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Influence of feedstock properties and pyrolysis conditions on biochar carbon stability as determined by hydrogen pyrolysis

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ABSTRACT

We produced 18 thermosequences of biochar from common feedstocks at ten temperatures from 300 to 900 °C to investigate their influence on carbon stabilization in biochar. Using hydrogen pyrolysis we were able to isolate the stable polycyclic aromatic carbon (SPAC) fraction that is likely to be resistant to mineralization on centennial timescales. SPAC formation was generally <20% of total organic carbon (TOC) at temperatures <450 °C and rises to >80% of TOC at temperatures above 600–700 °C depending on feedstock type. SPAC formation was retarded in feedstocks with high ash contents, and further retarded in those feedstocks when the final hold time at maximum pyrolysis temperature was reduced from one hour to 10 min. Given that aromatization of organic material in many feedstocks is usually completed by ca. 450 °C, the data suggests that a significant pool of aromatic biochar carbon exists in a 'semi-labile' form that may not be persistent on centennial timescales. For most feedstocks biochar yield and SPAC content are optimized at pyrolysis temperatures of 500–700 °C.

1. Introduction

Biochar is pyrogenic carbonaceous material (PCM) produced purposefully from waste organic feedstocks by controlled pyrolysis for use as a soil amendment [1]. Research over the past decade has demonstrated that biochar has considerable potential as a sustainable tool for carbon sequestration, soil amelioration, greenhouse gas emissions reduction and fertilizer runoff reduction, as well as waste management [1,2].

A basic requirement for the use of biochar as a carbon sequestration tool is that the carbon in the biochar is stable, meaning that a substantial fraction of the carbon sequestered is not re-mineralized on at least centennial timescales [3]. However, a variable component of the carbon in many biochars is degradable on annual to decadal timescales and hence does not contribute to long-term carbon sequestration [4,5]. In order to predict the long-term carbon sequestration capacity of biochar, a deeper, more predictive, understanding is needed of the biochar characteristics that confer resistance to environmental degradation and re-mineralization [3]. The stability of biochar is likely to be related primarily to feedstock type and pyrolysis conditions in the first instance, followed by secondary environmental factors (temperature, rainfall, soil type) at the site of incorporation into the soil.

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A number of approaches have been used to assess biochar stability. Incubation studies have directly measured carbon re-mineralization rates up to 8.5 years. Such studies have demonstrated the existence of a labile fraction (general <5%) in most biochars that is re-mineralized over weeks to months, and a 'stable' fraction with an apparent residence time commonly, although not exclusively, measured in centuries [6–9]. It is possible that the 'stable' fraction identified in incubation studies actually represents at least two pools, a 'semi-labile' pool with a residence time measured in years to decades and a 'stable' pool with a residence time measured in centuries to millennia [10]. The ability to determine the proportion of carbon in each of these longer turnover pools is pivotal to being able to predict the proportion of carbon in a biochar that is likely to have a minimum residence time of a century [10].

Biochar carbon in both the semi-labile and stable pools is dominated by polycyclic aromatic carbon compounds (PAC) [11]. At lower pyrolysis temperatures, the number of fused rings in an aromatic cluster is small, as shown by both BPCA analysis [12,13] and the "ring current" NMR spectroscopy method [14,15]. As temperature increases, the average number of rings in a cluster increases, leading ultimately to the development of ordered microcrystalline graphitic sheets at high temperature [11]. It has been demonstrated that PACs with a ring size <7 are degradable by micro-organisms [16] and hence are likely to form a component of the semi-labile pool and unlikely to contribute to a significant degree to the stable biochar carbon pool.

Moreover biochar's composition and structure can vary widely depending upon pyrolysis conditions and source feedstock and it is this variability that is likely to have a significant effect on their chemical stability in soils [17]. Some feedstocks can contain considerable amounts of organic nitrogen which becomes incorporated into the biochar's structure as thermally altered N (black nitrogen) in the form of heterocyclic aromatic N [18]. There has been a growing interest in how these structures will influence the stability of biochar in soils where more recent studies have shown that these structures may not be as recalcitrant as formerly thought [18–20]. Thus when considering mechanisms of stabilization of biochar in the environment both C and N aromatic structure's need to be taken into consideration.

A number of techniques have been proposed to determine the size of the stable carbon pool in biochars, on the assumption that the labile and semi-labile pools are small in most cases. Zimmerman [21] and Enders et al. [22], have suggested that decreasing volatile matter and O:C or H:C can be used to infer relative increases in stability, though this technique does not differentiate between semi-labile and stable pools, and hence cannot directly be used to quantify the relative sizes of these pools. An alternative technique uses hydrogen peroxide oxidation to accelerate the 'aging' and hence the oxidative loss of carbon from biochar. In combination with O:C or H:C, this technique has been used to estimate the proportion of biochar that will be stable over ca. one hundred year period (The 'Edinburgh Stability Tool') [10,23]. The results of the accelerated ageing experiments have demonstrated chemical behaviours for a range of biochars that are consistent with the hypothesis that biochars produced at higher temperatures exhibit more resistance to oxidative degradation, however separate quantification of a semi-labile and stable pool has yet to be achieved. There is currently no technique that has been shown to directly measure the stable pool of biochar carbon.

Hydrogen pyrolysis (hypy) has been demonstrated to be a technique of considerable utility for pyrogenic carbon isolation and quantification across a range of environmental matrices [24–26]. These studies have shown that the analytical window for hydrogen pyrolysis is PAC with the average ring cluster size greater than ca. 7 (coronene). Given that smaller PAC's are known to be degradable [16], this analytical window holds the promise of being able to directly measure the stable polycyclic aromatic carbon (SPAC) pool in biochars.

In recent years there has been a large number of thermosequence studies but many of these have been limited by the number of feedstocks and generally have a narrow pyrolysis temperature range (usually ca. 300 °C–600 °C; see Table S1 in supplementary information for references). These studies have employed a wide variety of methods to characterize different biochars and, moreover, have introduced a number of different methods for comparing the relative stability of different types of biochars. However the chemical heterogeneity of biochar has made it difficult to establish a single method suited to assessing biochar stability. In this study we produced biochar thermosequences from eighteen commonly-used feedstocks at ten temperatures from 300 to 900 °C under identical laboratory conditions. We have quantified the mass and carbon yield for each of these samples and used hypy to directly determine the size of the SPAC pool in each in order to better define the relationships between feedstock, pyrolysis temperature and the amount of carbon in each sample that is likely to contribute to long-term carbon sequestration.

2. Materials and methods

2.1. *Biochar feedstock*

Eighteen feedstocks were selected on the basis that they are in common use for biochar production and are deemed a waste product. These feedstocks have been divided into four categories; woods (hard, oil mallee, pine), residues (bagasse, corn stover, green waste, hay, paper-mill waste, peanut shells, rice husk, sugarcane trash, wheat chaff), manures (biosolids, dairy, feedlot, poultry) and macroalgae (saltwater and freshwater). Further feedstock source details and initial properties are provided in supplementary information, Table S2 and discussed below.

2.2. *Biochar production*

All feedstocks were dried at 60 °C to ca. 10% moisture (w/w) prior to pyrolysis. An aliquot of the feedstock (20–100 g) was loaded into a wire mesh basket suspended in a sealed 2 L stainless steel vessel which was itself placed inside a muffle furnace as described in Bird et al. [27]. The stainless steel vessel was constantly purged with dry nitrogen gas at 4 L min^{-1} and the furnace temperature was raised from