nitrate fertilization for e.g. 10 years (=having the social benefits for this time period) and thus incurring a reduced crop yield in that period leads to the following comparison of costs and benefits:

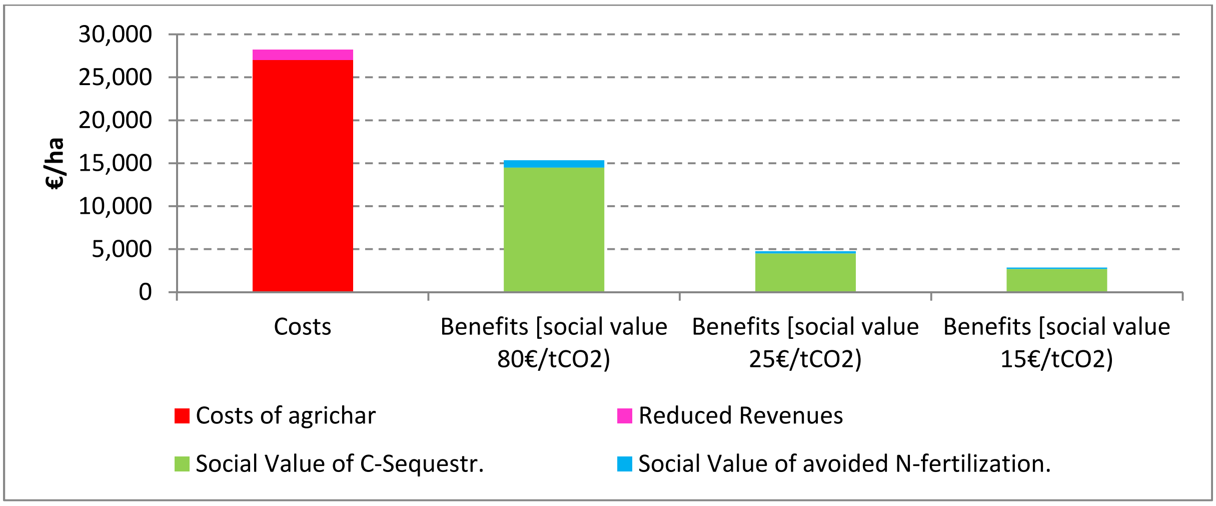

Figure 86: Comparison of costs and benefits of agrichar at alternative cultivation method

This comparison shows that costs for agrichar and reduced revenues due to reduced crop yields are much higher than social benefits from carbon sequestration and avoided N-fertilization. For break-even costs for agrichar would need to be even lower than required in the case of using both agrichar and N-fertilization as social benefits of avoided N-fertilization are lower than reduced revenues from reduced crop yield. This picture remains valid even when assuming the more optimistic assumptions of Woolf et al. (2011): Once again, benefits exceed costs only for the case of where one ton of carbon from agrichar is assumed to finally leading to an overall reduction of 4.7 tons CO_2eq. and where a social value of greenhouse gas reduction of € 80/tCO_2eq. is assumed. In all other cases, either where a lower social value of greenhouse gas reduction or a more conservative estimate of saved greenhouse gases per ton of agrichar (value 2.6 instead of 4.7) was assumed, costs once again exceed benefits.

Economic Conclusions

From a business economic viewpoint, currently high costs of agrichar are not balanced by only moderate increases in crop yields and thus agricultural revenues. Improved water retention due to agrichar, however, might justify agrichar as an adaptation measure to global

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[28] Klinglmüller (2013), pp58/59; „…the N_2O emissions from soil were also estimated as a result of N input to soil."

warming, especially when considering beside business economic aspects also overall economic aspects.

When not assuming total crop failures but only increased soil fertility, even an inclusion of avoided social (=societal) costs by sequestering carbon and thereby helping to mitigating climate change do not economically justify the application of agrichar. Price of agrichar would need to be decrease by at least 40 % to achieve a break-even from the overall economic viewpoint (if optimistic assumptions about the social value of sequestered carbon are applied; at pessimistic assumptions price for agrichar must decrease even more in order to break even).

When applying an alternative type of soil treatment of using agrichar but avoiding N-fertilization, a similar picture arises: Social benefits due to avoided N-fertilization and therefore reduced N_2O emissions are lower than reduced crop yields and thus revenues due to avoided N-fertilization. Also this kind of social benefits is much lower than social benefits from carbon sequestration.

Concluding it can be stated that agrichar cannot be applied economically at current costs and prices. Also when including external benefits of carbon sequestration and avoided N_2O emissions cost of agrichar still dominates. However, agrichar might be considered as an adaptation measure to global warming, especially from an overall economic point of view.

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2.8 WP 8: Coordination

WP leader: Gerhard Soja, AIT Austrian Institute of Technology, Tulln

Work package content:
Project management and reporting

The project coordinator held the contact with FFG and the project-specific representatives of FFG (Mag. Henrike Kamenik and DI Maria Bürgermeister). The composition of consortium agreements, the checks by the legal departments and the signatures of all partners were organized as well as the contracts with the farmers who provide the areas for the field experiments.

The partner consortium was complemented by several students who partly were financed by the staff costs of the project, partly from other sources.

PhD-student: Stefanie Kloß

Diploma students at AIT and BOKU: Jannis Bücker, Sonja Feichtmair, Franziska Rempt, Elena Anders.

Diploma students at BFW: Thomas Ochsenhofer, Michaela Klinglmüller.

These students are supervised by members of the consortium (Gerhard Soja, Andrea Watzinger, Bernhard Wimmer, Sophie Zechmeister-Boltenstern, Franz Zehetner). The students will graduate either at the University for Natural Resources and Life Sciences Vienna, at TU Cottbus or at University Stuttgart.

The PhD-work of S. Kloß has already resulted in the publication of a manuscript in a peer-reviewed journal (Journal of Environmental Quality 41, 990-1000, 2012). A second paper is already accepted (Journal of Plant Nutrition and Soil Science) and a third has been submitted.

The daily business of coordinating the individual workpackages was organized in the frame of meetings at two levels: on the one hand within the partner departments for the short-term planning of the staff directly involved, on the other hand by consortium meetings of all partners. All meetings regulating the daily project business within the AIT unit HET resulted in protocols (in German; AOB = Arbeitsorganisationsbesprechung), accessible to the project staff including technicians and students. For all partner meetings protocols were prepared, took, and distributed to the participants and project staff. These protocols are presented in Appendix A and give a chronological overview about the project work.

3. Conclusions

Conclusions from the results

The technologicl challenge to construct a lab-scale pyrolysis reactor that is able to produce several kg of biochar in one batch was mastered with the help of the engineering expertise of the WP 1 team. For the future, additional challenges will have to be met: the pre- or post-treatment modification of biochar will be a key to purpose-designed biochars. For future experimental reactor developments, the possibilities to activate biochar in a second step after pyrolysis or to add reactants during the process would offer more flexibility to diversify the biochar production. Also for commercial scale rotary kiln reactors this step should be facilitated because future applications of biochar will rather need different products for different purposes than a general type of biochar that suits for all purposes. Although the selection of feedstock and pyrolysis temperature are key processes that influence the quality of the output product, pre- or post-treatment steps will further adjust the char properties to the actual application needs.

The experimental design of the project with an extensive microlysimeter experiment under controlled greenhouse conditions and two field experiments proved very valuable to investigate several research questions in parallel. However, the limited financial scope of the project did not allow to extend the pot experiment design still further to a full-factorial design. In the 25 treatments the five factors biochar type, biochar concentration, nitrogen addition, soil type and vegetation were studied. The capacity constraints of the project only allowed for the investigation of each factor only with a selection of other co-factors. This allowed for the answering of basic questions but not all questions arising from comprehensive combinations of all treatments. Similarly, also the design of the field experiments had to be limited – without financial constraints, the installation of field experiments in more than 2 different soils and regions would have been an interesting option that waits for implementation in future projects.

