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Stability of pyrochar and hydrochar in agricultural soil - a new field incubation method

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ABSTRACT

The application of chars on soil offers an option to sequester carbon (C) and to improve soil fertility. Different types of chars are available as soil amendments, produced with mainly two different processes: pyrochar produced with pyrolysis and hydrochar produced with hydrothermal carbonization. However, there are few studies to assess the stability of these two char types in soils *in situ* at field sites. A 19-month *in-situ* field incubation was conducted in northern Germany. With a mini-plot method we were able to assess the decomposition dynamic of chars with few operational costs. Zinc was used as inert tracer mixed with the char in order to account mixing so that char losses could be accurately quantified. We used chars from *Miscanthus* (C4-plant) as feedstock with a higher δ13C value than the C3 plant derived soil C. Changes in δ13C value allowed the calculations of char-derived C in the soil at three sampling dates. While C derived from pyrochar did not change significantly over time, 23–30% of initial added hydrochar-C was mineralized after 19 months *in-situ* field incubation. There was no difference in the decomposition dynamics of the chars among the three field sites with different soil types. Moreover, we did not observe a decline in decomposition rates with time. For hydrochar the data were well fitted with a linear one-pool decay model. The average model derived mean residence times were 4 (95% confidence interval: 3–14) years for hydrochar and 60 (95% confidence interval: 16–224) years for pyrochar. Thus, while pyrochar has a higher potential for C-sequestration, faster mineralization of hydrochar compared to pyrochar showed their potential to act as a mid-term fertilizer through slow nutrient release to soils. Advantages of the Zinc method were the low price for application and analysis as well as the ability for farmers to manage their field in the course of their normal activities. However, variability in results gained from the Zinc method is not insignificant which mostly affect the calculated MRTs.

1. Introduction

Intensive land use and current agricultural practices have led to degradation of soil and to decreasing content of soil organic matter (SOM) (Lal, 2001; Lal, 2004; Lal and Bruce, 1999; Xue et al., 2015). New technologies are required to capture atmospheric C and store it in stabilized form in soil, in order to counteract the increased accumulation of C as CO_2 in the atmosphere and soil C losses. In the past ten years, long-term storage of atmospheric C in the soil to mitigate global warming has gained increasing attention. Application of carbonized biomass to agricultural soils could be an option to mitigate climate change, by fixing atmospheric C. Besides the ability to sequester soil C, several additional benefits are provided by biochar when it is mixed into agricultural soils. These include: increasing crop yield due to retention of plant-available nutrients in the rhizosphere (Lehmann and Joseph, 2009) as a result of increased soil pH and soil cation exchange capacity (CEC) (Liang et al., 2006); enhanced soil water-holding capacity (Glaser et al., 2002; Abel et al., 2013); decreasing greenhouse gas emissions of nitrous oxide (N_2O) and methane (CH_4) (Cayuela et al., 2013; Cayuela et al., 2014; Kammann et al., 2012; Spokas et al., 2009); and immobilization of toxic compounds such as heavy metals (Chen and Yuan, 2011). Up to 75% of carbon in crop residues, such as maize stovers, can be mineralized within one year, e.g. the mean residence time (MRT) for maize-C in soil ranges from 5 to 7 years (Ajwa and Tabatabai, 1994; Li et al., 2016). In contrast, amending soil with biochar has the advantage that it is much more recalcitrant to mineralization than its original feedstock.

