Characterization, stability, and plant effects of kiln-produced wheat straw biochar

O'Toole , A [1], K. Knoth de Zarruk[1], M. Steffens[2], and D. P. Rasse[1]*

[1]Bioforsk – The Norwegian Institute for Agricultural and Environmental Research. Frederick A. Dahls vei 20, Ås, Norway.

[2]Lehrstuhl für Bodenkunde, Department für Ökologie und Ökosystemmanagement, Wissenschaftszentrum Weihenstephan für Ernährung, Landnutzung und Umwelt, Technische Universität München, D-85350 Freising-Weihenstephan, Germany

**Corresponding author (adam.otoole@bioforsk.no)*

Abbreviations: *DMP, dry matter production; SWC, Soil water content; ^{13}C NMR, nuclear magnetic resonance spectroscopy.*

Abstract

Biochar is a promising technology for both improving soil quality and sequestering C in the long term. While modern pyrolysis technologies are being developed, kiln technologies often remain the most accessible method for biochar production. The objective of the present study was to assess biochar characteristics, stability in soil, and agronomic effects of a kiln produced biochar. Wheat-straw biochar was produced in a double-barrel kiln and analyzed by solid state ^{13}C NMR spectroscopy. Two experiments were conducted with biochar mixed into an Ap-horizon sandy loam. In the first experiment, CO_2 efflux was monitored for 3 months in plant-free soil columns across 4 treatments: 0, 10, 50 and 100 Mg biochar ha^{-1}. In the second experiment, ryegrass was grown in pots having received 17 and 54 Mg biochar ha^{-1} combined with four N rates from 144 to 288 kg N ha^{-1}. Our kiln method generated a wheat-straw biochar composed at 92% of aromatic structures. Our results suggest that the biochar lost less than 0.16% C as CO_2 over the 90-day incubation period. Biomass yields were not significantly modified by biochar treatments, except for a slight decrease at the 144 kg N ha^{-1} rate. Foliar N concentrations were significantly reduced by biochar application. Biochar significantly increased soil water content (SWC) and decreased plant wilting during periods of water stress. In conclusion our kiln-produced biochar was highly aromatic and appeared quite recalcitrant in soil. Increased SWC did not result in increased biomass yield, probably due to the timing of biomass growth and water depletion in the pots.

Introduction

Enhancement of C sinks and the reduction of fossil fuel emissions are the two strategies for mitigating climate change (IPCC, 2007). Agricultural soils have an important role to play as enhanced sinks for atmospheric C (Paustian et al. 1997). However, long term field research has confirmed that adding fresh crop residues to agricultural soils leads to large increases in soil C stocks in the short term but minimal increases in the long term (Powlson et al., 2008). Adding biochar (carbonized biomass) to soils has been suggested as a novel method for increasing soil C stocks in the long term due to the enhanced C stability of biochar as compared to that of fresh uncarbonized biomass (Lehmann et al., 2006; Cheng et al., 2008). In addition, biochar has been reported to enhance soil properties (Glaser, 2001; Grossman et al., 2010) and plant yields (van Zwieten et al. 2010a; Major et al., 2010b; Glaser et al., 2002). Reasons for this positive effect include pH increases in acidic soils (van Zwieten et al. 2010b) and subsequent reductions in exchangeable aluminum (Steiner et al. 2008); increases in cation exchange capacity and fertilizer efficiency (Glaser et al., 2002), and reductions in nutrient leaching (Major et al., 2010a).

Biochar is not a homogenous material. It can differ in its chemical and physical properties according to the type of feedstock, pyrolysis technology (Novak et al., 2009), and pyrolysis conditions used (Bruun et al. 2011b). Pyrolysis conditions influence the stability of biochar-C (Mašek et al. 2011) and the agronomic benefits from biochars (Hossain et al. 2010). Modern pyrolysis technologies for large-scale biochar production are few in number compared to traditional charcoal production technologies (Brown, 2009). Simple kiln and batch technologies are likely to be the first choice technology for small farmers and start-up biochar producers before larger scale systems become more prevalent and affordable. It is important therefore to determine whether kilns can create biochars that are suitable for carbon sequestration and soil improvement.

The objective of our study was to characterize kiln produced wheat straw biochar and investigate its effects on plant production as well as soil respiration as an approximate indicator for biochar-C stability.

Materials and Methods

Biochar Production

Wheat-straw biochar was produced using a two container kiln following the design of Gunther (2009). A container measuring 0.35 m in height (H) and 0.17 m diameter (D) was filled with approximately 870 g of straw (approx. 10-20 cm L, 20% moisture content) and compressed with a hand held pounding tool. The container was then placed upside down inside a larger container (0.50 m H and 0.45 m D) so that the straw was not exposed to O_2 during pyrolysis (Fig.1). The volume between the containers was filled with wood and burnt in order to heat the inner container. After all the outer container wood had burnt up (approx. 1 hr), the inner containers were removed, sealed with aluminum foil and left to cool. Temperatures were measured in the combustion zone at 45 minutes (the point where temperatures were highest). The combustion temperatures surrounding the pyrolysis chamber were measured at this point and ranged between 500 ºC - 900 ºC. Temperatures were not measured in the pyrolysis zone, but have been estimated to be around 500-600 degrees after we compared our data with NMR data and production process data available from Baldock & Smernik (2002). Twenty-five batches of biochar were produced with an average biochar yield of 24% ±4.7% from the original biomass. The batches were emptied into a larger barrel, mixed together, and sieved to 4-mm.

Biochar characterization

The wheat-straw biochar was characterized for nutrient content, pH, volatile matter and ash content, BET surface area, C and N content, and organic molecular structure. Ammonium and NO_3 were extracted with 2 M KCl and samples analyzed with a KONE instrument. Magnesium was measured according to Norwegian standard (2007). The pH was measured with 1g biochar in 20 ml of distilled water with an electrode probe connected to pH meter. (Orion Dual Star pH/ISE benchtop, Thermo Scientific). Shaking time was increased to 1.5 hr to increase equilibration between biochar surfaces and solution (Rajkovich et al., 2011) . Proximate analyses for volatile matter content were conducted according to ASTM E 871, 872 with the ash content determined according to ASTM D 1102. Specific surface area was measured by N adsorption–desorption isotherms at 77 K using a Micromeritics Tri Star 3000 instrument. Prior to analysis, the samples were dried at 120 °C and degassed overnight in a VacPrep 061 Degasser at 0.05 mbar, and 393K. The Brunauer–Emmet–Teller (BET) equation was used to calculate the specific surface area (Brunauer et al., 1938). The C and N contents were determined on a Leco CHN 1000 analyzer (Leco Corporation, MI, USA). Biochar quality was analyzed with solid state ^{13}C NMR spectroscopy (Bruker DSX 200 NMR spectrometer, Karlsruhe, Germany). The cross-polarization magic angle spinning (CPMAS) technique was applied with a ^{13}C -resonance frequency of 50.32 MHz and a spinning speed of 6.8 kHz. We used a contact time of 1 ms, a pulse delay of 2 s, accumulated 24883 scans and applied no line broadening. The ^{13}C chemical shifts were calibrated relative to tetramethylsilane (0 ppm). The region from 220 to 160 ppm was assigned to carbonyl (aldehyde and ketone) and carboxyl/amide C. Olefinic and aromatic C were detected between 160 and 110 ppm. O-alkyl and N-alkyl-C signals were found from 110 to 60 ppm and from 60 to 45 ppm. Resonances of alkyl C were assigned to the region 45 to -10 ppm.

Soil

A sandy loam Inceptisol (USDA classification) was collected from Utne farm, Rygge county, Norway (59°23'15'' N; 10°46'26'' E). The soil was air dried and sieved at 2 mm. The soil prior to biochar addition had a pH of 6.8. Soil pH within each pot was measured after biochar addition and before fertilization. The pH of the soil was determined with 1:1 w/w soil (18-37 grams per sample) and de-ionized water (pH 6.8). Each sample was shaken by hand with the added water for approximately 15 seconds before being measured by an electrode probe connected to a pH meter (Hanna instruments, HI931402). Soil bulk density was measured with 80 cm^3 sampling rings one week after soil, biochar amounts, and 2 L water had been added to pots. Four samples were taken from each treatment, and then weighed, dried in an oven at 105º C for 24 hours, and then re-weighed to determine the dry mass relative to its volume.