The design of the experiments that considered the possibility of long-term studies has already proved valuable. For studies outside and beyond the scope of our project soil has been sampled for additional analyses that were not possible in our project. The field experiments will be used for supplementary long-term effect studies in cooperation with FZ Jülich and the University of Gießen. So the original idea of creating the basis for long-term studies has already proved its worth and supports the integration in international networks.

An important result that will have impact on future applications of biochar is the realization of the ambiguous role of non-supplemented biochar for soil fertility. Nutrients are only released in short term from straw biochar but not from wood-based biochars. However, concerning other physico-chemical effects on the soil, straw biochar offers less benefits than other feedstocks. The combination of biochar with either mineral or organic fertilizers like compost is indispensable to avoid yield losses. Therefore the nutrient content of biochar has a negligible role for crop nutrition; rather it creates additional demand for nutrients to counteract the competition between biochar sorption sites and microbiological nutrient demand. A timely consideration of this nutrient demand creates additional costs for the farmer that lower the economic efficiency of the biochar production and application. The biochar-mediated decrease in greenhouse gas emissions, namely N_2O, is an advantage that is not rewarded financially because of the lack of financial instruments that consider soil in the frame of greenhouse gas accounting. Only regional campaigns that design locally adapted certificate trade systems have the possibility to account for soil greenhouse gas emissions but these are not yet wide-spread.

The problematic economical situation of biochar application to agricultural soils prevents currently a large-scale implementation of this technology as soil amendment. Although the quality of biochar nowadays is satisfying and the amendments can be applied without risk to any soils if modern biochar production techniques have been applied and the pollutant threshold values of the European Biochar Certificate are not exceeded, these achievements are not enough. At the moment the price of biochar cannot be translated into corresponding yield increases by the farmers. The additional benefits of biochar like reduced greenhouse gas emission, reduced nitrate leaching to groundwater, pollutant immobilization, long-term carbon sequestration in soil and increased soil water holding capacity do not translate into farmers' income. This is because partly these benefits are not yet reproducibly quantified under different environments, partly no financial remuneration systems exist. In future agricultural management strategies (e.g. ÖPUL follow-up) such effects could be related to benefit points that are related to financial support. Such considerations could change the economic assessment of biochar considerably but the basic quantitative functions necessary to connect ecological with financial effects will need a broader basis than a single study like this project can offer. If the scientific literature on individual aspects of biochar will be combined e.g. by meta-analytical techniques, quantitative assessments could be derived that are needed for such strategic considerations.

The supplementary work performed within this project has yielded important basic information on the adsorption of pollutants like heavy metals to biochar. These results were achieved by an extension of the seepage water and plant analyses from the microlysimeter experiment. Further work to explore the potential of biochar in soil remediation can build upon these results. If further basic and applied research is focused on the topic of heavy metal immobilization by biochar and preliminary results are confirmed, a new promising field of biochar application would open.

The field experiments and supplementary work on water holding capacity of biochar-amended soils have shown that during drought periods field crops may take advantage of prolonged water availability. This result appeared although the biochar was a "general-purpose" wood-based biochar not specially designed to withhold more water. If the feedstock selection will consider the porosity architecture of the original plant material and the pyrolysis conditions support a high specific surface area formation, biochar with improved water storage capacity could result. Studying the usability of suitable post-treatment modifications might open a field for further product developments.

The results of our project have provided new information not only for research but also for companies interested in commercializing biochar to a larger extent. In the first line these might be producers of composts who can take advantage of creating new compost varieties by the addition of biochar. But also the production of biochar itself with technical scale reactors can be a business opportunity if scientific results are considered and the economic frame conditions change. Whereas under current conditions an economically feasible production of biochar is not yet possible, a financial consideration of the different non-yield related benefits of biochar might change the situation.

The legal situation is one of the most important frame conditions that will determine the future importance of biochar as soil amendment. In Austria a large-scale application to agricultural soils is not yet allowed. But the Swiss example has shown that for certain production and application scenarios a framework can be created to legally allow for a regulated biochar use in agricultural soils. The results of our project can also contribute to create the necessary basis for Austrian national regulations if the EU-based regulations will take too long. Only with a reliable regulation framework biochar may become a real business opportunity and may hold up to its promises.

4. Outlook and Recommendations

It is not uncommon for scientific studies that the answers found raise even more new questions. Although plenty of answers have been extracted from the studies in response to the research questions that were the starting point of this project, these answers demand further explanations: about the causes and mechanisms behind, about validity in different environmental conditions and about effects that had not been suspected before but which have been observed. Specifically, the following questions could not be addressed in the limited frame of this project or have arisen during performance of the planned studies:

- Long-term effects of biochar application – which biochar effects can be found in the soil environment far beyond the project duration of 3 years?
- Are there differences in the efficacy of applying a large biochar dose only once or applying several small doses repeatedly?
- What are the interactions of compost and biochar concerning the nutrient supply from composts to plants or for other benefits of biochar?
- Are there effects of biochar on soil-borne diseases of economical relevance, on the efficacy of soil herbicides; are there effects on Diabrotica (Maiswurzelbohrer)?
- Which instrumentation would allow a deeper incorporation of biochar into soil?
- Which of the positive effects of biochar are still effective after an application rate that is still affordable for farmers (e.g. 10 t per ha)?
- How effective is the retention of nitrate under field conditions in groundwater protection zones?
- Which processes of soil nitrogen metabolism are most affected by biochar and what will be the effect of biochar-compost- mixtures?
- Can the water storage potential be increased by post-treatment or activation of biochar?
- What determines the progress of biochar surface aging and how does aging affect its characteristics?
- How can the relations between surface characteristics and biochar properties be elucidated by more sophisticated analytical techniques?
- Which steps in the biochar production process need technological development most urgently to lower the price of biochar?
- Will the deployment of molecular biological techniques reveal new or unknown effects of biochar on soil microorganisms?
- Is compliance with biochar quality standards like EBC or IBI enough to avoid any adverse effects of biochar in the future and to extend the legal permissions of biochar applications?

These questions are focused on the application of biochar as agricultural soil amendment which is by far not the only usage of interest. If other deployments of biochar are considered, this list of open research questions undoubtedly would grow fast as lightning. As the interest in biochar globally continues to rise and biochar sometimes even seems to have arrived earlier in economy than in science, it appears as highly recommendable to investigate the scientific questions mentioned above as soon as possible. Otherwise the risks become real that a reliable EU-wide legal framework will take time until the cows come home and that a significant economic branch operates in the twilight zone of assumptions without firm scientific evidence.

5. Literature

Relevant references are included in the chapters of the individual workpackages.

6. Appendices

Appendix A - Protocols of the consortium meetings

Appendix B – Published or accepted journal articles are uploaded as separate files

PROTOKOLL

der

1. Koordinationssitzung

Projekt:

BIOCHAR
for carbon sequestration in soils – Analysis of production conditions, biological effects in the soil environment and economics

Mittwoch, 3.3.2010

10.00 Uhr, Stadtbüro AIT am TechGate, 1220 Donaucitystr. 1, Ebene 2

Teilnehmer:

Horacek, Lair, Lauer, Liedtke, Soja, Watzinger, Wimmer, Zechmeister-Boltenstern, Zehetner

Allgemeines

Das Projekt befindet sich derzeit im Stand der Vertragsverhandlungen. Bei dieser Koordinationssitzung ging es primär um die erforderlichen Schritte zur Erfüllung der FFG-Auflagen und um Vorbereitung der praktischen Arbeiten für die ersten Monate der einzelnen Arbeitspakete, welche anhand der Beschreibungen im Antrag besprochen wurden.

