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The stability of low- and high-ash biochars in acidic soils of contrasting mineralogy

James Murray, Alexandra Keith, Balwant Singh*

Faculty of Agriculture and Environment, The University of Sydney, Sydney, NSW 2006, Australia

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ABSTRACT

The potential of biochar as a tool for long-term soil carbon (C) storage has led to an increasing interest in its use as a soil amendment. While much research has been conducted on the stability of high C and low ash biochars, the stability of low C (with relatively high inorganic C) and high ash biochars has been largely neglected. In light of this, an incubation experiment was conducted to compare and assess the stability of a high ash and low C biochar produced from tomato green waste and low ash and high C biochar produced from blue mallee biomass. The two biochars were applied at 2% and 4% (w/w) to two acidic soils of contrasting mineralogy, a Ferralsol and a Solonetz. The soil–biochar mixtures were incubated at 20 °C for 120 days. The CO_2–C mineralised was captured in NaOH traps and the source of C mineralisation determined by isotope analysis. The tomato biochar was mineralised (1.4–3.7%) to a greater extent than the blue mallee biochar (0.28–0.77%), possibly due to dissolution of the large quantity of inorganic C. In biochar amended soils, with the exception of the Solonetz applied with 2% blue mallee biochar, greater cumulative mineralisation (positive priming) of native SOC occurred as compared to their respective controls. Mean residence time for the two biochars suggests much greater potential of the blue mallee biochar for long-term soil C storage than the tomato biochar. However, the tomato biochar may have greater agronomic value, in particular a high liming potential, although field studies are required to confirm these results.

1. Introduction

In the last two decades, there has been a substantial research interest in the use of biochar technology for long-term carbon (C) storage in soil and for other environmental applications. Due to its high C content and the recalcitrant nature of C, biochar offers large climate-change mitigation potential (Glaser et al., 2002; Lehmann et al., 2006). In addition to long-term C storage, biochars may provide other favourable services in soils such as, increased nutrient storage and availability, improved soil structure, increased water holding capacity, acidity amelioration and decreased availability of inorganic and organic contaminants in soils (Chan et al., 2008; Atkinson et al., 2010; Namgay et al., 2010; Singh et al., 2010; Sohi et al., 2010; Devereux et al., 2013).

Biochar can be defined as the solid product resulting from the heating of organic residues under oxygen limited conditions. It is primarily produced with the intention of being applied to soil (Lehmann and Joseph, 2009). A large portion of the C in biochar is highly recalcitrant with a very long mean residence time (MRT). However, a small proportion of biochar C has been shown to mineralise in laboratory incubation studies, particularly during the initial stages (e.g. in the first few days to weeks) (Cheng et al., 2006, 2008; Zimmerman, 2010; Singh et al., 2012; LeCroy et al., 2013; Fang et al., 2014a). The stability of biochar in soils depends on several factors including properties of the biochar and soil, and the environmental conditions. The pyrolysis process used for biochar production converts other C in original organic matter into more complex and stable structures such as high molecular weight aliphatics and aromatic C (Paris et al., 2005; Keiluweit et al., 2010; Singh et al., 2014) through dehydration, decarbonylation and decarboxylation reactions (Schmidt and Noack, 2000; Cheng et al., 2006; Nguyen et al., 2010). These structures, and in particular aromatic structures, provide high intrinsic stability to biochar C and thus mineralisation occurs more slowly than in the soluble and low molecular weight organics in the original biomass (Brewer et al., 2012). The proportions of amphorous aromatic C (i.e. randomly

* Corresponding author. Tel.: +61 2 8627 1140.
E-mail addresses: james@bcg.org.au (J. Murray), alexandra.keith@sydney.edu.au (A. Keith), balwant.singh@sydney.edu.au (B. Singh).

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organised aromatic rings) and crystalline aromatic C (i.e. turbostatically aligned condensed polyaromatic sheets) are considered to govern the overall stability of biochar C in soils (Keiluweit et al., 2010; Singh et al., 2012; Wiedemeier et al., 2015). Biochars produced from wood generally contain a larger proportion of aromatic C and greater degree of aromatic condensation whereas biochars produced from organic litter and manure contain lesser amounts of aromatic C (Zimmerman, 2010; Enders et al., 2012; Singh et al., 2012; Wiedemeier et al., 2015).

Soil properties, in particular the C content and clay mineralogy, also influence the stability of biochar. Biochar has displayed lower mineralisation levels when applied to soils with low native organic C content compared to organic C rich soils (Kimetu and Lehmann, 2010). Research on biochar stability in soils of varying clay contents and clay minerals has suggested that clay mineralogy is integral in the level of biochar C mineralisation (Fang et al., 2014a, 2014b, 2015). The stabilisation of biochar through organo-mineral interactions, particularly involving Fe and Al oxides, is a major factor in reducing the rate of biochar C mineralisation.