Experiment 1 – Biochar effect on CO_2 evolution

A soil column experiment without plants was conducted in a greenhouse with night (8 hrs) and day (16 hrs) temperatures of 15 ºC and 20ºC. Twelve high-density polyethylene (PEH) columns, measuring 0.4 m H x 0.2 m D (inner) were sealed on a 0.3 m × 0.3 m PEH plate, and filled with either soil or soil/biochar mixtures. The experiment design consisted of 4 treatments: control (7 L of soil with no biochar [BC0]), and soil (7 L) mixed with biochar at 10, 50 or 100 Mg ha^{-1} (BC10, BC50, BC100). There were 3 replicates per treatment and columns. Column bases were fitted with sealed drainage tubes. During CO_2 measurement periods, drainage tubes were plugged with silicon stoppers. The CO_2 flux from each column was measured with an infrared gas analyzer (IRGA) EGM-4 (PP Systems, Hitchin, UK). A gasket-lined lid was designed to fit air-tight over the PEH columns. The lid included an inlet and outlet for connecting gas tubes to the IRGA. Soil respiration rates were derived over 3-min measurement periods and 23 measurements were taken throughout a 98 day period. Measurements were taken between 10:00-14:00 o'clock throughout

the study period. Columns were measured in the same order each time but the pots from each treatment were randomly placed on the table. Irrigation events involved watering the columns with 1.2 L tap water every 14 days. The amount of water was chosen to ensure saturation of the soil column and provide leachate samples that were used in another study.

Experiment 2 – Biochar effect on plant and soil characteristics

A pot experiment was carried out in the same greenhouse (and light conditions) using perennial rye grass (*Lolium perenne L.*). The pots were placed on a rectangular table with radiation from 3 lamps which were set to 315 µmol photons m^{-2} s^{-1}.

Factors were: (a) biochar quantities and (b) N fertilization. Biochar treatments were: No biochar (control); biochar at a rate of 17 Mg ha^{-1} (BC17) and 54 Mg ha^{-1} (BC54) and 4 replicates for each. The biochar amounts correspond to 10 and 30% of pot volume for BC17 and BC54. N fertilization rates were 144, 192, 240, and 288 kg N ha^{-1}. The 240 kg N ha^{-1} represented the recommended rate for perennial rye-grass in Norway (Bioforsk, 2011). Nitrogen fertilizer was applied in the form of YaraMila™ Fullgjødsel® 22-3-10. Previous biochar studies have shown limited positive effect on yield in the absence of fertilizer (Chan et al., 2007; van Zwieten et al. 2010b; Yeboah et al., 2009), therefore we excluded a biochar-and-no-fertilizer control treatment and instead tested treatments against the recommended fertilization rate as stated above.

Soil and biochar amounts were measured by weight and added to plastic pots measuring (0.175 m tall by 0.20 m diameter) and which had 7 small drainage holes drilled in the bottom. The control pots had 7.50 kg air dried soil in them, the BC17 pots: 6.36 kg air dried soil and 0.05 kg biochar (0.75% mixture w/w), and the BC54 pots: 4.68 kg air dried soil and 0.16 kg biochar (3.5% mixture w/w). Soil amounts varied between treatments in experiment 2 to ensure potting media volumes

and potential root space and water holding capacity were equivalent to that of the control, i.e. 5.2 L. Biochar was thoroughly mixed in soil prior to filling the pots. To ensure comparable bulk densities within treatments, the soil was poured 1 L at a time and compacted with a flat hand tool. Pots were then placed in the greenhouse and watered with 2 L water. After two weeks, the fertilizer was carefully mixed into the top 5 cm of soil and ryegrass was sown at 0.8 g pot^{-1}.

The watering regime was designed to simulate a growing season with adequate precipitation followed by a dry period. Over the first month, pots were weighed weekly and watered up to 60% of field capacity. In the second and third months, pots were given approximately half the amount of water and were left to dry until plant wilting was observed in at least 50% of pots. At this point equal amounts of water were given to all pots across all treatments. The degree of plant wilting in each treatment was visually estimated before the last watering and grass harvest. The wilting point was estimated by recording the SWC at the point at which plants wilted and did not regain turgidity. Volumetric SWC was measured with a hand held Delta-T SM200 and HH2 moisture meter. Micro-voltage was recorded in each pot prior to watering events (x 9) and later converted into volumetric SWC with a manufacturer supplied equation that specifically accounts for the soil organic matter content. Soil moisture measurements made with TDRs are reported to be accurate to 3% compared to gravimetric methods (Tsegaye et al. 2004)

The biomass was harvested at the end of each month for 3 months. The grass in each pot was cut at a height of 5 cm from the soil level. The fresh biomass was weighed, bagged, and dried in an electric oven at 60 ºC for 5 days. After drying, the biomass was weighed again to determine the net dry weight and moisture content. References to biomass yield in this paper refer to dry matter weights. The chemical properties of unfertilized soil and biochar, along with the nutrient

concentrations in harvested biomass from the 240 kg N ha^{-1} treated pots only were analyzed by Eurofins AS laboratory. Elemental content of harvested biomass from pots fertilized with 144, 240, and 288 kg N ha^{-1} rates were not measured due to cost constraints. Soil NH_4 and NO_3 were extracted with 2 M KCl and analyzed on a Konelab Aqua 60 (Thermo Clinical Labsystems). Plant available cations were measured using the Egners AL (Ammonium lactate) method (Krogstad, 1992). The extraction fluid was a mixture of ammonium lactate (0.1 mol L^{-1}) and acetic acid (0.4 mol) and had a pH of 3.75.

Data and statistical analysis

Yield and foliar nutrient concentration data were analyzed by two-way analysis of variance (ANOVA) and SWC and degree of plant wilting by one-way ANOVA using Sigma Plot software. All pair-wise multiple comparison procedures were performed using the Holm-Sidak method when ANOVA returned a statistical difference ($p < 0.05$). Significant results were those where $p < 0.05$. A repeated measures analysis was conducted on the CO_2 efflux data as a two-factor ANOVA in R (2012).

Results

Biochar characterization

The solid state ^{13}C NMR spectrum of the biochar sample showed one main peak at 126 ppm, representing the C in aromatic systems. Two smaller peaks at 262 ppm and -10 ppm represent spinning side bands of this peak. Two more peaks were found at 72 ppm and 21 ppm representing alkyl and O-alkyl C. Most of the C in the biochar was represented by aromatic C (92.2%) while O-alkyl C and alkyl C only explained 4.4% and 3.4% (Fig. 2) The surface area of the biochar was

195 24 m^2 g^{-1} and proximate analysis measured fixed carbon, volatile and ash contents of 69, 13, and
196 17% respectively, and pH 9.8 (Table 1.) Biochar was low in mineral N, but high in P-AL, K-AL,
197 Mg-AL, and Ca-AL content (AL= Ammonium Lactate extraction), compared to background soil
198 levels (Table 2). High Zn concentrations in the biochar were attributed to contamination from the
199 galvanized zinc coating of the inner containers (Table 2). Small flakes of Zn coating were observed
200 and removed from two of the biochar batches.

201

202 **CO_2 flux from soil incubations**

203 Cumulative CO_2 fluxes from soil columns after 98 days of incubation did not differ significantly
204 among treatments (Fig. 2). A repeated measure analysis confirmed the absence of significant
205 treatment or time-treatment interactions (data not shown). The indigenous soil organic matter
206 (from treatment BC0) lost 3.3% of its original C over the 98-day period (data not shown). We
207 subtracted CO_2 efflux measured in BC0 from that measured in BC10, BC50, and BC100 in order
208 to estimate the biochar-C mineralization rate for the incubation period. Mineralization of biochar-
209 C by the end of the 98-day period was estimated to be 0.14% and 0.16% in BC50 and BC100,
210 respectively (data not shown). Soil respiration from BC10 was actually lower than BC0 by 1.59%,
211 although not significantly so (data not shown).