Stand der Arbeitspakete

AP 1: Biomass and pyrolysis conditions for biochar production production efficiency

Liedtke organisiert das Material für die Adaption der Pyrolyse-Öfen (u.a. Stahlrohr ca. 0,3 m ID). Eine Ausbeute von 2 kg Biochar pro Pyrolyse erscheint realistisch. Bei den zu testenden Materialien werden keine Abfälle einbezogen (mögliche Probleme mit Abfallrecht). Als Biomasse-Ausgangsmaterial wird Stroh, Rebholz und Hackschnitzel verglichen (idealerweise sowohl von Buche als auch von Weichholz). Das pyrolysierte Material muss auf Elemente (C, N vorher und nachher) und PAK analysiert werden. Auch einige Pflanzenverträglichkeitstests sollten gemacht werden. Für die Produktion der großen Biochar-Menge für den Freilandversuch 2011 wird bei Bedarf mit den Betreibern der Holzvergasungsanlage St. Margareten/Gleisdorf Kontakt aufgenommen. Könnte die Pyrolyse im Ausland (http://www.pyreg.de/) ersparen. Bitte auch Artikel beachten:
http://www.ithaka-journal.net/pyrolysereaktor ; http://www.delinat-institut.org/ithaka_test/pyrolsereaktor

AP 2: Experimental setup for carbon sequestration and soil studies

Entsprechend der AP-Beschreibung wird ein Gefäßversuch (3 Biochar-Materialien, 2 Böden, 2 BC-Konzentrationen + Kontrolle; variable Kompost- oder Düngerzugabe geht sich nicht aus) noch vor dem

Sommer 2010 (mit Bepflanzung) sowie 2011 ein Mikro-Lysimeterversuch und der Feldversuch angelegt. Die beiden Böden sind optimalerweise aus der Region Kaindorf + Waldviertel (möglichst karbonatfrei). Fruchtfolge für den Gefäßversuch: Gerste, Zwischenfrucht (z.B. Gelbsenf), Leguminose (Rot- oder Weißklee). Der Klee kann dann gleich als ausdauernde Kultur für die Zeit nach Projektende bleiben. Bewässerung über selbstsaugende Dochte aus Wasservorrat. Mit den Grundbesitzern für die Feldversuche muss Kontakt aufgenommen werden und der FFG die engere Einbindung demonstriert werden. Mit Mag. Ninaus / Kaindorf wurde bereits ein Besuchstermin für den 15.3. vereinbart (Soja, Zehetner).
Isotopen-Versuch: es wird vereinbart, dass 2 Pflanzenarten in den Gewächshaus-Kabinen mit dem verschobenen 13C/12C-Verhältnis kultiviert werden: Weizen + Weide. Ziel ist möglichst hohe Biomasse. Soja kümmert sich um Erdgas-Versorgung und erforderliche Heizkanone. Horacek misst Erdgas aus der Seibersdorf-Versorgung. 15N wird nur als markierter Dünger im Gefäßversuch verwendet, nicht bei der BC-Produktion.
Die Ausbringungsmethodik von Biochar am Feld ist noch nicht völlig geklärt – eventuell gemeinsam mit Kompost. Für reibungslosen Einsatz vorhandener Geräte wäre Feinvermahlung und anschließende Pelletierung günstig, um ähnliche Körnung wie Kunstdünger zu erzielen. Vorgangsweise wird vor Feldversuch im 2. Jahr in Abstimmung mit Biochar-Produzenten festgelegt.

AP 3: Stability of biochar carbon pools

Inkubationen werden teilweise mit Ansätzen analog zu Gefäßversuchen gemacht, ein Teil erfordert zuvor die Produktion der 13C-Biochar. Auswahl für die Dissertationsstelle erfolgt am 5.3.

AP 4: Response of the soil microorganisms to biochar application

Beprobungen sowohl vom Gefäßversuch (evtl. eigene Gefäße dafür vorsehen, damit der Boden nicht zu sehr gestört wird) als auch vom Feldversuch. Schwerpunkt am Gefäßversuch, dort auch Varianten mit 13C-BC (beim Feldversuch nicht).

AP 5: Soil fertility after biochar applications

Im ersten Jahr werden vom Seibersdorfer Gefäßversuch Proben genommen und auf der Boku analysiert (Grundcharakterisierung, Makro- und Mikronährstoffe). Im Mikrolysimeterversuch werden N-Verbindungen im Leachate bestimmt. Gesamt-C-Bilanzierung soll versucht werden.

AP 6: Effects on non-CO_2 greenhouse gas emissions

Schwerpunkt der Messungen des BFW beim Gefäßversuch im 2. Jahr. Messkammer kann auf niedrige Kultur aufgesetzt werden, deswegen Klee günstig. Stechzylinderproben sind aus eigenen Töpfen zu entnehmen (wegen Störung). Ergebnisse werden zur Modell-Parametrisierung eingesetzt.

AP 7: Economic evaluation of biochar production and application

Der FFG-Forderung nach einer Akzeptanzanalyse wird durch Einplanung von 2 Workshops mit den Stakeholdern entsprochen.

Zusammenfassende To-Do-Liste (als Erinnerung; ersetzt nicht Arbeitsplan und sonstige Vereinbarungen)

Aktion	Wer	Bis
Kontakt mit Region Kaindorf	Lauer	8.3. (Anmerkung: bereits erfolgt und weitergeleitet)
Organisation CO_2-Anreicherung	Soja	03-2010
Messen Erdgas in Seibersdorf	Horacek	03-2010
Weidenstecklinge, Gerstensaatgut	Soja	03-2010
CO_2-Sensor für Glashaus	Soja	03-2010
nächster Termin: 28.6., 10 h Achtung, Verschiebung der Lokalität auf Boku / Bodenforschung - Bibliothek, 1190 Wien, Peter Jordan-Str. 82	Soja	Einladung aussenden Mitte Juni
Entwurf Konsortialvertrag	Soja	03-2010

Ende der Besprechung: 13.30 h

Gerhard Soja, 5.3.2010

AUSTRIAN INSTITUTE OF TECHNOLOGY

PROTOKOLL
der
2. Koordinationssitzung

Projekt:

BIOCHAR for carbon sequestration in soils – Analysis of production conditions, biological effects in the soil environment and economics

Montag, 28.6.2010

10.00 Uhr, Universität für Bodenkultur, Institut für Bodenforschung

Teilnehmer:

Horacek, Kloß, Lauer, Liedtke, Soja, Watzinger, Wimmer, Zechmeister-Boltenstern, Zehetner

Allgemeines

Nach Vorlage des unterschriebenen Fördervertrags steht der Abschluss der Konsortialverträge im Vordergrund (Voraussetzung für Auszahlung der 1. Förderrate). Administrative Schwierigkeiten bei einzelnen Partnern sollen in den nächsten Tagen behoben werden. Im Weiteren werden die Projektfortschritte anhand der Arbeitspaket-Gliederung besprochen. Der von der FFG geforderte Text über das Projekt für die Homepage wurde mit 28.6. übermittelt.

Stand der Arbeitspakete

AP 1: Biomass and pyrolysis conditions for biochar production production efficiency

Der Versuchs-Pyrolysereaktor wurde gebaut und anhand einiger Durchgänge erprobt und optimiert. Sammlung flüchtiger Fraktionen ist möglich. Als Versuchs-Materialien sind derzeit Stroh und Rebholz vorhanden, ab dieser Woche stehen auch Hackschnitzel von 3 verschiedenen Baumarten zur Verfügung. Zuerst sollen die Variationen der Versuchsparameter an einem Material (Stroh) durchgespielt werden, bevor die anderen Biochar-Arten nur mehr mit 1 od. 2 Parametervariationen zum Vergleich mit den Stroh-Ergebnissen produziert werden.

Der Versuchsreaktor der EVN in Dürnrohr sollte besichtigt werden, um die dortigen Produktionsbedingungen im Vergleich zum Labor-Reaktor abschätzen zu können. Die größere Menge Biochar für die Versuche wird möglicherweise als "Auftragspyrolyse" in Dürnrohr produziert und beim Laborreaktor steht nur die Variation der Prozessparameter im Vordergrund. Die Versuchsdurchgänge sollen möglichst bis Ende Sept. 2010 abgeschlossen werden.