Biochar addition to soil also affects the mineralisation of native soil organic C (SOC), what is known as the 'priming effect' (PE). The majority of research on biochar C stability and its PE have focussed on biochars produced from wood or grasses with high C and low ash contents. Conversely, the stability of low C and high ash biochars and their PE have remained poorly understood. Additionally, little attention has been drawn to the stability of the inorganic C present in these types of biochars. It is important to rectify this, as biochar is produced from a wide range of feedstocks and the stability of C in these biochars must be determined to assess their true C storage potential in soils. While the long-term stability of biochar C is a major determinant for the potential use of biochar as a C sequestration tool, any associated PE of biochar C on SOC should also be considered. The complex interactions between biochar, soil organic matter and soil biota produce PE responses. Published studies have shown both positive (increased mineralisation) and negative (decreased mineralisation) PE of biochar on native SOC, with the time frame of the experiments being a major impact on the results (Keith et al., 2011; Zimmerman et al., 2011; Fang et al., 2014a, 2014b). The initial positive priming found in these studies is generally considered due to the co-metabolism of the labile fraction of C in biochars (Keith et al., 2011). After the depletion of the labile C fraction of the biochar, the remaining highly recalcitrant C produced a negative PE at later stages of the incubation experiment. Negative priming of biochar has also been attributed to changes in biochar properties with ageing. For instance, the surface of biochar particles develops negative charge through oxidation reactions that leads to increased sorption of soil organic matter to biochar particles (Bailey et al., 2011; Lin et al., 2012).

The contrasting reports on the PE of biochar on native SOC from past studies have resulted in much conjecture surrounding the PE of biochar C on native SOC. The high ash and low C biochars may have significant effects on soil properties (e.g. addition of nutrients or liming effect), which may result in increased microbial activity or positive priming on native SOC in biochar amended soils. It is therefore important to quantify the stability of biochar C and any associated PE of both low and high ash biochars before a sustainable and viable agricultural management plan incorporating biochar can be implemented.

The aim of our study was to compare the stability of a high ash and low C biochar, and a low ash and high C biochar in two acidic soils with differing clay mineralogy in an incubation experiment. We hypothesised that (i) the high ash-low C biochar would mineralise more rapidly than the low ash-high C biochar and; (ii) the Fe and Al oxides dominated soil would provide greater stabilisation to biochar C compared to the phyllosilicates dominated soil.

2. Materials and methods

2.1. Biochar and soil

Biochar was produced from two different feedstocks: tomato green waste comprising leaf and stem material, and blue mallee (*Eucalyptus polybractea*) consisting of woody material that had been used for eucalyptus oil production. The tomato biochar was produced by slow pyrolysis with a maximum heating temperature of 550 °C using the Daisy Reactor at Pacific Pyrolysis, Somersby, Australia. The blue mallee biochar was made by slow pyrolysis with a maximum heating temperature of approximately 500 °C in a batch pyrolysis unit at Biochar Energy Systems Pty. Ltd., Bendigo, Australia. The two biochars were oven dried at 105 °C for 24 h and ground to <2 mm for the incubation experiment and laboratory analyses.

Two acidic soils, a Ferralsol (from Wollongbar, NSW, Australia, 28.816627 °S, 153.39827 °E) and a Solonetz (from Ingham, Queensland, Australia, 18.592655 °S, 146.01427 °E), were collected from 0 to 15 cm depth for use in the incubation experiment. The areas from which the two soil samples were collected were dominated by C4 vegetation. The soils were selected based on their significantly different $\delta^{13}C$ isotopic signals compared to that of the biochars and their contrasting clay mineralogy. The soils were air dried and ground to <2 mm for the incubation experiment.

2.2. Biochar and soil characterisation

Total C, N and H contents were analysed using a Truspec CHN Leco analyser as well as a vario MAX CNS elemental analyser for greater accuracy of C and N contents. Additionally, the inorganic C content of the biochars were ascertained by treating biochar samples with 2 M HCl to dissolve carbonates before analysis of the total C using a vario MAX CNS elemental analyser (Midwood and Boutton, 1998). The electrical conductivity (EC) and pH of soil and biochar samples were analysed at the start and conclusion of the experiment in mixtures of 1:5 soil/biochar and water after shaking for 30 min. The $\delta^{13}C$ analysis of the fresh soil and biochar was measured using Isotope Ratio Mass Spectrometer (IRMS; Delta V Thermo Finnigan) (Keith et al., 2011). Random powders and basally oriented clay fractions of the soils were analysed by X-ray diffraction (GBC MMA diffractometer; monochromatic CuKα radiation at 35 kV, 28 mA) for the identification of clay minerals (Brown and Brindley, 1980). For the identification of phyllosilicates, orientated clay samples were Mg-saturated, Mg-saturated and ethylene glycol solvated, K-saturated and K-saturated and heated to 550 °C before the analysis.

Cation exchange capacity (CEC) of the experimental soils was determined using the silver thiourea method (Rayment and Higginson, 1992). Soil particle size analysis (PSA) was undertaken using the hydrometer method after dispersing the samples with sodium hexametaphosphate. The ash content of the biochars was determined using the standard test method for chemical analysis of wood charcoal (ASTM-International, 2007). The water extractable organic C (WEOC) of the two biochars was extracted by combining biochar and water in a 1:10 ratio and continuously shaking for 24 h at 50 °C (Lin et al., 2012). The total C content in the extracts was analysed using a total organic C (TOC) analyser (Shimadzu TOC-VCPN). Characteristics of the experimental soils and biochars are presented in Table 1.

2.3. Incubation experiment

The incubation experiment was conducted using 200 g soil (oven dry basis) in 2 L airtight glass jars. The treatments consisted