212 **Plant Yield**

213 Biochar additions did not significantly modify cumulative biomass yields. Within individual
214 harvests, biochar had no significant effect for harvest-1 & -2 but induced a significant yield
215 reduction in harvest-3 (Table 3, Figure 4). Harvest-3 yield reductions were more pronounced for
216 BC17 than for BC54 (Figure 4). Increased rates of N fertilization significantly increased harvest-
217 2 & -3 and cumulative biomass yields, while inducing a significant yield reduction for harvest-1

(Table 3, Figure 4). A significant cumulative yield reduction was observed at 144 kg N ha^{-1}. Significant biochar × N interactions were observed on biomass yields for harvest-3 ($p<0.001$) and cumulative totals ($p<0.05$), but not for havest-1 or -2 (Table 3).

Biochar effects on foliar nutrient concentration

Foliar concentrations of N, Ca, and Mg were significantly reduced by biochar addition in harvest-1 and -2 (Table 4). Potassium foliar concentrations were significantly increased by biochar application at all 3 harvests (Table 4), most likely due to the high extractable amounts present in the biochar (Table 2). Phosphorus and S foliar concentrations showed no clear trends between biochar treatments over all three harvests (Table 4). Zinc concentrations were significantly higher in biochar treatments (Table 2).

Soil pH, bulk density, and Soil water effects (Experiment 2)

The pH of the biochar was 9.8 (Table 1). Soil pH increased after biochar additions from 6.8 (±0.02) in control soil to 7.01 (±0.04) and 7.67 (±0.03) in BC17 and BC54, respectively. Soil bulk density was reduced from 1.56 g cm^{-3} (±0.04) in the control, to 1.46 g cm^{-3} (±0.03) in the BC17 and 1.24 g cm^{-3} (±0.02) in BC54 (data not shown). Biochar additions significantly increased ($p<0.05$) SWC for all measurements throughout the 3 months of the trial (Fig. 5). During the final month of the experiment when pots were not watered for up to two weeks, many of the plants wilted. Plant wilting was significantly reduced ($p= 0.039$) by 53% in BC54 and 31% in BC17 compared to the control (data not shown). Biochar additions on average prevented SWC descending below the wilting point of the control soil in the final month (Fig. 5).

Discussion

The tested kiln method was sufficient to fully carbonize the wheat straw and transform alkyl and O-alkyl C to aromatic (aryl) C as confirmed by the solid state ^{13}C NMR experiments (Fig. 2). High aromatic content in biochar has been linked to increased recalcitrance of biochar-C decomposition in soils (Novak et al., 2009). The degree of aromaticity of our kiln-produced wheat-straw biochar appeared similar to that of a switchgrass biochar produced under controlled slow pyrolysis conditions at 500°C, i.e. from 82% to 93% (Novak et al., 2009, Brewer et al., 2009), and to that of corn-stover biochar from 730°C gasification, i.e. 87% (Brewer et al., 2009). Krull et al. (2009) and Baldock and Smernik (2002) analyzed biochar made from both wood and grass using solid state ^{13}C NMR spectroscopy and found greater proportions of aromatic C in biochar with increasing pyrolysis temperatures. The proportion of aromatic C in grass biochar pyrolyzed at 600 degrees for one hour was 88% (Baldock & Smernik, 2002), which is near to 85.8% aryl C in our wheat straw biochar pyrolyzed between an estimated 500-600 degrees for one hour.

The stability of the kiln produced wheat straw biochar was also inferred by the similar CO_2 efflux from control and biochar-amended soil columns (Fig. 3). Approximate biochar decomposition was less than 0.2% over the 98-day period. Our results are similar to those of Bruun et al. (2011), reported that wheat-straw biochar produced between 500 and 575°C lost <5% of its carbon when incubated with soil. Ninety percent of the loss occurred within the first 20 days and 10% of the recorded loss in the next 100 days. Similarly, Smith et al. (2010) using natural abundance ^{13}C tracing reported no significant CO_2 production after 50 days of incubation from switchgrass biochar produced by slow pyrolysis at 500°C. The fraction of labile and semi-labile carbon has been reported to decrease with increasing pyrolysis temperatures (Mašek et al. 2011). In their

study, pyrolysis temperatures of 550 °C yielded a labile C fraction of approximately 10% wt. of the produced biochars.

Biochar mineralization rate in soils appears to decrease rapidly with time, as the labile fraction is progressively mineralized (e.g. Smith et al., 2010). Longer term incubations do not suggest any increase in biochar degradation rate with time, such as for a 2-year field decomposition study in tropical conditions (Major et al., 2010a). Both the NMR-derived molecular structure data and 90-day mineralization rate suggest that our wheat-straw biochar has good properties for long-term C storage in soils, despite having been produced with a simple kiln technology where temperature control was not possible. We did not use labeled C methods and therefore we could not correct for the possible contribution of a priming effect induced by the biochar. However, a potential positive priming effect would lead to a relative decrease in the proportion of biochar-derived CO_2 as compared to that of SOM-derived CO_2. In other words, the presence of a positive priming effect would mean that our biochar mineralization rates are overestimates of the true values.

Cumulative biomass yields over the 3-month period were not significantly modified by biochar application rate, however a small but significant decline was observed in the third harvest (Table 3, Fig. 4). Crop yields and plant biomass are generally increased by biochar addition, although some negative responses have also been observed (Jeffery et al., 2011). For cereal crops, recent field trials in northern latitudes have reported positive biochar effects on yields. Vaccari et al. (2011) reported yield increases in durum wheat up to 30% when 30 and 60 Mg ha^{-1} of biochar and 122 kg N ha^{-1} were applied to a silt loam. Gaythorne-Hardy et al. (2009) also found field plots amended with 50 Mg ha^{-1} and at least 100 kg N ha^{-1} had increased spring barley yields compared to no-biochar control plots. In China, Zhang et al. (2012) observed significant yield increases of

16% from kiln produced wheat straw biochar applied at 10 and 40 t ha^{-1}. For ryegrass, Wisnubroto et al. (2011) report that biochar increases dry matter production (DMP) under ample N fertilization, but reduces DMP in non-fertilized controls. Our results give further evidence that ryegrass DMP are negatively impacted by biochar addition at low N fertilization rates. Our results suggest that adequate N fertilization is needed when biochar is applied to soils cultivated under ryegrass, at least for the initial season of biochar incorporation.

Nitrogen deficiency is the likely cause for our slight reduction in DMP at the third harvest. Foliar N concentration in harvest-1 and -2 was significantly reduced by biochar addition under normal N fertilization rate. These findings suggest that biochar somewhat reduced soil N availability to plants. We observed a significant negative N × biochar interaction on yield at the third harvest (Table 3). By contrast, Chan et al. (2007) found significant biochar x N fertilizer interactions leading to increased yields. Biochar effects appear soil dependent. Radish DMP increased in an acid ferrasol but decreased in an alkaline calcarosol (Van Zwieten et al., 2010b). Yeboah et al. (2009) reported a decrease in N recovery with biochar application to a silt loam but found an increase in a sandy loam.

Nitrogen adsorption and microbial immobilization are potential explanations for the reduction in N availability. The volatile matter (VM) content of our biochar was 13%, which suggests that some labile C might have remained in the biochar despite the apparent low mineralization rates. Volatile matter (VM) includes the labile carbon fraction of biochar which is accessible to microbes as an energy source (Zimmerman, 2010). High VM in biochar have been linked to N immobilization and to subsequent reductions in corn growth (Deenik et al., 2010). In this latter study, macadamia biochars were produced with differing VM levels of 6.3 and 22.5%. The high VM biochar

312 significantly reduced and the low VM biochar significantly increased growth relative to the
313 fertilized control. Positive effects on biomass growth from low VM biochar were independent of
314 pH effects. Further research is needed to determine more accurately at what percentage and under
315 what conditions VM matter in biochar can lead to reduced yields.

