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Effects of temperature and processing conditions on biochar chemical properties and their influence on soil C and N transformations

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ABSTRACT

There have been limited studies of how the pyrolysis process and activation conditions affect the chemical properties of biochar and how these properties alter soil carbon (C) and nitrogen (N) transformations when used as an amendment. This study compared the chemical properties of biochars produced through slow pyrolysis at 200, 400 and 600 °C, in the presence or absence of steam and CO_2 activation at 800 °C. Quantitative solid-state ^{13}C nuclear magnetic resonance spectroscopy and elemental analysis were used to evaluate processing condition effects on biochar chemical properties. Biochars were added at a rate of 0.75% by weight and soils were incubated for 28 d, during which soil inorganic N and CO_2 and N_2O emissions were determined. Thereafter, adsorption of ammonium (NH_4^+) and nitrate (NO_3^-) – N were investigated further. While constituents of biochar feedstock were not altered at pyrolysis temperature of 200 °C, NMR data showed that biochars produced at 400 and 600 °C converted >82% of labile C constituents to aromatic C structures, which increased their recalcitrance. Also the later pyrolysis temperatures increased biochar cation exchange capacity (CEC) and pH, however, exposure to steam and CO_2 activation decreased their CEC. Compared to unamended soil, amendment with biochar produced at 200 °C significantly increased cumulative CO_2 and N_2O emissions by more than 3 fold, whereas those produced at 400 °C had no effect on CO_2 emissions but had a similar effect on cumulative N_2O emissions. Biochar produced at 600 °C had no effect on either CO_2 or N_2O emissions. In contrast, activation of biochar significantly decreased cumulative CO_2 emissions by 18%. Amendment with biochars produced at 400 and 600 °C and activated biochars significantly decreased soil inorganic N, which was attributed to their increased adsorptive capacity for NH_4^+ by 62–81%. This study highlights the importance of production conditions for designing biochars for use as amendments to sequester soil C and N, by promoting the formation of stable soil organic matter and by increasing retention of soil inorganic N. From a soil amendment perspective, this study suggests that activation of biochar did not benefit soil C and N transformations.

1. Introduction

Biochar is the dark-colored, carbon (C) rich residue of pyrolysis of plant biomass under oxygen (O_2) limiting conditions, specifically produced for use as a soil amendement (Sohi, 2012). Benefits of biochar amendment to soil quality and the environment include increased storage of stable organic C (Lehmann, 2007; Woolf et al., 2010), reduced CO_2 and N_2O emissions (Ameloot et al., 2013) and enhanced soil inorganic N (NH_4^+ and NO_3^-) retention (Ding et al., 2010; Zhao et al., 2013b). There is increasing interest in using biochar and activated biochar as a soil amendment to adsorb NH_3/NH_4^+ (Taghizadeh-Toosi et al., 2011) as a mechanism to reduce N losses as N_2O emissions (Bruun et al., 2011) or through NH_3 volatilization (Sarkhot et al., 2012).

The chemical characteristics of biochars can be highly variable (Spokas, 2010) depending on the feedstock composition and the pyrolytic conditions under which the biochar is produced (Brewer et al., 2011; Zimmerman et al., 2011). For instance, biochars produced from switchgrass and corn stover have lower aromatic C contents but higher ash contents than those produced from woody materials (Brewer et al., 2011). Exposure of biochars to steam and CO_2 at temperatures >700 °C (Azargohar and Dalai, 2006) drives off

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volatile compounds and increases their surface area and porosity (Azargohar and Dalai, 2008). As a soil amendment, the later properties enhance biochar's capacity for adsorption and retention of nutrients and water (Ippolito et al., 2012; Hale et al., 2013; Sun and Lu, 2014).

Other critical parameters in biochar production are the highest pyrolysis temperature, the rate of temperature increase, and the duration of the heating period (Keiluweit et al., 2010). With increasing pyrolysis temperature constituents of the biomass are transformed (cellulose at 240–350 °C, hemicelluloses at 200–260 °C, and lignin at >280 °C) to aromatic C structures characteristic of biochars (Keiluweit et al., 2010; Wiedner et al., 2013), and this contributes to their stability in soils (Luo et al., 2011). In addition to aromatic C, biochars contain variable quantities of labile C, depending on highest pyrolysis temperature (Bruun et al., 2011; Ameloot et al., 2013), and this would affect CO_2 and N_2O emissions from biochar-amended soils (Scheer et al., 2011; Zheng et al., 2012). Because of the varying chemical properties of biochars and their interactions with soils, the mechanisms regulating biochar effects on the soil biological processes are not well understood (Lehmann et al., 2011).

Biochar effects on soil biological processes can influence soil N transformations. Studies have shown that amendment with biochar can accelerate soil inorganic N transformations by increasing net N mineralization (Nelissen et al., 2012), by increasing nitrification (Song et al., 2013), and by enhancing denitrification (Cayuela et al., 2013). These results can be explained by biochar increased mineralization of recalcitrant soil organic N (Nelissen et al., 2012), enhanced abundance of ammonia oxidizers (Song et al., 2013) and promotion of denitrification by transformation of electrons to soil denitrifying microbes (Cayuela et al., 2013). Other studies report no effect of biochar additions on soil inorganic N transformations (Schomberg et al., 2012; Cheng et al., 2012). Biochar has been shown to adsorb inorganic N (NH_4^+ and NO_3^-) in the leachates, depending on production temperature (adsorption of NO_3^- at >600 °C) and feedstock (Yao et al., 2012). Available information on activated biochar effects on the adsorption and desorption of NH_4^+ and NO_3^- compared with biochar in retention of soil inorganic N is lacking. Therefore, there is limited information on the effect of production conditions on the chemical properties of biochar and their effects on soil biological processes, i.e. N mineralization, nitrification, CO_2 and N_2O emissions.