AP 2: Experimental setup for carbon sequestration and soil studies

Für den Gefäßversuch wurde bereits 1 Boden beschafft (Traismauer, sandig-schluffig, kalkhaltig, hoher pH). Kaindorf wird im Juli und Waldviertel im August beschafft. Die Anlage des Gefäßversuches ist daher nicht vor Ende August zu erwarten. Auf Grund der Jahreszeit wird es besser sein, die vorgesehene Reihenfolge der Versuchspflanzen Gerste und Gründüngung umzukehren.

Diskussion um Topfversuche und Gefäßgrößen – der Mikrolysimeterversuch soll in Gefäßen durchgeführt werden, in denen auch die Gasemissionen gemessen werden können. Zechmeister-Boltenstern zeigt ein Mustergefäß; AIT wird die Herstellbarkeit solcher Gefäße mit größerem Durchmesser zu erträglichen Kosten prüfen. Ionenaustauschersäckchen unter Lochplatte könnten für Nitrat-/Ammoniumsammlung (integrativ über 2 Wochen) verwendet werden.

Isotopen-Versuch: die CO_2-Kanone für Erdgas-/Methanbetrieb wurde angeschafft, die Installation macht aber noch Probleme. Weiden und Weizen sind schon stark im Wachsen; Weiden sollten zurückgeschnitten werden, wenn tatsächlich CO_2-Anreicherung erfolgt.

AP 3: Stability of biochar carbon pools

Stefanie Kloß hat die ausgeschriebene Dissertationsstelle mit 1.6. angetreten. Inkubatoren wurden am Institut angeschafft.

AP 4: Response of the soil microorganisms to biochar application

Bei den Bodenbeschaffungs-Aktionen an den Freilandstandorten müssen für mikrobiologische Bestimmungen gekühlte Proben gezogen werden.

AP 5: Soil fertility after biochar applications

Grundcharakterisierung der Freilandböden an Boku und in Seibersdorf (S. Kloß) Gefäßformen und Wasserversorgung (Selbstbewässerung, installierte Bewässerung, manuelle Bewässerung) für den Pflanzengefäß- und Mikrolysimeterversuch sind noch zu klären.

AP 6: Effects on non-CO_2 greenhouse gas emissions

Wahl der Gefäßtypen – siehe AP 2.

AP 7: Economic evaluation of biochar production and application

Verschiebung des ersten Milestones wegen verzögerter FFG-Vertragsausstellung ist derzeit leicht kompensierbar.

Zusammenfassende To-Do-Liste (als Erinnerung; ersetzt nicht Arbeitsplan und sonstige Vereinbarungen)

Aktion	Wer	Bis
Konsortialvertrags-Unterschriften	alle	2.7.2010
AIT-Unterschriften, Weiterleitung unterschriebener Kons.Verträge an FFG	Soja	Juli 2010
Boden-Probenahme Kaindorf	Wimmer, Zehetner	Juli 2010
Boden-Probenahme Waldviertel	Soja, Wimmer	August 2010
Organisation Besichtigung Pyrolyse Dürnrohr	Soja	Juli 2010
Entscheidung über Topfvarianten bei Gefäßversuch	Wimmer, Soja	August 2010
nächster Termin: 18.10., 13 h, Boku	Soja	Einladung aussenden ca. 10.10.

Ende der Besprechung: 13.30 h

Gerhard Soja, 28.6.2010

PROTOKOLL

Zwischenbesprechung zu WP 2

Projekt:

BIOCHAR
for carbon sequestration in soils – Analysis of production conditions, biological effects in the soil environment and economics

Dienstag, 17.8.2010

9.00 Uhr, Universität für Bodenkultur, Institut für Bodenforschung

Teilnehmer:

Bücker, Kloß, Rempt, Soja, Wimmer, Zehetner

Allgemeines

Hauptthemen der Besprechung sind Klärung von Details der Anlage des Gefäßversuchs und der Probenahme im Waldviertel am 18. August.

Gefäßversuch

Der Entwurf von Bernhard Wimmer bezüglich Spezifität der Varianten und voraussichtlich benötigte Menge Biochar und Boden wird unter Einbeziehung der Vorschläge von Kloß, Soja und Zehetner diskutiert und geringfügig modifiziert. Die für die Versuchsanlage letztgültige Version ist aus dem beigefügten Excel-File ersichtlich. Wimmer weist auf die Risikofaktoren des hohen Betreuungsaufwands, insbesondere bei Bewässerung, Sickerwassersammlung und Analytik hin. Diesem soll durch Zusammenarbeit in der Betreuung (und fallweisen gegenseitigen Vertretung) durch Bücker, Kloß und Rempt begegnet werden. In der Zeit nach Ende der Diplomarbeiten von Bücker und Rempt soll die Betreuung der 3. Kultur entweder durch eine weitere Diplomarbeit oder durch die Mithilfe von Schlögl / Mayer / Kobe sichergestellt werden (Organisation: Soja).

Die Projektmitarbeit der StudentInnen wird fachlich wie folgt aufgeteilt:

Bücker: Sickerwassersammlung, -analytik, Pflanzennährstoffaufnahme. Thema der Studienarbeit (Arbeitstitel): Leaching characteristics of biochar-ameliorated agricultural soils (10-12/2010). Thema der Diplomarbeit (Arbeitstitel): Nutrient dynamics in biochar-ameliorated agricultural soils and crops (01-06/2011).

Kloß: Biochar-Analytik im Boden, Abbauversuch mit Biochar, Inokulationsversuch, 13C-markierte Biochar, biologische Wirkungen von Biochar auf Klee als 3. Folgekultur. Arbeitstitel der Dissertation wurde bereits früher festgelegt.

Rempt: PLFA-Analytik von unmarkiertem Material von Boden-MO, Pflanzenwachstum und Ertrag, Chlorophyllfluoreszenz-Messungen. Arbeitstitel der Master-Thesis wurde bereits früher festgelegt.

Für die Entscheidung über die Biochar-Arten im Gefäßversuch wird auf die ausständigen Analysedaten gewartet. Anlage des Versuches im September, erste Kultur: Phazelie.

Zerkleinern der Biochar auf gleichmäßige Größe vor der Einmischung in den Boden: Besichtigung einer Mühle im Labor Holzforschung. Klärung der Verwendbarkeit mit Dr. Buksnowitz (Zehetner?).

Zusätzliche Analysen, welche für eine vollständigere Charakterisierung der verschiedenen produzierten Biochars nützlich wären (hinsichtlich Publikationsfähigkeit der Ergebnisse):

- wasserextrahierbare PAK (nach Norm; Information bei Wimmer; Soja fragt bei Mapag wegen verwendeter Extraktionsmethodik nach),
- Schwermetalle + Si (Analysen auf Boku),
- Kationen-Austauschkapazität (Analysen auf Boku),
- elektronenmikroskopische Aufnahmen (Wimmer erkundigt sich bei AIT, Zehetner auf Boku über die Möglichkeiten),
- Wasserspeicherfähigkeit (pF-Analysen) oder alternativ Wasserhaltekapazität.

Höhere Pyrolyse-Temperatur für Biochar-Vergleich wäre noch interessant (Mengen im Labormaßstab, Soja → Liedtke).

Probenahme Waldviertel 18.8.

Gewinnung von 4 vollen Kisten + ca. 10 Säcken mit je ca. 20-30 kg Boden, da vom sandigen Boden die größte Menge benötigt wird. Teilnehmer: Wimmer, Kloß, Rempt, Frank, Henriquez-Martinez, Soja. Fahrzeuge: Boku-Bus + AIT-Bus.