316

317 Foliar concentration of Ca and Mg were reduced in biochar pots vs. control (Table 4). This result
318 was unexpected, as our biochar contained large quantities of Ca and Mg (Table 2). Increases in Ca
319 and Mg uptake with biochar additions have been observed in maize plants (Major et al., 2010b).
320 For common beans, Rondon et al. (2007) observed consistent increases in biomass Mg content,
321 while Ca biomass concentrations increased or decreased depending on both varieties and biochar
322 quantities. However, the most probable explanation for our reduction in plant Mg and Ca
323 concentrations comes from the high Zn concentrations detected in our biochar, which may have
324 competed for cation exchange sites. High Zn supply has been previously found too reduce Ca foliar
325 concentrations (Ruano et al., 1987). High levels of Zn present in our biochar (Table 2) were likely
326 caused by contamination from the zinc galvanized surface of the containers that the biochar were
327 in during pyrolysis. However, Zn was likely to be largely bound to biochar surfaces as foliar
328 concentrations from biochar amended pots, ranging from 56-171 mg kg^{-1} over 3 harvests (Table
329 4), did not exceed phytotoxic limits for perennial ryegrass (210 mg kg^{-1}) (Davis and Beckett,
330 1977). Nevertheless, caution should be shown for the choice of material for producing biochar in
331 kilns, in order to minimize the risk of heavy metal contamination to biochar and soils.

332

333 Volumetric SWC significantly increased in our biochar treatments as compared to the control (Fig.
334 5), which is in accordance with other studies (Tryon, 1948; Glaser, 2001; and Chan et al. 2007).
335 Although we did not directly measure available soil water, we did observe wilting reductions up

to 51% in BC54 at the end of a two week dry period. This suggests that the BC54 treatment increased available soil water for ryegrass. However, this effect did not translate into increased DMP in our experiment. This could be because the biomass regrew quickly after each harvest and initial watering, and thus the water deficient periods occurring 1-2 weeks later had little bearing on final DMP.

Increases in SWC by biochars appear largely driven by their often-reported high surface areas and porosity (Thies and Rillig, 2009; Downie et al. 2009). Surface area of our biochar was 24 m^2 g^{-1} (Table 1), with a micropore structure well-defined on the on a SEM picture (Fig. 6). Biochar surface area generally increases with temperature as volatile matter is released from micropores (Downie et al. 2009). Production temperatures and heating times for our kiln-produced biochar appear most closely related those of slow pyrolysis, i.e. 400-600 degrees for ~ 1 hour. The surface area of our wheat-straw biochar was substantially higher than that reported for a wheat-straw biochar produced with slow pyrolysis at 525 °C, i.e. 0.6 m^2 g^{-1} (Bruun et al., 2011a), but within the range of 0.1 – 235 m^2 g^{-1} found by Spokas et al. (2011) for *Pinus* under slow pyrolysis at ~ 500 °C. Although reported surface area measurements of slow pyrolysis chars are variable they could be generally expected to increase the total surface area of sand soils such as used in our study and aid in increasing water retention.

We have documented here the properties of one kiln-produced biochar and its plant and soil effects. But as there are multiple kiln designs emerging for small-scale biochar production further studies are required to make more general assertions about kiln-produced chars, their effects on plant growth and soil conditions, and their utility for carbon sequestration.

Acknowledgments

This study has been made possible through funding from the Norwegian Research Council's Food Research Program as part of the project: NFR/192856 'Creating a scientific basis for an integrated evaluation of soil-borne GHG emissions in Norwegian agriculture' led by Department of Plant and Environmental Sciences (IPM), at the the University of Life Sciences, Norway (UMB). We would also like to thank Pr. Bishal Situala (Noraric, UMB) who was co-supervisor for the main author during his masters work and who facilitated partial funding. Thanks also to Hege Bergheim and Dr. Morten Grønli who helped with biochar production and lab analysis.

References

Baldock, J. A. and R. J. Smernik. 2002. Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red pine) wood. *Org. Geochem.* 9:1093-1109. doi:10.1016/S0146-6380(02)00062-1

Bioforsk. 2011. Fertilizer handbook: Pasture and animal feed crops. Available at: http://www.bioforsk.no/ikbViewer/page/prosjekt/tema/artikkel?p_dimension_id=19190&p_ menu_id=19211&p_sub_id=19191&p_document_id=47257&p_dim2=19603 (verified 10 April 2012).

Brewer, C. E., K. Schmidt-Rohr, J.A. Satrio, and R.C. Brown. 2009. Characterization of biochar from fast pyrolysis and gasification systems. *Environ. Progress & Sustainable Energy*. 28:386-396.

Brown, R. 2009. Biochar production technology. In: J. Lehmann and S. Joseph, Editors, Biochar for environmental management: Science and technology. Earthscan, London, p.127-147.

Brunauer, S., P. H. Emmett, and E. Teller. 1938. Adsoption of gases in mulitmolecular layers. *J. Am. Chem. Soc*. 60:309-319

Bruun, E. W., Ambus, P., Egsgaard, H., & Hauggaard-Nielsen, H. 2011a. Effects of slow and fast pyrolysis biochar on soil C and N turnover dynamics. *Soil Biology and Biochemistry*, 46:73-79. Elsevier Ltd. doi:10.1016/j.soilbio.2011.11.019

Bruun, E.W., H. Hauggaard-Nielson, N. Ibrahim, H. Egsgaard, P. Ambus, P.A. Jensen, and K. Dam-Johansen. 2011b. Influence of fast pyrolysis temperature on biochar labile fraction and short term carbon loss in a loamy soil. *Biomass Bioenerg.* 35:1182-1189.

Chan, K.Y., L. van Zwieten, I. Meszaros, A. Downie, and S. Joseph. 2007. Agronomic values of greenwaste biochar as a soil amendment. *Aust. J. of Soil Res.* 45:629-634.

Cheng, C.H., J. Lehmann, J.E. Thies, and S.D. Burton. 2008. Stability of black carbon in soils across a climatic gradient. *J. Geophys. Res.* 113:G02027

Davis, R. D. and P. H. T. Beckett. 1978. Upper Critical Levels of Toxic Elements in Plants. II. Critical Levels of Copper in Young Barley, Wheat, Rape, Lettuce and Ryegrass, and of Nickel and Zinc in Young Barley and Ryegrass. *New Phytol.* 1:23-32

Deenik, J., T.McClellan, G.Uehara. 2010. Charcoal volatile matter content influence plant growth and soil nitrogen transformations. *Soil Sci. Soc. Amer. J.* 4: 1259-1270.

Downie, A., Crosky, A. and P. Munroe. 2009. Physical properties of biochar. In: J. Lehmann and S. Joseph, Editors, Biochar for environmental management: Science and technology. Earthscan, London. p.14-32.

Gaythorne-Hardy, A., J. Knight, and J. Woods. 2009. Biochar as a soil amendment positively interacts with nitrogen fertiliser to improve barley yields in the UK. IOP Conf. Series: Earth and Environmental Science 6. Available online: http://iopscience.iop.org/1755-1315/6/37/372052/pdf/1755- 1315_6_37_372052.pdf (verified 16 Mar.2011)

Glaser, B. 2001. The 'Terra Preta' phenomenon: a model for sustainable agriculture in the humid tropics. *Naturwissenschaften.* 88:37–41.

Glaser, B., J. Lehmann, and W. Zech. 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal – a review. *Biol. Fertil. Soils.* 35:219–230.

Grossman, J. M., O'Neill, B. E., Tsai, S. M., Liang, B., Neves, E., Lehmann, J., and Thies, J. E. 2010. Amazonian anthrosols support similar microbial communities that differ distinctly from those extant in adjacent, unmodified soils of the same mineralogy. Microbial ecology, 1:192-205. doi:10.1007/s00248-010-9689-3

Gunther, F. 2009. The simplest of the simple: A two-barrel charcoal retort. Available online: http://www.holon.se/folke/carbon/simplechar/simplechar.shtml (verified 17 Mar. 2011).