Biochar is the solid charcoal product produced from thermal transformation under anaerobic conditions (pyrolysis) of biomass, such as wood and other agricultural or forestry residues, digestates and sewage sludge, which is intended to act as a soil conditioner and/or a C storage medium (Hale et al., 2013; Lehmann and Joseph, 2009). In this study, two processes were used for the production of char intended for use in agricultural systems: i) Slow pyrolysis, which involves carbonization of biomass at processing temperatures of above 300 °C under oxygen-free conditions with a process duration of hours to days (Bridgwater, 2012); and ii) hydrothermal carbonization (HTC), which is a low-temperature transformation process (temperatures between 180 and

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300 °C) performed in the presence of water and high pressure (2.0–2.5 MPa) for several hours (Funke and Ziegler, 2010; Libra et al., 2011; Wiedner et al., 2013a; Yu et al., 2004). In the following, we refer to the solid product derived from pyrolysis as 'pyrochar' and to the solid product derived from HTC as 'hydrochar'. Pyrochar is characterized by high recalcitrance to degradation or mineralization (Glaser et al., 2002) and a high degree of aromaticity (Keiluweit et al., 2010; Lehmann et al., 2006). Hydrochar has recently been receiving increasing attention since the wet feedstock can be carbonized without pretreatment by drying (Funke and Ziegler, 2010). The main characteristics of hydrochar are lower specific surface area (SSA) compared with pyrochar (Eibisch et al., 2013; Titirici et al., 2008) and a lower degree of carbonization, and thus less aromatic carbon (C), compared with pyrochar. Furthermore, hydrochar has a higher H:C and O:C ratio, which means that it has higher amounts of plant-derived surface functional groups on chars' surface (Schimmelpfennig and Glaser, 2012).

As agricultural soil amendment, char degradation maybe more relevant than C sequestration, because nutrients incorporated into char can be released (Abiven et al., 2011). Thus, depending on the specific use, there is competition between the stability and functionality of char. The more stable the char, the lower its functionality due to the smaller number of functional groups on particle surfaces (Schimmelpfennig and Glaser, 2012). However, in order to evaluate the potential of different chars as an agricultural amendment and as an option to mitigate climate change, it is necessary to know their stability once they are applied to soils.

Laboratory incubation studies suggest high resistance of pyrochar to mineralization (Bamminger et al., 2014; Gajić et al., 2012; Kuzyakov et al., 2014; Lu et al., 2014). It is generally agreed that most chars can be mineralized, but the mineralization rate differs depending on environmental conditions (Zhao et al., 2015) and the quality of the char. However, most studies on the stability of char are conducted as incubation studies in the laboratory, with limited transferability to *in situ* soil conditions. Moreover, environmental factors affecting char mineralization in laboratory studies are not comparable to those in field conditions. MRTs estimated from incubation studies show slow char-C mineralization and lifetimes of millennia (Bamminger et al., 2014; Fang et al., 2014; Gajić et al., 2012; Kuzyakov et al., 2014), whereas MRTs derived from field experiments show shorter lifetimes of decades to centuries (Jones et al., 2012; Malghani et al., 2014). No previous study has conducted a systematic comparison of the recalcitrance of pyrochars and hydrochars from the same feedstock in field experiments. Moreover, most of the field studies conducted to date to investigate decomposition have used small plots, which are often defined by rings or frames where soil tillage is not possible. We therefore developed a new field incubation method (mini-plot approach) to examine the mineralization of different char types in arable soils under regular tillage and where crops are grown under common agricultural practices. In this study, the mini-plot approach was used to assess the stability of two char types under field conditions.

2. Materials and Methods

2.1. Production of pyrochar and hydrochar

The feedstock for both hydrochar and pyrochar was chopped aboveground biomass of the C4-plant *Miscanthus x giganteus*. Pyrochar was carbonized in a Pyreg reactor (Wiedner et al., 2013b)(PYREG GmbH, Dörth, Germany) at 750 °C for 0.75 h. Hydrochar was produced with water (1 kg dry weight (dw) *Miscanthus* to 10 kg water) in a tabular reactor (3 m^3) at 200 °C and 2 MPa for 11 h by AddLogicLabs GmbH/SmartCarbon AG (Jettingen, Germany). To catalyze the dehydration process in order to increase C content in the solid product, citric acid powder was added to the *Miscanthus* (0.03 kg citric acid/kg dw *Miscanthus*) (Wang et al., 2010). Both chars were dried at 40 °C and sieved at <2 mm. The C and N content were determined by dry combustion (TruSpec, LECO Corp., St. Joseph, USA). The oxygen and hydrogen content of chars and the feedstock were determined with an elemental analyzer (Vario EL3, Elementar, Hanau, Germany) and the zinc content was analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES; Varian Liberty 150, Agilent, Palo Alto, USA). The pH value of the chars was determined in 0.01 M $CaCl_2$ with a volume ratio of 1:5 (char:solution). Basic characteristics of the feedstock, pyrochar and hydrochar are presented in Table 1.