Ende der Besprechung: 13.00 h

Gerhard Soja, 17.8.2010

PROTOKOLL
der
3. Koordinationssitzung

Projekt:
BIOCHAR
for carbon sequestration in soils – Analysis of production conditions, biological effects in the soil environment and economics

Freitag, 17.12.2010
10.00 Uhr, TechGate, Donaucitystr. 1, Level 2 (Seminarraum Nanotechnologie)

Teilnehmer:
Bücker, Klinglmüller, Kloß, Lauer, Rempt, Soja, Watzinger, Wimmer, Zechmeister-Boltenstern, Zehetner

Allgemeines

Der von der FFG verlangte Zusatzvertrag zum Konsortialvertrag liegt als Entwurf vor und steht in Diskussion zwischen den Rechtsabteilungen von AIT und Joanneum. Nach aktueller Information wurde eine kleine Modifikation vereinbart (siehe Mail vom 20.12.10)– erfordert daher neue AIT-Unterschriften (Organisation Soja).

Zwischenbericht ist bis Ende März vorzubereiten – separate Aussendung durch Soja.

Stand der Arbeitspakete

AP 1: Biomass and pyrolysis conditions for biochar production production efficiency

Nach der Externalisierung der Arbeitsgruppe Liedtke wurde der Versuchsreaktor leihweise HET überlassen, um die restlichen Chargen für den Gefäßversuch herzustellen, inklusive des 13C-markierten Materials (Organisation Bücker). Die Analytik der verschiedenen Biochars ist im Laufen, Ergebnisse sollen in einer Publikation bis März zusammengefasst werden (siehe Präsentation Kloß).

AP 2: Experimental setup for carbon sequestration and soil studies

Der Gefäßversuch wurde durch gemeinsame Anstrengung eines großen Teams (Organisation Wimmer) in der zweiten Novemberhälfte im Glashaus Seibersdorf fertig installiert (25 Varianten mit n=5). Die Gefäße basieren auf Kanalrohren, Außendurchmesser 25 cm, Höhe 40 cm, Volumen 15,2 l, 2-schichtige Sand-Drainage und Sickerwasser-Sammlung. Berücksichtigte Versuchsfaktoren Bodentyp, Biochar-Ausgangsmaterial, Biochar-Menge, Pyrolyse-Temperatur, N-Versorgung, Bepflanzung (aus Kapazitätsgründen nur teilfaktorielle Anlage möglich; siehe Liste im Attachment). Die Aufstellung erfolgte im randomisierten Block-Design. Auf den bepflanzten Varianten (18 von 25) wurden Senf angebaut (50 Samen auf 0,0434 m² pro Gefäß). In einigen Gefäßen wurden TDR-Sonden zur

Verfolgung des Wassergehalts als Basis für die Bewässerung eingebaut (Aufzeichnung mit Datenlogger im Laufen). Für die Nährstoff-Versorgung wurde ein 15:15:15-Volldünger (entsprechend 40 kg N/ha) bei den Standardvarianten (N_{100}) verwendet. Bei N_0-Varianten ist noch mit PK-Dünger auszugleichen. Bei Folgekultur Gerste soll mit getrennter N- und PK-Düngung gearbeitet werden.

Der Feldversuch ist vorzuplanen (Organisation Biochar – Soja). Anlage Traismauer voraussichtlich März. Vorsc

AP 3: Stability of biochar carbon pools. Anlage des Versuches mit 13C in der ersten Jännerhälfte (Kloß und Zehetner).

AP 4: Response of the soil microorganisms to biochar application: Rempt arbeitet an der Analysen-Vorbereitung der bisherigen Beprobungen.

AP 5: Soil fertility after biochar applications: Analytik der Sickerwassersammlungen durch Bücker in Vorbereitung. Anionen inkl. Phosphat bei HET möglich, Methodik für photometrische Ammonium-Bestimmung wird vom FBW zur Verfügung gestellt.

AP 6: Effects on non-CO_2 greenhouse gas emissions: Treibhausgas-Analysen durch BFW bisher zu 2 Terminen, vom ersten Termin liegen vorläufige Auswertungen vor (siehe Präsentation Klinglmüller).

AP 7: Economic evaluation of biochar production and application: Datenerhebung ist im Anlaufen, erstes Deliverable wird bis zum ersten Zwischenbericht verschoben (verzögertes Anlaufen wegen Vertragskomplikationen).

Zusammenfassende To-Do-Liste (als Erinnerung; ersetzt nicht Arbeitsplan und sonstige Vereinbarungen)

Aktion	Wer	Bis
Kontakt Kampichler EVN	Soja	Ende 12/2010
REM-Analytik bei AIT klären	Soja	Ende 12/2010
REM-Analytik bei BFW klären	Klinglmüller	Ende 12/2010
PAK-Analytik auf der Boku klären	Zehetner	Ende 12/2010
PK-Düngung auf N0-Varianten ergänzen	Soja	Ende 12/2010
NH4-Analytikmethode an AIT	Zechmeister	Ende 12/2010
Vorbereitung Zwischenbericht – Template aussenden	Soja	Ende 01/2011
nächster Termin: 24.3.11, 13 h (Boku)	alle	Soja Einladung aussenden bis ca. 17.3.11

Ende der Besprechung: 13.00 h

Gerhard Soja, 19.12.2010

PROTOKOLL
der
4. Koordinationssitzung

Projekt:
BIOCHAR
for carbon sequestration in soils – Analysis of production conditions, biological effects in the soil environment and economics

Donnerstag, 24.3.2011
13.00 Uhr, Universität für Bodenkultur, Institut für Bodenforschung, Seminarraum

Teilnehmer:
Bücker, Feichtmayer, Frank, Kitzler, Klinglmüller, Kloß, Lauer, Soja, Watzinger, Wimmer, Zechmeister-Boltenstern, Zehetner

Allgemeines

Von der FFG werden die Auflagen als erfüllt angesehen. Daher ist erste Zahlungsrate möglich - ausständige Rechnungen sind an Soja zu schicken, ebenso ausständige Kapitel des Zwischenberichts (bis Anfang nächster Woche).
Vorschlag: Einfacherer Austausch von Datenfiles durch Einrichtung eines FTP-Servers. Organisation durch Wimmer bei AIT.
Bei der EGU-Tagung (4.-8.4.2011) werden 2 Poster mit bisherigen Projektergebnissen durch Kloß und Klinglmüller präsentiert.
Bücker stellt seine Arbeiten bei einem AIT-Seminar am 5.5. vor (13 h, UFT Tulln).

Stand der Arbeitspakete

AP 1: Biomass and pyrolysis conditions for biochar production production efficiency

Die Ergebnisse der chemischen Charakterisierung verschiedener Biokohlen wurden für einen Artikel in J. Environ. Qual. durch S.Kloß zusammengefasst (Einreichung am 1.3.2011).

AP 2: Experimental setup for carbon sequestration and soil studies

Gefäßversuch: nach Ernte der ersten Kultur (Senf) wurde Sommergerste angebaut. Ist derzeit im Jungpflanzen- und Bestockungsstadium. Nach Ernte der Gerste wird als 3. und letzte Kultur Rotklee angebaut (ca. Juni).

Der Feldversuch Traismauer wurde planmäßig am 16.3. angelegt (Versuchsplan und weitere Details siehe Präsentations-PDF). Einsatz einer rumänischen Biokohle (Nadelholz : Laubholz = 4:1), da weder EVN noch Pyreg zeitgerecht liefern konnten. Anlage des Versuchs in der Steiermark am 31.3. durch das gleiche 6-Personen-Team wie in Traismauer + Franz Zehetner. Einarbeitung der Biokohle mit Kreiselegge des Landwirts geplant, AIT-Gartenfräse wird als Reserve mitgenommen. Ersatztermin bei Schlechtwetter: 6. April.

AP 3: Stability of biochar carbon pools. Abbauversuch mit 13C wurde angelegt und läuft planmäßig. Weiteres siehe Präsentations-PDF. 13C-Biokohle sollte noch charakterisiert werden (Parameter, sofern genug Material da ist: C/N, FTIR, STA, Asche, BET, RFA, PAK).