Hossain, M.K., V. Strezov, K.Y. Chan, and P.F. Nelson. 2010. Agronomic properties of wastewater sludge biochar and bioavailability of metals in production of cherry tomato (*Lycopersicon esculentum*).*Chemosphere* 78:1167–1171.

IPCC, 2007. Climate change 2007: The physical science basis. Contribution of working group 1 to the forth assessment report of the intergovernmental panel on climate change. Cambridge University Press, Cambridge.

Jeffery, S., F. G. A.Verheijen , M. van der Velde, & A. C. Bastos. 2011. A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. *Agriculture, Ecosystems & Environment*, 1:175-187. Elsevier B.V. doi:10.1016/j.agee.2011.08.015

Knicker, H., K.U. Totsche, G. Almendros, F.J. González-Vila. 2005. Condensation degree of burnt peat and plant residues and the reliability of solid-state VACP MAS ^{13}C NMR spectra obtained from pyrogenic humic material. *Org. Geochem*. 10:1359-1377.

Krogstad, T. 1992. Methods for soil analysis (In Norwegian). Institute for Soil Science, Norwegian Agricultural College, Ås, Norway.

Krull, E.S., Baldock, J.A., Smernik, R. and Skjemstad, J.O. 2009. Characterization of biochar, In: Lehmann and Joseph (editors.), Biochar for Environmental Management: Science and Technology, Earthscan Publishers Ltd.

Lehmann, J., J. Gaunt, and M. Rondon. 2006. Bio-char Sequestration in Terrestrial Ecosystems – A Review. *Mitig. Adapt. Strat. Glob. Change*. 11:395-419.

436 Major, J., J. Lehmann, M. Rondon, and C. Goodale. 2010a. Fate of soil-applied black carbon:
437 Downward migration, leaching and soil respiration. *Glob. Change Biol.* 16:1366-1379.

438 Major, J., Rondon, M., Molina, D., Riha, S. J., & Lehmann, J. 2010b. Maize yield and nutrition
439 during 4 years after biochar application to a Colombian savanna oxisol. *Plant and Soil*,
440 333(1-2), 117-128. doi:10.1007/s11104-010-0327-0

441 Mašek, O., Brownsort, P., Cross, A., & Sohi, S. 2011. Influence of production conditions on
442 the yield and environmental stability of biochar. *Fuel*. doi:10.1016/j.fuel.2011.08.044

443 In Norwegian Standard. 2007. Water quality- Determination of selected elements by inductively
444 coupled plasma optical emission spectrometry (ISO 11885:2007).

445 Novak, J. M., I, Lima, Gaskin, J.W., C.Steiner, K. C. Das, M. Ahmedna, and D. W Watts.
446 2009. Characterization of designer biochar produced at different temperatures and
447 their effects on a loamy sand. Science, 843:195-206.

448 Paustian, K., O. Andrén, H.H. Janzen, R. Lal, P.Smith, G.Tian, H.Tiessen, M.Van Noordwjik,
449 P.L.Woomer. 1997. Agricultural Soils as a sink to mitigate CO_2 emissions. *Soil use*
450 *and manage.* 4: 230-244.

451 Powlson, D.S., A.B. Riche, K. Coleman, M.J. Glendining, A.P. Whitmore. 2008. Carbon
452 sequestration in European soils through straw incorporation: Limitations and
453 alternatives. *Waste Manage.* 28:741–746.

454 R statistics software. 2012. R Foundation for statistical computing, Vienna, Austria.

455 Rajkovich, S., Enders, A., Hanley, K., Hyland, C., Zimmerman, A. R., & Lehmann, J. 2011.
456 Corn growth and nitrogen nutrition after additions of biochars with varying properties
457 to a temperate soil. Biology and Fertility of Soils, 3:271-284.

458 Rondon, M.A., J. Lehmann, J. Ramírez, and M. Hurtado. 2007. Biological nitrogen fixation
459 by common beans (*Phaseolus vulgaris* L.) increases with bio-char additions. *Biol.*
460 *Fertil. Soils*. 43:699–708

461 Ruano, A., J. Barceló, and C. Poschenrieder. 1987. Zinc toxicity-induced variation of mineral
462 element composition in hydroponically grown bush bean plants. *J. Plant Nutr*. 4:373-
463 384.

464 SigmaPlot for Windows Version 11. 2008. Wpcubed GmbH, Germany.

465 Smith, J., H. Collins, and V. Bailey. 2010. The effect of young biochar on soil respiration.
466 *Soil Biol. Biochem*. 42:2345-2347.

467 Steiner, C., B. Glaser, W.G. Teixeira, J. Lehmann, W.E.H. Blum, and W. Zech. 2008. Nitrogen
468 retention and plant uptake on a highly weathered central Amazonian Ferralsol
469 amended with compost and charcoal. *J. Plant Nutr*. 171:893–899.

Thies, J.E. and M.C. Rillig. 2009. Characteristics of biochar: Biological properties. In: Lehmann and Joseph (Editors) Biochar for Environmental Management: Science and Technology. Earthscan Publishers Ltd. London., p. 85-105.

Tryon, E.H. 1948. Effect of charcoal on certain physical, chemical, and biological properties of forest soils. *Ecol. Monogr*. 18:81-115.

Tsegaye, T. D., Tadesse, W., Coleman, T. L., Jackson, T. J., & Tewolde, H. 2004. Calibration and modification of impedance probe for near surface soil moisture measurements. *Canadian Journal of Soil Science*, 2:237-243.

Vaccari, F.P., S. Baronti, E. Lugato, L. Genesio, S. Castaldi, F. Fornasier, and F. Miglietta. 2011. Biochar as a strategy to sequester carbon and increase yield in durum wheat. *Eur. J. Agron*. 34:231-238.

Van Zwieten, L., S. Kimber, A. Downie, S. Morris, S. Petty, J. Rust, and K.Y. Chan. 2010a. A glasshouse study on the interaction of low mineral ash biochar with nitrogen in a sandy soil. *Aust. J. Soil Res*.48:569-576.

Van Zwieten, L., S. Kimber, S. Morris, K.Y. Chan, A. Downie, J. Rust, S. Joseph, and A. Cowie. 2010b. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant Soil.* 327:235-246.

Wisnubroto, E., M. Hedley, and M. Camps Arbestain. 2011. The use of biochar from biosolids to improve soil functions of sandy soils. NZBRC Workshop 2011, February 10-11, Massey University, Palmerston North, New Zealand

Yeboah, E., P. Ofori, G.W. Quansah, E. Dugan, and S. Sohi. 2009. Improving soil productivity through biochar amendments to soils. Afr. J. Environ. Sci. Technol. 3:34-41.

Zimmerman, A.R. 2010. Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). *Environ. Sci. Technol.,* 4:1295-1301.

Zhang, A., Bian, R., Pan, G., Cui, L., Hussain, Q., Li, L., Zheng, J., et al. (2012). Effects of biochar amendment of soil quality, crop yield and greenhouse gas emission in a Chinese rice paddy: A field study of 2 consecutive rice growing cycles. *Field Crops Res.*, 127, 153-160. Elsevier B.V. doi:10.1016/j.fcr.2011.11.020.

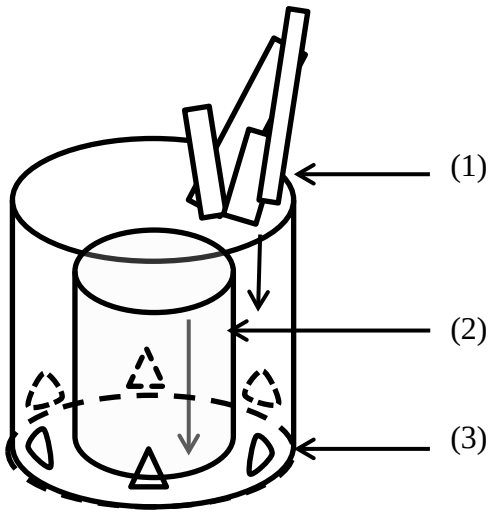


Fig. 1. Double-container biochar kiln. (1) Scrap wood filled the space and was burnt to heat the biochar feedstock in the inner container (2) The inner container, containing straw, was turned upside down to prevent air entry to the pyrolysis zone (3) 6 x Air vents were cut in the outer container to assist updraft combustion.