2.2. Experimental design for in situ field ageing

Three arable sites in the North German lowlands (mean annual temperature 8.8 °C, mean annual precipitation around 600 mm) were chosen to incubate the chars *in situ*. These three sites, located in Bortfeld (siltic Cambisol), Volkmarsdorf (cambic Planosol) and Querenhorst (arenic Planosol), differ mainly in their soil texture (Table 2). All sites were managed according to common regional agricultural practices, such as conventional tillage (mouldboard ploughing and/or chisel ploughing) to a depth of around 25–27 cm and inorganic fertilization (potassium nitrate and/or ammonium nitrate). The C3-crops grown at the sites were: i) barley (2012), winter wheat (cover crop), sugar beet (2013) (Querenhorst); ii) barley (2012), mustard (cover crop), sugar beet (2013) (Volkmarsdorf); and iii) potatoes (2012), sugar beet (2013) (Bortfeld).

A randomized block design was used at three sites. In March 2013, the two different types of char were mixed into the soil in triplicate mini-plots (70 cm × 70 cm) in blocks at each site, so that every site had nine mini-plots: three amended with pyrochar (soil + pyrochar + zinc), three with hydrochar (soil + hydrochar + zinc) and three as a control (soil + zinc). The distance between mini-plots within blocks was 200 cm. In each mini-plot, soil was excavated to a depth of 25 cm and placed in a cement mixer with 3.9 kg hydrochar (dw) or 3 kg pyrochar (dw) in order to achieve thorough mixing. The char amendment rate was designed to double the soil C content and corresponded to 50 Mg char-C ha^{-1}(62 Mg pyrochar ha^{-1} (82% C content) and 79 Mg hydrochar ha^{-1} (64% C content)). Elemental zinc powder (particle size <45 μm; Merck, Darmstadt, Germany) was added to the soil or soil-char mixture at a concentration of 450 mg kg^{-1} soil as an inert tracer. This increased the natural zinc concentration in the soil seven-fold, from a background concentration of about 50 mg Zn kg^{-1} soil to a final concentration of around 500 mg Zn kg^{-1} soil. This was done to allow correction for blending or attenuation with the surrounding soil after the mixture was returned to the mini-plot, e.g. due to tillage, as the mini-plots were not physically separated from the field site and thus mixing with the surrounding soil was possible. The centre of each plot was marked by inserting a metal bar (5 cm × 1 cm) to below the plough horizon, i.e. to a depth of 35–40 cm, to make a precise relocation easier. In addition, the centre point of each plot was georeferenced by GPS. The advantage of the mini-plots was that the farmers could manage the field sites with the research plots in the same way as their other fields. Soil samples were taken in March 2013, immediately after mixing of soil with char (designated T_0), and again after seven months (October 2013; designated T_1) and after 19 months (October 2014; designated T_2). On all sampling occasions, five randomly distributed soil cores of depth 25 cm were taken with a split-tube sampler (5 cm diameter) from each plot. At T_0, an additional six randomly distributed soil samples were taken to determine the original zinc concentration for each experimental field site (designated Zn_0). All samples were dried at 40 °C and sieved to ≤2 mm and a subsample was finely ground for further analysis. Zinc concentration (T_0, T_1, T_2) was determined after extraction by microwave *aqua regia* digestion using ICP-OES (Varian 725-ES, Agilent, Palo Alto, USA).

2.3. Correction of C stocks with the mini-plot approach

Char mineralization was calculated by changes in SOC content and its isotopic values. A C stock correction was applied in order to account