The aim of the research was to evaluate how production method altered biochar's effect on soil C and N transformations when used as a soil amendment. The specific objectives of the study were (i) to evaluate the effects of pyrolysis temperature, 200, 400 and 600 °C, with and without steam and CO_2 activation at 800 °C, on biochar chemical properties, (ii) to determine effects of biochars on soil inorganic N transformations, (iii) to determine effects of biochars on soil CO_2 and N_2O emissions, and (iv) to determine the sorption-desorption potential of biochars for soil inorganic N (NH_4^+ and NO_3^-). We hypothesized that: (i) increasing pyrolysis temperature during biochar production would decrease subsequent soil CO_2 and N_2O emissions, and (ii) activation of biochar, by increasing it's capacity for inorganic N adsorption, would alter transformations of soil N.

2. Materials and methods

2.1. Soil

Soil for this study was collected from the topsoil layer (0–15 cm) of an experimental plot, which has been managed in a corn (*Zea* mays L.)-soybean (*Glycine max* L.)-winter wheat (*Triticum aestivum* L.) rotation, located at the Elora Research Station (43°39′ N, 80°35′ W), University of Guelph, Ontario, Canada. The soil is a silt loam (27% sand, 56% silt and 17% clay) classified as a Gray Brown Luvisol belonging to the London Series (Hoffman et al., 1963). The soil has a pH of 7.5 and contains 2.8% total C, 0.2% total N, 13.1 mg kg^{-1} NO_3^- and 2.6 mg kg^{-1} exchangeable NH_4^+. The soil has a cation exchange capacity (CEC) of 25.0 cmol kg^{-1} and contains 0.1 mg g^{-1} potassium (K), 4.0 mg g^{-1} calcium (Ca), 0.4 mg g^{-1} magnesium (Mg), and 0.02 mg g^{-1} phosphorus (P). Soil pH was determined in a 1:2.5 (w/v) ratio of air dried soil to deionized water. Soil total C and N were determined by a dry combustion method using a LECO TruSpec microanalyzer (Agri-Food Laboratories, Guelph, ON, Canada). Inorganic N (NH_4^+, NO_3^-) was extracted with 0.5 M K_2SO_4 (soil weight: extract volume ratio 1:5) and determined by colorimetric methods (Kamphake et al., 1967; Krom, 1980; Kempers and Luft, 1988) using an Autoanalyzer (Technicon AutoAnalyzer II, U.S.A). Soil CEC was determined by ammonium acetate (pH 7.0) and using a method described by Hendershot et al. (2007). Soil nutrients including K, Ca, Mg, and P were extracted by 0.1 mol L^{-1} $BaCl_2$ (1:60, w/v) and determined using an ICP-OES optical spectrometer (Agri-Food Laboratories, Guelph, ON, Canada). The field soil samples were passed through a 2-mm sieve, air-dried and stored at ambient temperature prior to the incubation experiment.

2.2. Biochar and activated biochar production

Biochar and activated biochar was produced by a slow pyrolysis treatment of hardwood (oak [*Quercus*])-based wood pellets followed by a steam and CO_2 activation process. The activation treatment was used to produce a biochar with greater surface area and porosity (Alaya et al., 2000; Yang and Lua, 2003).

Prior to the biochar production, the woody material were dried at 60 °C for 12 h to reduce the moisture content, ground and sieved to <2 mm to minimize temperature gradients in the material during the pyrolytic process.

Slow pyrolysis and the activation were performed in a muffle furnace (Thermolyne) in which a stainless-steel reactor core (length 15 cm, diameter 4 cm) was placed to contain ground woody material (~55 g). The muffle furnace was equipped with a vent (3.2 cm diameter) to allow purging with nitrogen (N_2) gas to remove O_2. Pure N_2 (99.995%) gas was flushed through the muffle furnace at a rate of 150 mL min^{-1}, 30 min prior to heating, during the slow pyrolysis, and as the biochar cooled to room temperature overnight.

The pyrolysis parameters including temperature, heating rate and dwell time were set using the programmable controller associated with the muffle furnace.

Table 1
Effects of temperature and activation conditions on chemical properties of biochars. All analyses were determined in triplicate.

Property	Woody material	BC 200	BC 400	BC 600	ActBC 200	ActBC 400	ActBC 600
Total C (%)	48.5	48.8	42.7	45.5	30.6	30.3	37.1
Total N (%)	0.2	0.2	0.3	0.4	0.5	0.5	0.4
C:N ratio	242.5	256.8	129.5	111.0	66.5	65.8	88.4
pH	7.2	4.6	6.9	9.5	9.6	9.6	9.6
CEC (cmol kg^{-1})[a]	nd[b]	54.2	61.1	97.0	33.7	36.2	42.6
Phosphorus (mg g^{-1})	0.3	0.3	0.6	0.6	0.8	0.8	0.8
Potassium (mg g^{-1})	1.3	1.3	3.8	4.4	5.9	5.9	6.2
Calcium (mg g^{-1})	3.9	3.9	11.8	13.9	17.3	17.3	20.2
Magnesium (mg g^{-1})	0.4	0.4	1.5	1.8	2.2	2.2	2.5
Sodium (mg g^{-1})	0.2	0.2	0.4	0.5	0.6	0.6	0.7

BC200, 400 and 600: Wood biochar was produced at 200, 400 and 600 °C, respectively.
ActBC200, 400 and 600: Wood biochar (200, 400 and 600 °C) was activated by steam and CO_2 at 800 °C.
[a] CEC: Cation exchange capacity.
[b] nd: Not determined.