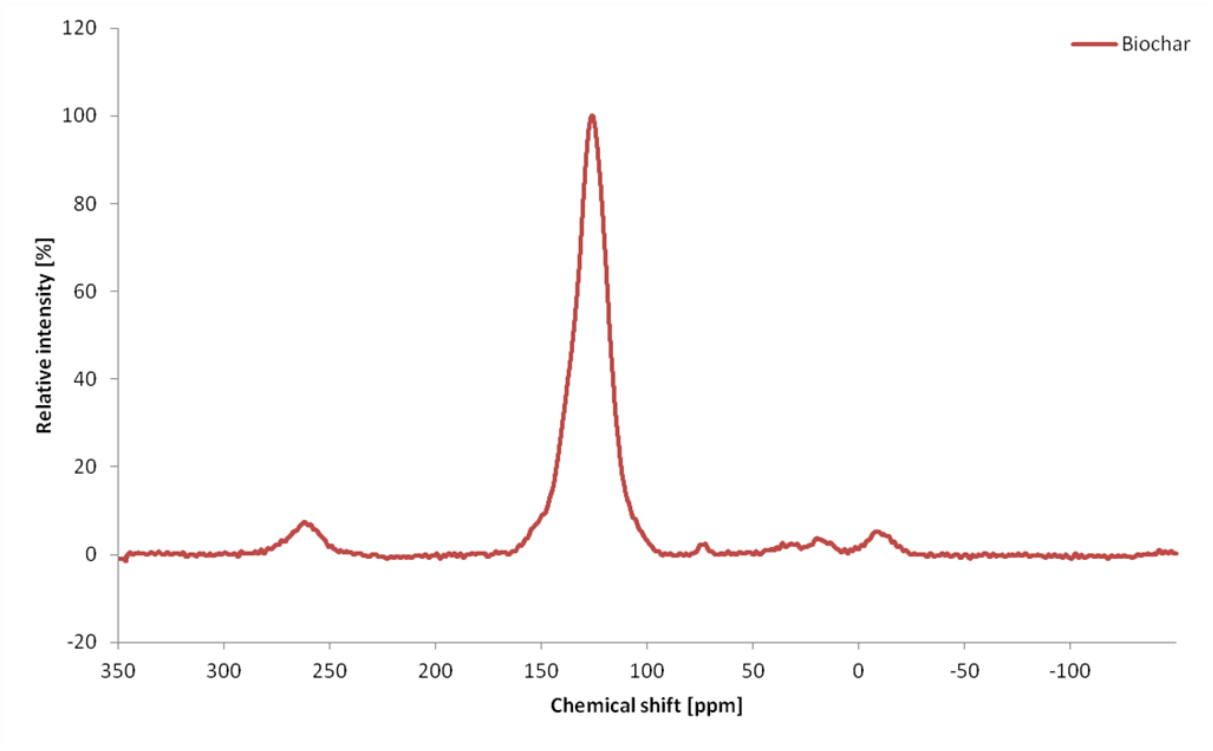
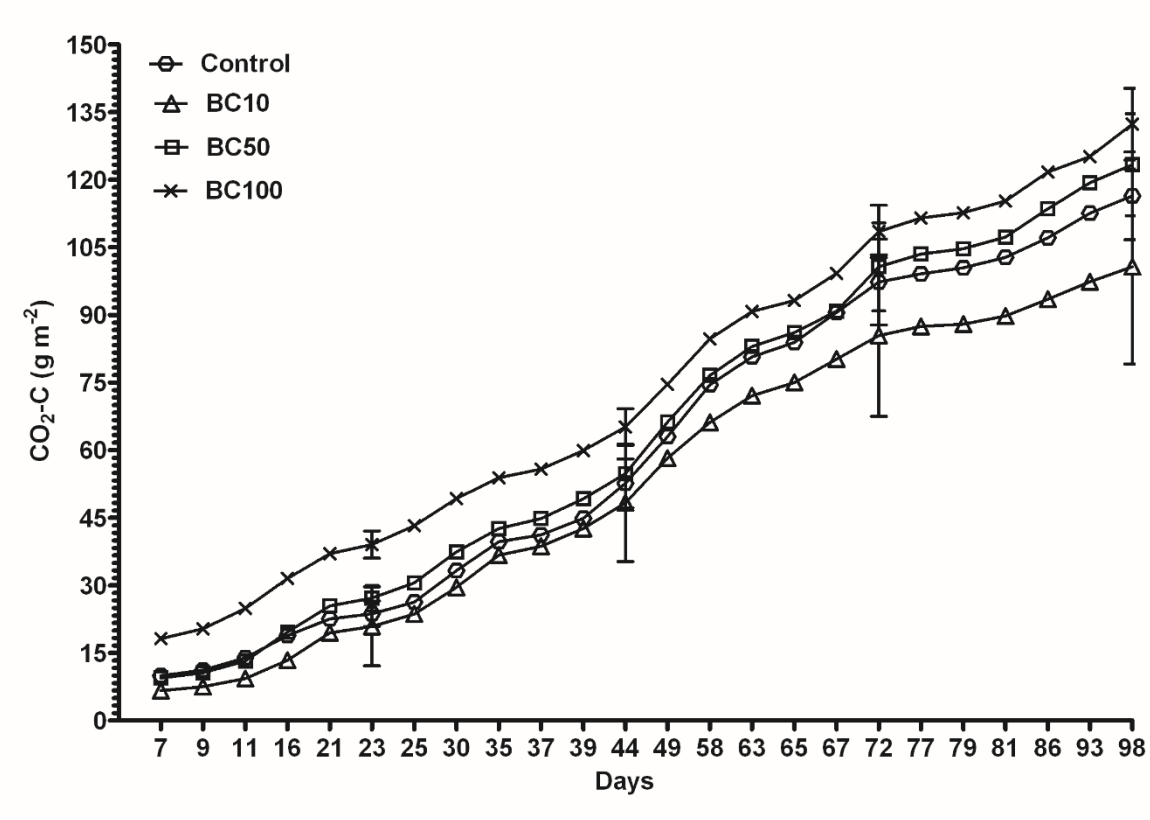


Fig. 2. Quality of the produced biochar as analysed by solid state ^{13}C NMR spectroscopy. The main peak at 126 ppm represents C in aromatic systems and contains 92.2% of the total spectrum (including spinning side bands at 262 ppm and at -11 ppm),

516



517

518 **Fig. 3. Cumulative CO_2-C evolved over 98 days. (error bars ± one standard error of the**
519 **mean shown for every 6th measurement for the sake of visual clarity, *n*=3).**