AP 4: Response of the soil microorganisms to biochar application: Rempt arbeitet intensiv an den Analysen.

AP 5: Soil fertility after biochar applications: In der Vorwoche wurde die 4. Sickerwasserprobenahme durchgeführt, die 5. ist für erste Mailhälfte vorgesehen. Analysedaten von 3 Terminen vorhanden. (weitere Details siehe Präsentations-PDF)

AP 6: Effects on non-CO_2 greenhouse gas emissions: Treibhausgas-Analysen durch BFW im Plan, vom 1.-3. Termin liegen vorläufige Auswertungen vor (siehe Präsentation Klinglmüller).

AP 7: Economic evaluation of biochar production and application: Berichtsbeitrag liegt vor, erste Wirtschaftlichkeitsabschätzungen verschiedener Produktionsverfahren vorhanden. Sozioökonomik wird im nächsten Bericht behandelt.

<u>Zusammenfassende To-Do-Liste </u>(als Erinnerung; ersetzt nicht Arbeitsplan und sonstige Vereinbarungen)

Aktion	Wer	Bis
Proben für REM organisieren	Watzinger	04/2011
REM-Aufnahmen	Kitzler	04/2011
FTP-Server einrichten	Wimmer	Ende März
Beprobung Feldversuch für MO	Watzinger	Ende Feldversuch
Analysemöglichkeit bei Boku für Nährstoff-Elemente, Schwermetalle (inkl. Kosten)	Zehetner	04/2011
Menge für PAK-Analytik bei Mapag klären	Soja	Ende März
Konsortialvertrag-Auszug bezüglich Datennutzung versenden	Soja	Ende März
Auf Ergänzungsbedarf des Aspekts Datennutzung prüfen	Zechmeister	Ende März
nächster Termin: 4.10.2011, 13 h TechGate	Soja	Einladung aussenden bis 26.9.

Ende der Besprechung: 16.15 h

Gerhard Soja, 25.3.2011

PROTOKOLL
der
5. Koordinationssitzung

Projekt:
BIOCHAR
for carbon sequestration in soils – Analysis of production conditions, biological effects in the soil environment and economics

Dienstag, 4.10.2011
13.00 Uhr, TechGate, Donaucitystr. 1, Level 2, gr. Seminarraum

Teilnehmer:
Feichtmayer, Horacek, Kitzler, Kloß, Lauer, Soja, Watzinger, Zehetner

Allgemeines

Nachforderungen der FFG zur Abrechnung – wurden an Partner bzw. AIT-Buchhaltung weitergegeben.
To-do-Liste vom 24.3.: siehe aktualisierten Präsentations-File vom 4.10.
Am FTP-Server sollen accepted papers und Poster zum Informationsaustausch hinterlegt werden.
Aktuelle Ergebnisse: siehe PDFs der Präsentationen (Kitzler, Kloß, Kloß für Rempt, Soja, Watzinger).
Diskussion der Autorenschaft bei Publikationen: 2 Vorschläge für Vorgangsweise bei Artikel werden bei nächstem Meeting weiter diskutiert bzw. entschieden, wenn mehr Teilnehmer dabei sind. Formulierung im Konsortialvertrag lässt Interpretationsspielraum (siehe Folie).
Anregung: zusammenfassende Publikation quer über alle AP zum Ende des Projekts
Geplante Tagungsteilnahmen – siehe Folien.
Nächster Termin: 1.3.2012 (13 h, TechGate, Level 2)

Stand der Arbeitspakete

AP 1: Biomass and pyrolysis conditions for biochar production production efficiency

Artikel in J. Environ. Qual. ist in Druck (S. Kloß). Arbeiten zum AP 1 beendet

AP 2: Experimental setup for carbon sequestration and soil studies

Gefäßversuch: Rotklee als 3. Folgekultur im Glashaus Tulln. 1. Schnitt gegen Jahresende 2011. Freilandversuch: beide Standorte beerntet, Ertrag Gerste ausgewertet. Details siehe PDF-Attachments.

AP 3: Stability of biochar carbon pools.

Abbauversuch mit 13C wurde bereits teilweise beprobt, Aufbereitung in Arbeit. Endergebnis braucht gesamte Projektlaufzeit.

AP 4: Response of the soil microorganisms to biochar application:

Watzinger stellt Ergebnisse vor – siehe attachment. Master thesis von F. Rempt wurde eingereicht, Kurzvorstellung des Pflanzenteils durch S. Kloss.

AP 5: Soil fertility after biochar applications:

Sickerwasserproben wurden analysiert, Studienprojekt Bücker als Basis des Posters für Biocharsymposium in Halle. Masterthese wird gesamte Sickerwasser-Analytik umfassen.
Vorstellung der vorliegenden Ertragsauswertungen Gefäßversuch (Senf + Gerste) und Freiland (Gerste) – Präsentation vom Biocharsymposium in Halle (G. Soja).
Elementanalysen der Pflanzen noch ausständig.

AP 6: Effects on non-CO_2 greenhouse gas emissions:

Treibhausgas-Analysen durch BFW im Plan, werden auch bei Klee fortgesetzt. Präsentation B. Kitzler vom Biocharsymposium in Halle vorgestellt.

AP 7: Economic evaluation of biochar production and application:

Zwischenbericht über weitere Datenerhebungen seit letztem Zwischenbericht; wird für nächsten Zwischenbericht zusammengefasst.

Zusammenfassende To-Do-Liste (als Erinnerung; ersetzt nicht Arbeitsplan und sonstige Vereinbarungen)

Aktion	Wer	Bis
Vorkulturen auf den Versuchsfeldern definieren	Soja	11/2011
Einladung für nächsten Termin: 1.3.2012, 13 h, AIT (TechGate, Level 2)	Soja	Mitte 02/2012
Dioxin-Analytik für Feldversuchs-Biochar	Soja	11/2011

Ende der Besprechung: 17.40 h

Gerhard Soja, 5.10.2011

PROTOKOLL
der
6. Koordinationssitzung

Projekt:
BIOCHAR
for carbon sequestration in soils – Analysis of production conditions, biological effects in the soil environment and economics

Donnerstag, 1.3.2012
13.00 Uhr, TechGate, Donaucitystr. 1, Level 2, gr. Seminarraum

Teilnehmer:
Anders, Feichtmayer, Horacek, Karer, Kitzler, Klinglmüller, Kloß, Lauer, Ochsenhofer, Soja, Watzinger, Wimmer, Zechmeister-Boltenstern, Zehetner

Allgemeines

Zweck der Besprechung war die Vorstellung und Diskussion der im letzten Halbjahr neu erarbeiteten Ergebnisse sowie die Abstimmung der weiteren Arbeiten.

To-do-Liste vom 4.10.'11: siehe aktuelles Präsentations-File

Aktuelle Ergebnisse aus den Arbeitspaketen: siehe PDFs der Präsentationen (Kitzler, Kloß, Bücker, Soja, Watzinger, Lauer).

Diskussion der Autorenschaft bei Publikationen unter Bezugnahme auf die Vorschläge bei der Besprechung vom 4.10.2011: Bei Grundsatz-Publikationen mit Gesamtdarstellung alle Ko-Autoren anführen (Variante a) auf Folie). Bei der Publikation von Teilergebnissen Schwerpunkt auf Einbeziehung der mitgewirkt habenden Autoren (entsprechend scientific practice; Variante b) auf Folie).

Anregung: zusammenfassende Publikation quer über alle AP zum Ende des Projekts. Möglicher Schwerpunkt: N-Bilanzen bzw. N-cycles.

Die Hypothese, dass in gemäßigten Breiten Biochar auf ärmeren Böden deutlichere Wirkung zeigt als auf besseren Böden, scheint sich zu bestätigen.

