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Chars produced by slow pyrolysis and hydrothermal carbonization vary in carbon sequestration potential and greenhouse gases emissions

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ABSTRACT

Bio-char, biomass that has been deliberately charred to slow its rate of decomposition, has been proposed as an amendment with the potential to sequester carbon and improve certain soil properties. Slow pyrolysis (temperature ≤ 500 °C) and hydrothermal carbonization (low temperature, high pressure) are two efficient methods to produce bio-char with high yield and are applicable to a broad range of feedstocks. Chars made using slow pyrolysis (PC) and hydrothermal carbonization (HTC) of the same feedstock material (corn, C4) differed in physical appearance, chemical properties and decomposition behavior. We added these HTC and PC chars as amendments to three soils with C3-derived organic matter that differed in clay content, pH, and land use (managed spruce forest, unmanaged deciduous forest and agriculture), and compared their impacts on carbon sequestration and net greenhouse gas (CO_2, $^{13}CO_2$, N_2O and CH_4) emissions. HTC addition (1% w/w) significantly increased CO_2 emissions in all three soils ($p < 0.001$), with much of the extra C derived from HTC decomposition. In contrast, PC addition (1% w/w) had almost no impact on deciduous forest soil and actually decreased CO_2 emission from the agricultural soil. HTC treatment resulted in increased CH_4 emission from all soils but reduced N_2O fluxes in the agricultural and spruce forest soils. PC amendment had no significant effect on CH_4 emission, and resulted in intermediate levels of N_2O emission (between control and HTC treatments). Although both HTC and PC chars were produced from the same feedstock, PC had markedly higher potential for carbon sequestration than HTC.

1. Introduction

The annual growth rate of atmospheric CO_2 was 1.9 ppm in the past decade (2000–2009), reflecting a continuing, large, imbalance between carbon (C) release to the atmosphere and removal by natural sinks (Peters et al., 2012). One proposed mitigation strategy is to enhance land C sinks by removing C from the atmosphere and storing it in a form that is stable over a long period of time. Soils provide a large global reservoir of C stabilized for decades to centuries (Schmidt et al., 2011) and therefore practices that increase soil C storage have received much attention. Recent attention has been to add charred biomass (bio-char), which has been demonstrated to persist in tropical 'anthroposols' for up to thousands of years, in order to store C in soils (Lehmann, 2007). Bio-char, resulting from pyrolysis of biomass that enriches overall carbon content and slows degradation, has been proposed as an amendment that can potentially sequester carbon and improve certain soil properties such as soil fertility (Sohi et al., 2010).

The concept of bio-char amendment was derived from the study of Amazonian dark earth soils, also known as anthroposols. These soils were managed by indigenous people living in the Amazon basin between 600 and 8700 years ago (Grossman et al., 2010), and are characterized by higher C content and greater microbial diversity compared to unamended adjacent soils with similar mineralogy (Grossman et al., 2010; Navarrete et al., 2010; O'Neill et al., 2009). The soils are also characterized by the presence of charred particles, suggesting that char lasts hundreds to thousands of years at these sites. Thus amendment with bio-char is widely hypothesized to increase carbon storage capacity, although this effect is largely unquantified and depends on many factors (Liang et al., 2010). One such factor is the method used for bio-char production. Large differences in the composition of bio-char produced using different methods can result in timescales for persistence in soils, ranging from millennia (Forbes et al., 2006; Liang et al., 2008) to decades (Steinbeiss et al., 2009).

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Two thermal degradation processes, in the presence and absence of water, are most commonly used to carbonize biomass. Both methods efficiently produce large amounts of char, have high rates of carbon recovery, and can be applied to a broad range of feedstock. These properties make them optimal from a soil amendment point of view (Fuertes et al., 2010; Titirici et al., 2007).

The most efficient process for char production under dry conditions is slow pyrolysis. This method derives from methods for charcoal production used by mankind for millennia (Ogawa and Okimori, 2010). Slow pyrolysis uses moderate heating rates over a long period of time, and ultimately leads to 30–45% C yield as bio-char (Bruun et al., 2012). However, this process is not suitable for carbonization of most agricultural wastes due to the requirement for drying of the feedstock prior to and/or during the reaction.

In contrast, hydrothermal carbonization (HTC) makes use of a range of unconventional biomass feedstocks, such as sewage sludge, animal wastes and compost (Titirici et al., 2007), without the need for drying prior to char production. Although HTC was discovered in the early 20th century during studies of natural coal formation, to date there are only a few studies about its potential use for C sequestration (Funke and Ziegler, 2010; Rillig et al., 2010; Schimmelpfennig and Glaser, 2012). In hydrothermal char production processes, the wet biomass mixture is heated to temperatures of up to 220–240 °C in a high-pressure reactor. Steam pressures reach up to 20 bar, and very little gas (1–5%) is generated, so that most organics remain either in dissolved form or transform into brown coal (Libra et al., 2010). Various carbonaceous materials with different sizes, shapes, and surface functional groups are synthesized during HTC but a large proportion of the initial carbon (40–54%) remains in soluble form (Hu et al., 2010). Among the advantages of the HTC process is the use of non-traditional feedstock that could provide a continuous feedstock stream for this process and less carbon losses during the char generations.