520

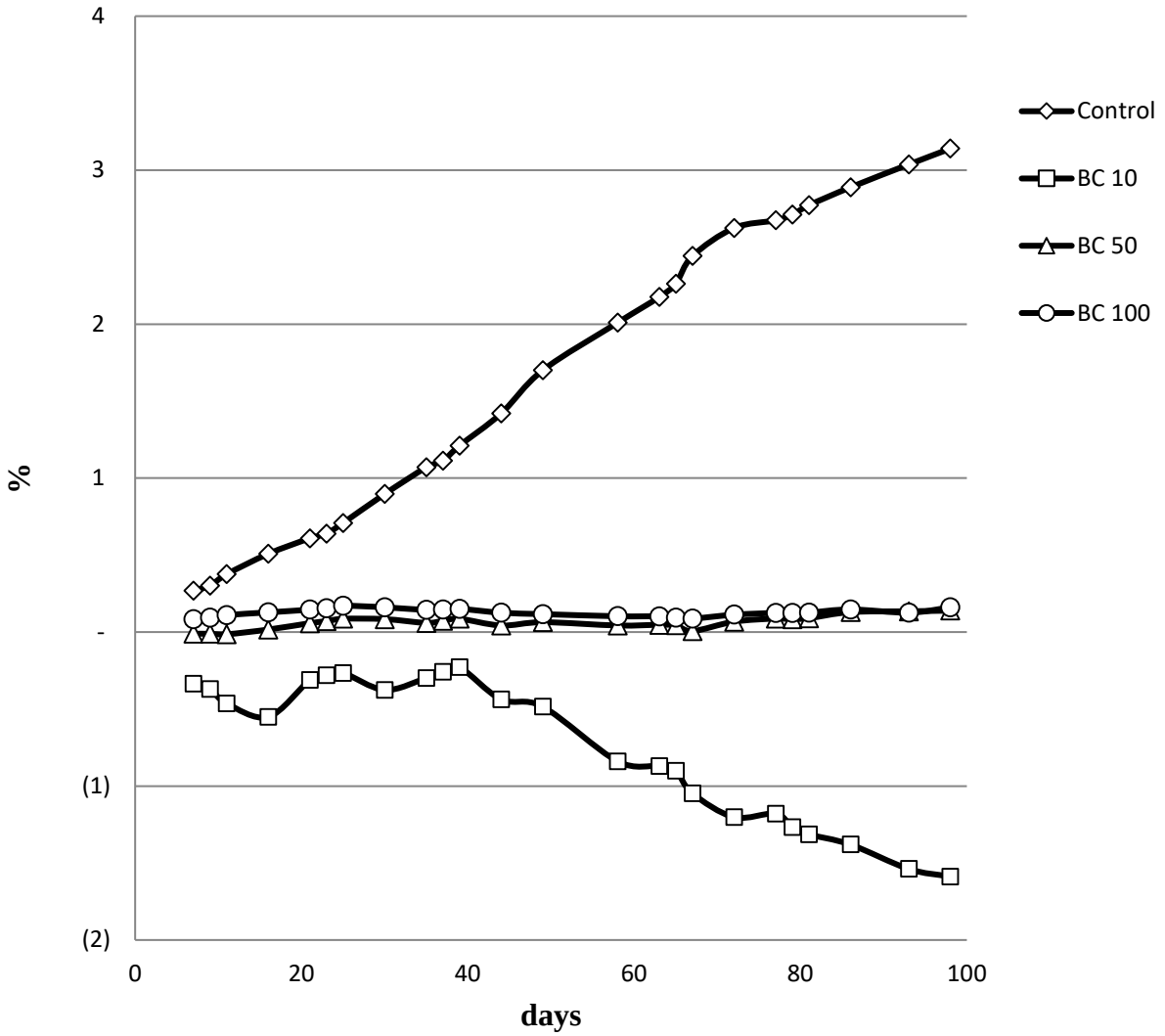
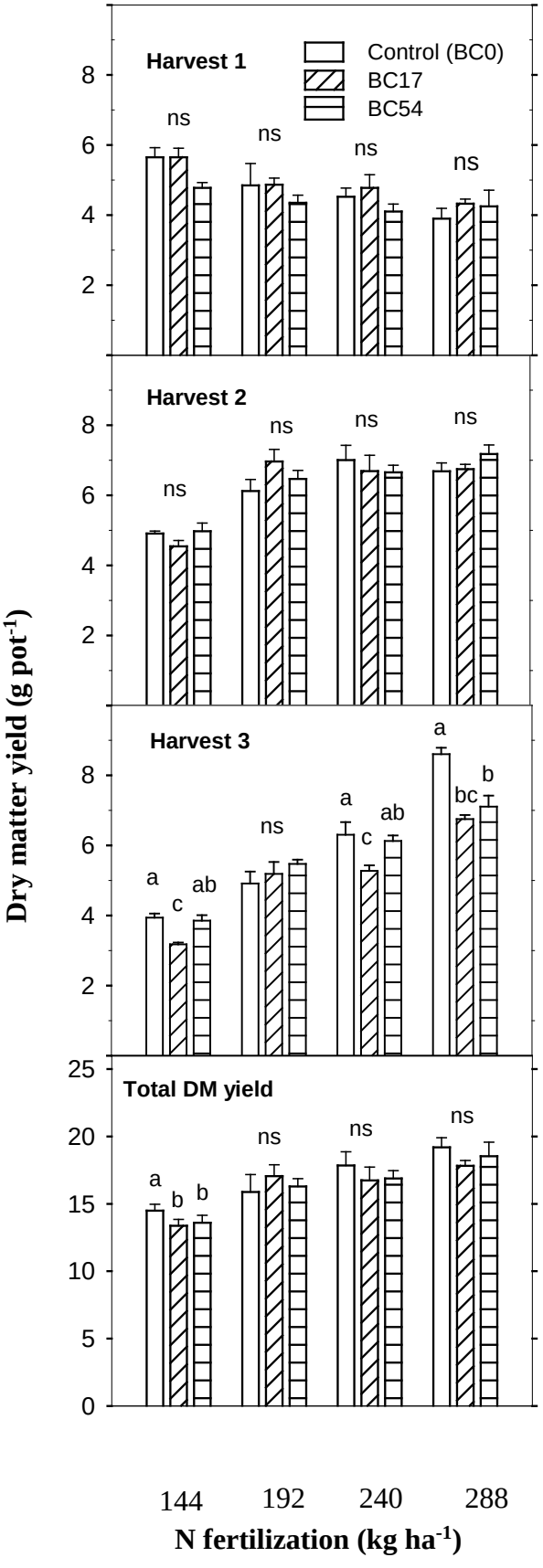
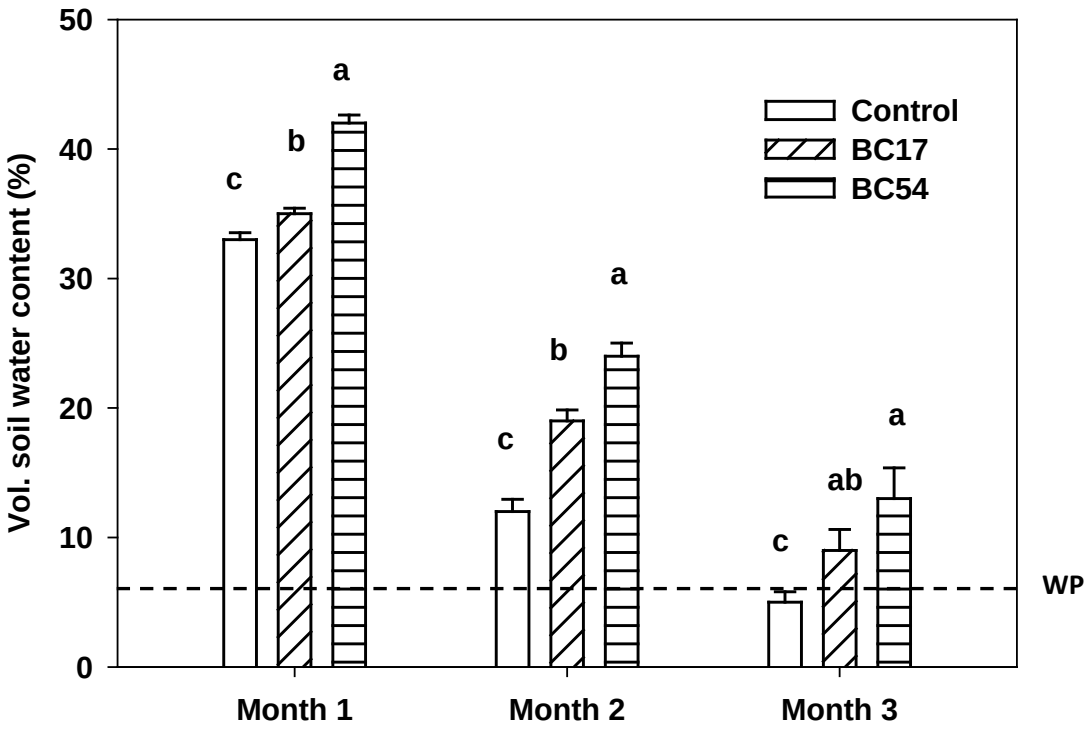


Figure X. Biochar-C loss as a % of Total-C after Control/Native-C respiration has been subtracted.



