



Designer, acidic biochar influences calcareous soil characteristics



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ARTICLE INFO

Article history:

Received 6 December 2014

Received in revised form 19 May 2015

Accepted 27 May 2015

Available online 12 June 2015

Keywords:

Biochar

Soil water

Micronutrients

Microbial enumeration

Nitrate–nitrogen

ABSTRACT

In a proof-of-concept study, an acidic (pH 5.8) biochar was created using a low pyrolysis temperature (350 °C) and steam activation (800 °C) to potentially improve the soil physicochemical status of an eroded calcareous soil. Biochar was added at 0%, 1%, 2%, and 10% (by wt.) and soils were destructively sampled at 1, 2, 3, 4, 5, and 6 month intervals. Soil was analyzed for gravimetric water content, pH, NO₃-N, plant-available Fe, Zn, Mn, Cu, and P, organic C, CO₂ respiration, and microbial enumeration via extractable DNA and 16S rRNA gene copies. Gravimetric soil water content increased with biochar application regardless of rate, as compared to the control. Soil pH decreased between 0.2 and 0.4 units, while plant-available Zn, Mn, and P increased with increasing biochar application rate. Micronutrient availability decreased over time likely due to insoluble mineral species precipitation. Increasing biochar application raised the soil organic C content and remained elevated over time. Increasing biochar application rate also increased respired CO₂, yet the CO₂ released decreased over time. Soil NO₃-N concentrations significantly decreased with increasing biochar application rate likely due to microbial immobilization or denitrification. Depending on application rate, biochar produced a 1.4 to 2.1-fold increase in soil DNA extracted and 1.4- to 2.4-fold increase in 16S rRNA gene abundance over control soils, suggesting microbial stimulation and a subsequent burst of activity upon biochar addition. Our results showed that there is promise in designing a biochar to improve the quality and water relations of eroded calcareous soils.

Published by Elsevier Ltd.

1. Introduction

Biochar is the carbonaceous solid byproduct from thermochemical conversion of carbon-based organic materials that commonly contain elevated cellulose, hemicelluloses, or lignin contents (Spokas et al., 2012). The thermochemical conversion process is known as pyrolysis and occurs when carbon-containing substances are introduced to elevated temperatures in the absence of oxygen at varying residence times, yielding biochar. Pyrolysis temperature may be varied to design a biochar with specific end-product characteristics (Novak et al., 2014).

In general, increasing pyrolysis temperature tends to increase biochar total nutrient content, specific surface area, and pH. Increasing pyrolysis temperature increases loss of easily decomposable substances (Munoz et al., 2003; Kloss et al., 2012), volatile compounds (Cantrell et al., 2012), and elements such as O, H, N, S and thus concentrates other nutrients (e.g., C, Ca, Mg, K) (Antal and Grønli, 2003; Kim et al., 2012; Kinney et al., 2012). However,

pyrolysis conducted at specific temperatures can favor the accumulation of certain nutrients in biochar. For example, total N content tends to be maximized between 300 and 400 °C due to the presence of heterocyclic N-containing compounds (Cantrell et al., 2012), while total P content decreases above 760 °C due to volatilization (Knicker, 2007).

Increasing pyrolysis temperature removes acidic functional groups and causes biochar to become more basic (Novak et al., 2009b; Li et al., 2002; Ahmad et al., 2012; Cantrell et al., 2012). In three biochars studied, Enders et al. (2012) showed that as pyrolysis temperature increased from 300 to 600 °C, biochar pH increased. In addition, greater pyrolysis temperatures promote minerals such as KOH, NaOH, MgCO₃, and CaCO₃ to separate from the solid organic matrix, resulting in elevated pH values (Cao and Harris, 2010; Knicker, 2007). Although this would create a biochar well suited for acidic soil conditions because the biochar may act as a liming source, elevated pyrolysis temperatures would not create biochars conducive for use under arid soil conditions. Aridic soils may, however, benefit from biochars with lower pH. Thus, an opportunity exists to develop biochars for the ~1 billion ha (Agrostats, 2009) of soils in arid and semi-arid climatic regimes globally.

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The inherent variability of biochars when used as a soil amendment suggests that the production of biochars can be designed for specific situations (Ippolito et al., 2012a). As an example, Novak et al. (2014) showed that nutrient enriched and nutrient poor feedstocks could be co-blended and pyrolyzed to produce a more nutrient-balanced biochar. In theory, this co-blended biochar can be used on soils without excessively adding plant-available nutrients. However, as outlined by Novak et al. (2014), the designer biochar concept is still in its infancy and requires further evaluation of designer biochar performance in other agricultural soils containing diverse fertility or physical characteristics.

To that end, we expanded the findings of Ippolito et al. (2012b) who suggested that a low pyrolysis temperature, low pH biochar could improve environmental quality by reducing nutrient losses in calcareous soils. Here, in a proof-of-concept study we designed a low pH, steam activated biochar for potentially improving the soil physicochemical status of an eroded calcareous soil in south-central Idaho. Topsoil in many locations of the area have been eroded due to ~100 years of flood irrigation, leaving the calcareous subsoil (pH 7.8–8.2; USDA-NRCS, 2001) exposed. Subsoil organic C content has been measured as about half of the soil surface (0.45% vs 0.94% organic C; Robbins et al., 2000) in this area of south-central Idaho. Lower organic matter content in eroded soils has been shown to significantly reduce available soil water content as compared to non-eroded soils (e.g., Frye et al., 1982). Thus, our hypotheses were that increasing application rates of an acidic pH biochar to an eroded calcareous soil will (1) improve the soil water status by reducing evaporative losses, (2) lower soil pH and (3) increase plant nutrient availability. In theory, an acidic pH designed biochar could neutralize excess soil OH⁻ groups and thus increase micronutrient concentration by increasing the dissolution of micronutrient carbonate mineral phases.