The net greenhouse gas effects of char amendment depend not only on the potential to sequester atmospheric CO_2, but also the changes in the overall consumption or emission of methane and nitrous oxide. Biophysical processes responsible for CH_4 and N_2O emissions from soils are considerably altered with incorporation of biomass, fertilizer or bio-char into soils. A large proportion of published literature agrees that pyrolysis char suppress N_2O emissions from soil majorly due to its effect on soil moisture, soil aeration and NO_3^- runoff/leaching (Kammann et al., 2012; Taghizadeh-Toosi et al., 2011; van Zwieten et al., 2010). The only reported results about HTC char showed initial decrease in N_2O emissions but this effect was not observed on later stages of field experiment (Kammann et al., 2012) In contrast, the reported impacts of pyrolysis char on CH_4 fluxes are inconsistent, with positive (Feng et al., 2012; Yu et al., 2012), negative (Spokas and Reicosky, 2009; Zhang et al., 2010), or neutral influence on emissions (Kammann et al., 2012; Yoo and Kang, 2012). These effects were highly moisture dependent, and a full explanation of the impact of HTC on CH_4 fluxes is lacking.

Chars made from slow pyrolysis and HTC differ in physical appearance and chemical properties (Fuertes et al., 2010). The objective of this study was to evaluate the overall greenhouse effect of amendment with the two types of char by continuous monitoring of trace gases emissions from three different soils. The two chars used were produced from the same corn-based feedstock. We used differences in the natural abundance of $\delta^{13}C$ to track bio-char carbon (reflecting C4 origin of corn) from the organic matter in the amended soil, which reflected a pure C3 origin. In addition to CO_2, we monitored the effect of soil amendment on the production of CH_4 and N_2O. To our knowledge, this is the first study to compare the net greenhouse gas effect of soil amendment with slow pyrolysis and HTC chars.

2. Materials and methods

2.1. Soil sampling and characterization

Two forests soils (Cambisols) and one agricultural soil were collected from three different locations within the Thüringen state in Germany: a deciduous forest (DF) within the Hainich National Park; a spruce forest (SF) near Ölknitz village; and an agricultural soil (AG) from research plots located near the Max-Planck Research Institute for Biogeochemistry in the city of Jena. Together, these soils span a broad range of vegetation types and soil properties, including soil texture, which ranged from clay loam (DF) to sandy loam (AG). At each site 5–6 subsamples of the upper 15 cm of mineral soil were collected. The SF and AG soils were processed at field moisture. The DF soil was very wet when sampled, and was dried at room temperature to 20% of gravitational moisture content prior to processing. Soils were first passed through a 4 mm mesh size sieve to remove all plant material and large roots. Samples were then homogenized to produce a single, composite sample and stored at 4 °C prior to incubation. Sub-samples of the homogenized soils were dried at 40 °C for physical and chemical analyses.

Soil water holding capacity was measured by the volumetric method using char free soils (Livingston and Topp, 2007). Soil carbon and nitrogen concentrations were measured from ball-milled sub-samples by elemental analysis ("Vario Max", Elementar Analysensysteme GmbH, Hanau) before and after incubation. Organic carbon concentration was determined by calculating the difference between elemental analyses of the total carbon concentration and soil inorganic carbon concentration (Steinbeiss et al., 2008). Soil mineral N (NO_3^- and NH_4^+), dissolved organic carbon (DOC) and soil microbial biomass were determined by extraction before and after incubation (Karsten et al., 2007). For DOC analysis, 10 g of moist soil sample was suspended in 50 mL 0.05 M K_2SO_4 and shaken on a low speed reciprocal shaker for 1 h. Supernatant was filtered and analyzed ("high TOC" Elementar Analysensysteme GmbH, Hanau). Soil microbial biomass was determined by chloroform fumigation-extraction (Brookers et al., 2007). Unless otherwise stated, all measurements and are reported as the mean and standard variation of triplicate analyses.

The $\delta^{13}C$ of soil organic carbon was measured by a coupling an elemental analyzer to an isotope ratio mass spectrometer ("Bianca" Delta^{Plus}XL). Values are reported as $\delta^{13}C$ in per mill (‰) calibrated relative to the VPDB reference standard using NBS19 (Werner and Brand, 2001), and represent repeated measurements with a standard deviation of less than 0.3‰.

2.2. Bio-char production and characterization

Slow pyrolysis char (henceforth pyro-char, or PC) was produced from corn silage that was air dried (70 °C) and ground to less than 4 mm. The ground silage was sealed in aluminum foil to avoid aeration, with a small hole on one side of the foil to let gaseous products out. Samples were heated from room temperature to 500 °C at a rate of 10 °C per min and held at 500 °C for 2 h. After cooling, the resulting PC was passed through a 2 mm sieve and stored at 4 °C until the incubation experiment.

Hydro-char (HTC) from the same corn silage was obtained commercially from the carbon solutions Company Ltd, Kleinmachnow Germany. The delivered material was slurry (10% solids). Before we used it as an amendment, this slurry was freeze-dried at −50 °C and the resulting solid material was passed through a 2 mm sieve.

Elemental concentrations of C, N, and H in both types of char were measured from ball-milled subsamples using an elemental analyzer (VarioMax Elementar Analysensysteme GmbH, Hanau).