527 **Fig. 4 . Dry matter yield at each harvest and total accumulated dry matter yield as a function of**
528 **biochar additions and applied fertilizer rates (error bars denote standard error of the mean,**
529 **ns=not significant, different letters within a given fertilizer rate denote significance p<0.05).**



530

531 **Fig. 5. Volumetric soil water content, bars with different letters denote significance where p<0.05).**
532 **Error bars are standard error of the mean. Dotted line shows the estimated wilting point (WP) of**
533 **the control soil.**

534

535

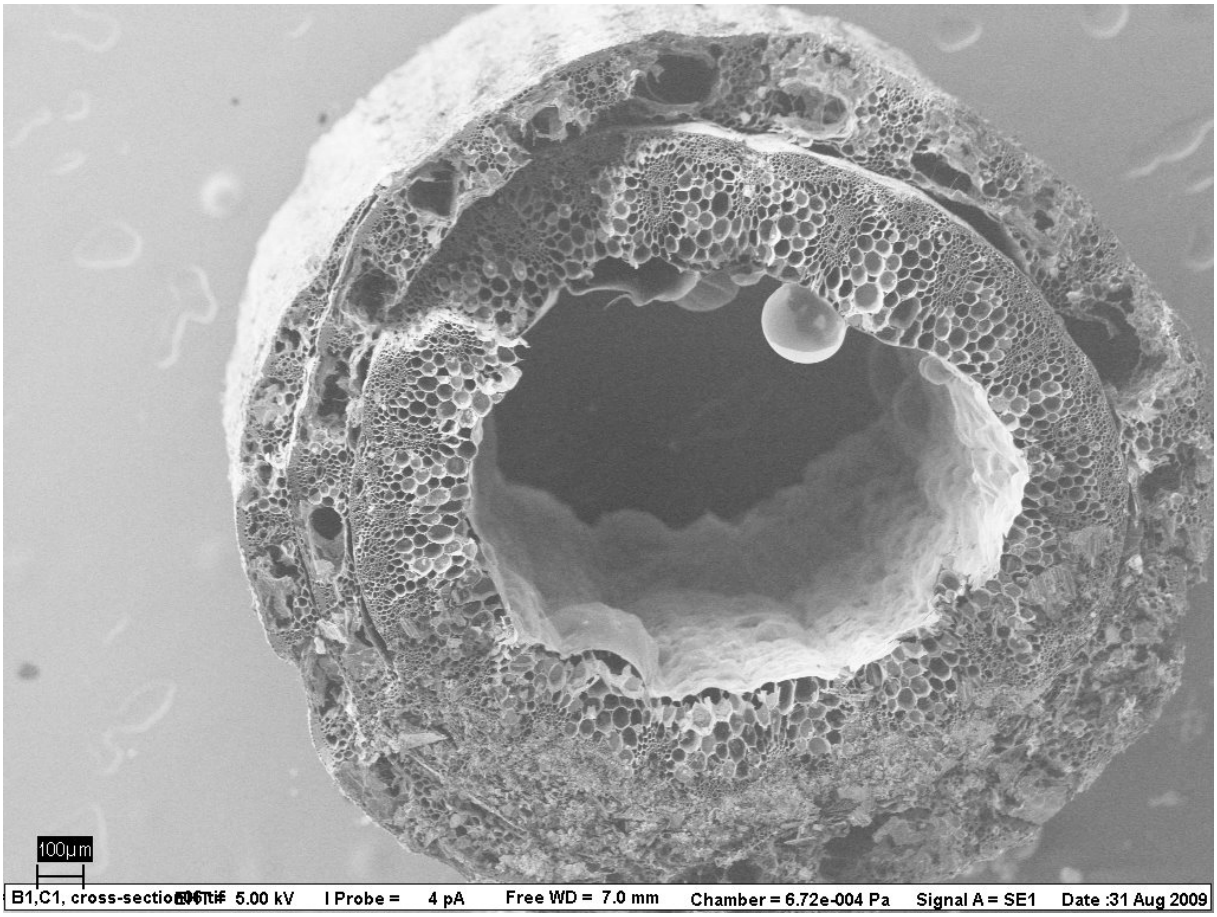


Fig.6. Scanning electron microscope image showing the cross section of a carbonized wheat straw stem.

Table 1. Selected properties of wheat straw biochar

	Fixed Carbon (%)	Volatile Matter (%)	Ash (%)	pH	BET-N_2 Surface area (m^2 g^{-1})
Biochar	69	13	17	9.8	24

539

540

Table 2. Selected chemical properties of soil and biochar at start of experiment

	----------extractable nutrients----------						------total elemental analysis---------			
	NH_4-N	NO_3-N	P-AL	K-AL	Mg-AL	Ca-AL	P	Zn	C	N
Soil	6.35	12.5	320	130	150	95	1400	68	12000	1000
Biochar	1.55	<4	720	7700	490	3800	-	6000	717000	9600

541

1 **Table 3. Factorial Analysis of biochar and N on DM production**

Factor	Harvest 1	Harvest 2	Harvest 3	Cumulative
Biochar	Ns	Ns	***	Ns
N	***	***	***	***
Biochar x N	Ns	Ns	***	*

2 *, **, *** significant at the 0.05, 0.01, and 0.001 probability levels respectively. Ns= non-significant.

Table 4. Element concentrations in harvested biomass on a dry matter basis (only for pots applied with 240 kg N ha^{-1})

	N	P	K	Ca	Mg	Zn
	----------%----------					mg kg^{-1}
Harvest-1						
Control	6.28^{a}	0.46^{a}	7.40^{b}	0.79^{a}	0.39^{a}	62.25^{c}
	(±0.05)	(±0.02)	(±0.07)	(±0.01)	(±0.01)	(±2.29)
10% BC	6.11^{b}	0.46^{a}	7.83^{ab}	0.63^{b}	0.32^{b}	86.50^{b}
	(±0.04)	(±0.01)	(±0.11)	(±0.01)	(±0.01)	(±5.66)
30% BC	5.85^{c}	0.48^{a}	8.33^{a}	0.60^{b}	0.32^{b}	165.00^{a}
	(±0.04)	(±0.05)	(±0.59)	(±0.03)	(±0.02)	(±16.05)
Harvest-2						
Control	5.43^{a}	0.36^{a}	4.53^{b}	1.13^{a}	0.60^{a}	46.25^{c}
	(±0.13)	(±0.02)	(±0.07)	(±0.03)	(±0.02)	(±1.89)
10% BC	4.69^{b}	0.46^{a}	6.45^{a}	0.81^{b}	0.41^{b}	91.50^{b}
	(±0.17)	(±0.02)	(±0.13)	(±0.01)	(±0.01)	(±10.64)
30% BC	4.10^{b}	0.51^{a}	6.98^{a}	0.61^{c}	0.32^{c}	171.50^{a}
	(±0.22)	(±0.02)	(±0.26)	(±0.02)	(±0.01)	(±11.05)
Harvest-3						
Control	2.51^{a}	0.48^{a}	3.33^{c}	1.03^{a}	0.55^{a}	46.25^{c}
	(±0.32)	(±0.01)	(±0.09)	(±0.03)	(±0.02)	(±2.17)
10% BC	1.85^{a}	0.40^{b}	4.48^{b}	0.68^{b}	0.36^{b}	56.75^{b}
	(±0.02)	(±0.01)	(±0.09)	(±0.03)	(±0.02)	(±5.20)
30% BC	1.91^{a}	0.43^{ab}	5.13^{a}	0.48^{c}	0.27^{c}	85.25^{a}
	(±0.10)	(±0.03)	(±0.17)	(±0.01)	(±0.01)	(±6.92)

± standard error shown. Within each harvest, different letters denote significance (P<0.05), n=4.