2. Materials and methods

2.1. Initial soil analysis, biochar analysis, and experimental setup

The experimental setup and design has been described elsewhere (Ducey et al., 2013). Briefly, subsoil was obtained near Kimberly, Idaho (42° 31' 07.50" N, 114° 22' 33.50" W), was classified from the Portneuf series (coarse-silty, mixed, superactive, mesic Durinodic Xeric Haplocalcid), and was part of an eroded soil experiment whereby the topsoil (0–30 cm) was removed (Robbins et al., 1997, 2000; Lentz et al., 2011). The top 30 cm of exposed subsoil was collected, air-dried, and passed through a 2-mm sieve. Initial soil analysis included pH (Thomas, 1996) and EC (Rhoades, 1996) using a 1:1 soil:deionized water extract, NO₃-N using a 2 M KCl extract (Mulvaney, 1996), and total C and N by dry combustion (Nelson and Sommers, 1996). Soil inorganic C was determined using a modified pressure–calimeter method (Sherrod et al., 2002) and organic C was determined by difference between total and inorganic C. The amount of CaCO₃ present in the soil was determined by converting inorganic C to CaCO₃. Soil total elemental concentrations were determined by HClO₄–HNO₃–HF–HCl digestion (Soltanpour et al., 1996) followed by analysis using inductively coupled plasma atomic emission spectrometry.

Biochar feedstock was full maturity switchgrass (*Panicum virgatum*), dried at 40 °C, and then hammer milled to pass a 6-mm sieve. Switchgrass was pyrolyzed at 350 °C under N₂ gas, then steam activated at 800 °C and allowed to cool down to room temperature; for more detailed information regarding biochar production see Ducey et al. (2013). Lower pyrolysis temperatures (e.g., 350 °C) helps retain acidic functional groups and lower ash contents, causing biochar to be more acidic (Ahmad et al., 2012; Cantrell et al., 2012; Enders et al., 2012; Novak et al., 2009b). Steam activation

can remove tar-like compounds with a subsequent increase in surface area (e.g., Borchard et al., 2012), and thus may lead to an increase in nutrient retention. Biochar surface area was determined by N₂ adsorption isotherms using the Brunauer, Emmett, and Teller (BET) equation (Brunauer et al., 1938), pH was determined in deionized water (1% w v⁻¹; Novak et al., 2009b), EC via a saturated paste extract (Rhoades, 1996), and total C and N, NO₃-N, and total elements as previously described. Soil and biochar physicochemical characteristics are presented in Table 1.

Switchgrass biochar was thoroughly mixed into soil (300 g), by hand, at 0%, 1%, 2%, or 10% (by wt.), and a completely randomized experimental design with four replicates was utilized; six sets of four replicates of each treatment were created for destructive sampling, described below. Although likely not conducive for use in production agricultural settings, the 10% biochar application rate was utilized in order to identify upper level benefits or detriments to the soil. Soil and biochar mixtures were placed in 8 cm × 8 cm × 8 cm plastic pots lined with a plastic liner to inhibit leaching. All pots were then placed in a constant temperature growth chamber (22 °C, 30% humidity) and watered twice weekly with reverse osmosis-treated water to bring all pots to 80% of field capacity (by wt.). Field capacity was determined prior to the experiment by using four of the plastic pots lined with cheesecloth and filled with 300 g soil only (no biochar), saturated, and allowed to freely drain for 48 h. Soil bulk density was also determined after mixing biochar into soils by filling a 100 mL graduated cylinder with the soil mixture, tapping the cylinder gently on a countertop, and topping off the cylinder with additional soil mixture. A soil–biochar-mixture weight per unit volume was then determined.

2.2. Destructive soil sampling

Pots were destructively sampled at 1, 2, 3, 4, 5, and 6 month intervals. At time of sampling, soils were analyzed for pH, and NO₃-N (as previously described), and for available Fe, Zn, Mn, and Cu using a diethylenetriaminepentaacetic acid (DTPA) extraction (Lindsay and Norvell, 1978). Substrate induced CO₂ respiration was determined by thoroughly mixing 50 g of moist soil, 0.5 g of glucose, 0.01 g of K₂HPO₄, and 0.075 g of NH₄Cl in a 100 mL mason jar, as described by Dungan et al. (2003). A vial containing 5 ml of 1 M NaOH was placed inside the jar and the jars were sealed. Following 24 h of incubation at room temperature the vials were removed, excess BaCl₂ was added to the NaOH, phenolphthalein indicator was added, and the NaOH was titrated to a clear endpoint with 1 M HCl; measurements were made in duplicate for all soils.

Table 1

Properties and total elemental analysis of the switchgrass biochar and Portneuf subsoil.

Property	Units	Switchgrass biochar	Portneuf subsoil
Surface area	m ² g ⁻¹	219	ND
pH		5.8	7.6
EC	dS m ⁻¹	0.70	0.77
Ash	%	5.86	ND
Total C	%	88.0	2.98
Inorganic C	%	ND ^a	2.02
Organic C	%	ND	0.96
CaCO ₃	%	ND	16.8
Total N	%	0.68	0.08
Organic N	%	0.68	0.08
NO ₃ -N	mg kg ⁻¹	2.6	18.1
P	mg kg ⁻¹	700	300
Fe	mg kg ⁻¹	100	7000
Zn	mg kg ⁻¹	10.3	28.0
Mn	mg kg ⁻¹	64.6	220
Cu	mg kg ⁻¹	3.4	4.83

^a ND = not determined.

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