Geplante Tagungsteilnahmen – siehe Folien.

2. Zwischenbericht: bitte Template unbedingt beachten. Für die einzelnen Arbeitspakete wird ein Absatz für die Zusammenfassung und ein Absatz Ausblick benötigt. Rücksendung der Beiträge an Soja bitte bis 11.4.2012.

Projekt-Laufzeitverlängerung um 3 Monate – wird bei Übersendung des 2. Zwischenberichts offiziell angesucht; von FFG informelle Zustimmung.

Nächster Termin: 26.9.2012 (13 h, TechGate, Level 2)

Stand der Arbeitspakete

AP 1: Biomass and pyrolysis conditions for biochar production production efficiency: abgeschlossen.

AP 2: Experimental setup for carbon sequestration and soil studies
Gefäßversuch: Rotklee als 3. Folgekultur im Glashaus Tulln. In der nächsten Woche wird ein Austrocknungsversuch begonnen, anschließend 2. Schnitt, Düngung (N: 100 % = 50 kg/ha, PK überall gleich), und 3. Aufwuchs. Anregung: Berechnung der Gesamt-N-Bilanzen für den Gefäßversuch.
Freilandversuch: Kaindorf – Winterweizen im Herbst von Hr. König angebaut. Traismauer: Sonnenblume wird im April gesät.

AP 3: Stability of biochar carbon pools.
Abbauversuch mit 13C: nächste Beprobung 01-2013. Endergebnis braucht gesamte Projektlaufzeit. Details siehe PDF-Attachment S. Kloss.

AP 4: Response of the soil microorganisms to biochar application:
Watzinger stellt Ergebnisse vor – siehe attachment. Master thesis von F. Rempt beendet und akzeptiert. E. Anders arbeitet für ihre Master thesis als Fortsetzung über die Langzeitwirkungen. Kleine Töpfe werden weiter erhalten und in ca. 1 Jahr nochmals beprobt.

AP 5: Soil fertility after biochar applications:
Master thesis von J. Bücker beendet und akzeptiert.
Nährstoff- und Spurenstoffgehalte in Böden/Pflanzen: siehe PDF der Präsentation von S. Kloß im Attachment.

AP 6: Effects on non-CO_2 greenhouse gas emissions:
Treibhausgas-Analysen durch neue Diplomarbeit von T. Ochsenhofer fortgesetzt. M. Klinglmüller ist an der Fertigstellung ihrer Diplomarbeit. Bei Klee sind im Vergleich zu den Vorkulturen sehr geringe Emissionen festzustellen. Weiteres siehe PDF der Präsentation von B. Kitzler im Attachment.

AP 7: Economic evaluation of biochar production and application:
Siehe PDF der Präsentation von M. Lauer im Attachment. Schwerpunkt der Untersuchungen wird auf slow pyrolysis gelegt, da für höheren Biokohle-Ertrag relevanter. Anfragen bezüglich Quantifizierungen für die Berechnungs-Ansätze werden über G. Soja verteilt.

Zusammenfassende To-Do-Liste (als Erinnerung; ersetzt nicht Arbeitsplan und sonstige Vereinbarungen)

Aktion	Wer	Bis
FTP-Server Informationen versenden	Wimmer	erledigt
Gaia-Artikel vorbereiten	Zehetner et al.	Deadline Juni 2012
Zusammenführung der Ergebnisse für Gemeinschaftspublikation	Soja et al.	im Anschluss
Dioxin-Analytik organisieren	Soja	03-04/2012
Zwischenbericht – Beiträge	alle WP-Leiter	11.4.2012

Kontakt zu Hood-Nowotny bezüglich ihrer Ergebnisse	Soja	03/2012

Ende der Besprechung: 17.50 h

Gerhard Soja, 3.3.2012

AUSTRIAN INSTITUTE OF TECHNOLOGY

PROTOKOLL
der
7. Koordinationssitzung

Projekt:
BIOCHAR
for carbon sequestration in soils – Analysis of production conditions, biological effects in the soil environment and economics

Mittwoch, 26.9.2012
14.00 Uhr, TechGate, Donaucitystr. 1, Level 2, gr. Seminarraum

Teilnehmer:
Anders, Karer, Kitzler, Kloß, Ochsenhofer, Watzinger, Wimmer, Zechmeister-Boltenstern, Zehetner

Allgemeines

Zweck der Besprechung war die Vorstellung und Diskussion der seit März neu erarbeiteten Ergebnisse sowie die Abstimmung der weiteren Arbeiten.

To-do-Liste vom 26.9.'12: siehe aktuelles Präsentations-File

Aktuelle Ergebnisse aus den Arbeitspaketen: siehe PDFs der Präsentationen (Ochsenhofer, Kloß, Anders).

Nächster Termin: wird elektronisch koordiniert (TechGate, Level 2)

Stand der Arbeitspakete

AP 1: Biomass and pyrolysis conditions for biochar production production efficiency: abgeschlossen.

AP 2: Experimental setup for carbon sequestration and soil studies

Gefäßversuch: Rotklee steht seit der 3. Ernte im Freiland (wird in geringer Intensität weiter gepflegt).
Freilandversuch: Beide Kulturen geerntet, daher abgeschlossen.

AP 3: Stability of biochar carbon pools.

Abbauversuch mit 13C: nächste Beprobung 01-2013. Endergebnis braucht gesamte Projektlaufzeit.

AP 4: Response of the soil microorganisms to biochar application:

Ergebnisse siehe attachment. Master thesis von Sonja Feichtmayer beendet, Defensio am 11.10.. E. Anders arbeitet für ihre Master thesis als Fortsetzung über die Langzeitwirkungen. Kleine Töpfe werden weiter erhalten und in ca. 1 Jahr nochmals beprobt.

AP 5: Soil fertility after biochar applications:

siehe PDF der beiden Präsentationen von S. Kloß im Attachment.

AP 6: Effects on non-CO_2 greenhouse gas emissions:

Siehe PDF der Präsentation von T. Ochsenhofer im Attachment.

AP 7: Economic evaluation of biochar production and application:

M. Lauer fällt krankheitsbedingt für längere Zeit aus.

Zusammenfassende To-Do-Liste (als Erinnerung; ersetzt nicht Arbeitsplan und sonstige Vereinbarungen)

Aktion	Wer	Bis
Vorkulturen auf den Versuchsfeldern definieren	Soja	11/2011
Einladung für nächsten Termin: per doodle	Soja	Mitte 10/2012
Paper Anders et al., EJSS, Gefäßversuche Freiland PLFAs	Anders	15.10.2012
Watzinger et al., Inkubation (mit Sonja	Andrea	15.10.2012
Karer et al., Freilandversuch	Jasmin	12/2012 oder 2/2013
Klinglmüller et al., Treibhausgase Topfversuch	Barbara	06/2013
Kloss et al., Adsorptionsversuche	Steffi	12/2012
Kloss et al. Topfversuch	Steffi	Bereits reviewed
Bücker et al., Topfversuch	Jannis	Work in progress?
Ordner auf FTP anlegen: Literatur und Projektpublikationen	Bernhard	5.10.2012
Literaturbezeichnung: Autor_stichwort_Zeitschrift_Jahr	alle	16.10.2012
Kloss et al., Schwermetalle im Topfversuch	Steffi	2013

Gasdaten Traismauer/Kaindorf an Elena	Barbara	1.10.2012
REM-Bilder auf FTP legen	Barbara	1.10.2012
Verteidigung Sonja	ALLE	11.10.2012 9:00
N-task force meeting		1.10.2012 14:00

Ende der Besprechung: 16.30 h

Protokollführung: Bernhard Wimmer
Kompilation: Gerhard Soja, 27.9.2012

AUSTRIAN INSTITUTE OF TECHNOLOGY

PROTOKOLL
der
8. Koordinationssitzung

Projekt:
BIOCHAR for carbon sequestration in soils – Analysis of production conditions, biological effects in the soil environment and economics

Dienstag, 12.3.2013
13.00 Uhr, TechGate, Donaucitystr. 1, Level 2, gr. Seminarraum

Teilnehmer:
Gunczy, Karer, Kitzler, Kloß, Soja, Wimmer, Zehetner

Allgemeines

Zweck der Besprechung war die Vorstellung und Diskussion der seit der letzten Besprechung im September neu erarbeiteten Ergebnisse sowie die Abstimmung des Projektabschlusses.

To-do-Liste vom 12.3.'13: siehe aktuelles Präsentations-File

Aktuelle Ergebnisse aus den Arbeitspaketen: siehe PDFs der Präsentationen (Soja, Kloß AP3, Kloß AP5).

Nächster Termin: wird elektronisch koordiniert für 1. Juliwoche, mit abschließendem Abendessen (TechGate, Level 2)

Zugangsdaten zum FTP-Server stehen zur Erinnerung im Präsentations-File. Ein komplettes Up-to-date-Halten der Publikationen ist wegen der enormen Zunahme der Biochar-Literatur unmöglich.

Es wird geplant, S. Kloss über ein FemTech-Stipendium beim BFW nach Ende des Projekts länger in die Thematik einzubinden.

Termin für die Beiträge zum Endbericht: Ende Juni an Soja. Template wird ausgesendet.

Stand der Arbeitspakete

AP 1: Biomass and pyrolysis conditions for biochar production production efficiency: abgeschlossen.

AP 2: Experimental setup for carbon sequestration and soil studies: abgeschlossen.

AP 3: Stability of biochar carbon pools. Siehe Präsentation Kloß im Attachment. Es ist noch zu klären, ob sich CO_2 vom Abbau wieder als CO_3^{--} niederschlägt und daher zu einer Unterschätzung führt.

AP 4: Response of the soil microorganisms to biochar application:
Andrea Watzinger erkrankt, Besprechung des WP beim nächsten Meeting. Artikel wurde eingereicht.

AP 5: Soil fertility after biochar applications: Siehe Präsentationen Kloß und Soja (Vortrag beim Humus-Symposium Kaindorf) im Attachment. Im Endbericht werden bei den Pflanzen sowohl Konzentrationen als auch Entzüge angegeben, in der Publikation Karer et al. nur Entzüge (+ Grafiken Erträge). Schwermetall-Adsorptionen werden in Kooperation mit Oburger genauer untersucht; Synchotron-Messungen werden in Taiwan durchgeführt (Proben wurden rechtzeitig hingeschickt). Geplante Publikationen siehe PDF Kloß.

AP 6: Effects on non-CO_2 greenhouse gas emissions: Ergebnisse von B. Kitzler in der Präsentation G. Soja integriert. Gemeinsame Publikation Klinglmüller + Ochsenhofer in Vorbereitung (aber nicht für den ursprünglich geplanten Proceedingsband)

AP 7: Economic evaluation of biochar production and application: S. Gunczy ersetzt den krankheitsbedingt verhinderten M. Lauer und führt die Arbeiten zum AP 7 bis Ende Juni zu Ende.

Zusammenfassende To-Do-Liste (als Erinnerung; ersetzt nicht Arbeitsplan und sonstige Vereinbarungen)

Aktion	Wer	Bis
Rückfrage Jannis	Gerhard	Ende März (erledigt)
Aussendung Template Endbericht	Gerhard	Ende April
Publikationen Graber → Stefan	Gerhard	Nächste Woche (erledigt)
Aussendung Doodle für nächste Besprechung 1. Juliwoche	Gerhard	Nächste Woche

Meta-Analyse Jefferey → Stefan	Jasmin	Nächste Woche
FemTech-Antrag Steffi	Barbara + Steffi	März

Ende der Besprechung: 17.00 h

Gerhard Soja, 16.3.2013

PROTOKOLL
der
9. Koordinationssitzung

Projekt:
BIOCHAR
for carbon sequestration in soils – Analysis of production conditions, biological effects in the soil environment and economics

Dienstag, 2.7.2013
15.30 Uhr, TechGate, Donaucitystr. 1, Level 2, gr. Seminarraum

Teilnehmer:
Gunczy, Karer, Kitzler, Klinglmüller, Kloß, Soja, Watzinger, Wimmer, Zechmeister-Boltenstern, Zehetner

Allgemeines

Bei dieser Besprechung stand der Abschluss des Projekts im Vordergrund, wobei die wichtigsten Ergebnisse zusammengefasst, der Status des Endberichts besprochen und die „lessons learned“ aus dem Projekt gemeinsam überlegt wurden.

Die To-do-Liste besteht in der Fertigstellung der noch nicht übersandten Arbeitspakete bis Ende Juli an Soja.

Aktuelle Ergebnisse aus den Arbeitspaketen: siehe PDFs der Präsentationen (Gunczy AP7, Kloß AP3, Kloß AP5, Klinglmüller AP6).

Der Endbericht inklusive Abrechnung wird von der FFG bis Ende Sept. 2013 eingefordert. Die Anmerkungen der FFG bei der letzten Zwischenabrechnung sind zu beachten.

Stand der Arbeitspakete

AP 1: Biomass and pyrolysis conditions for biochar production production efficiency: abgeschlossen.

AP 2: Experimental setup for carbon sequestration and soil studies: abgeschlossen.

AP 3: Stability of biochar carbon pools. Siehe Präsentation Kloß im Attachment (einschließlich Ausblick auf fertigzustellende Ergebnisse und lessons learned).

AP 4: Response of the soil microorganisms to biochar application: Artikel-Einreichung wurde überarbeitet.

AP 5: Soil fertility after biochar applications: Siehe Präsentation und Status Publikationen von Stefanie Kloß im PDF (Attachment). Einschließlich Hinweise auf weitere Vorhaben und lessons learned.

AP 6: Effects on non-CO_2 *greenhouse gas emissions:* Siehe Präsentation Michaela Klinglmüller im PDF (Attachment) – Ergebnisse der gemessenen Treibhausgas-Emissionen wurden durch eine Wirtschaftlichkeits-Abschätzung eines Biochar-Einsatzes ergänzt.

AP 7: Economic evaluation of biochar production and application: Siehe Präsentation Stefan Gunczy im PDF (Attachment). Der Abschluss der Arbeiten wird für Ende Juli avisiert.

Lessons learned

Zusätzlich zu den in den AP3- und AP5-Beschreibungen erwähnten Schlussfolgerungen wurden bei gemeinsamer Diskussion folgende Punkte angeführt:

- Langfristigkeit der Versuchsansätze ist schon in der Planungsphase zu berücksichtigen.
- Für die Analytik der Biochars wären wesentlich mehr Parameter zur Interpretation der Eigenschaften hilfreich. Im laufenden Projekt wurden einige Verfahren zwar teilweise eingebaut (z.B. durch Messungen taiwanesischer Kooperationspartner), ein größeres Analyenspektrum wäre aber wünschenswert: Salzgehalt, FTIR, ESEM, NMR, Röntgen-Absorptionsspektroskopie, FISH.
- Besonders die Aging-Effekte bedürfen genauerer Oberflächen-Analytik.
- Mehr molekularbiologische Techniken für die Bodenmikrobiologie bzw. Proteomik wären wünschenswert
- Stickstoff-Prozesse und Brutto-Umsatzraten für N sollten besser charakterisiert werden
- Biochar aus anderen Reststoffen als land-/forstwirtschaftliche Ernterückstände würde neue Eigenschaften eröffnen (z.B. Klärschlamm).
- Stärkere Unterscheidung zwischen grundlagennaher Forschung ohne Wirtschaftlichkeitsbezug und Anwendungs-Forschung mit dem Ziele einer wirtschaftlichen Umsetzung wünschenswert.

Ende der Besprechung: 19.00 h

Gerhard Soja, 7.7.2013