



Quantification and characterization of chemically- and thermally-labile and recalcitrant biochar fractions

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HIGHLIGHTS

- The labile biochar fraction may have a lower C:N ratio than the whole biochar.
- Different extraction methods yield different sizes for biochar labile fractions.
- Chemical addition reactions cause underestimation of biochar labile fractions.
- C and N can be accurately determined for biochar labile fractions.
- N release or immobilization from biochar in soils depends on biomass feedstock.

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ABSTRACT

The C:N ratios of biochar labile fractions is important for assessing biochar stability and N cycling in soil. Here we compare chemically and thermally labile fractions for nine biochars produced from five biomass feedstocks using four production techniques. Biochar fractionation methods included proximate analysis, hot water extraction, acid and base extractions (0.05 M, 0.5 M, 1 M, 2 M, 3 M, and 6 M of either H₂SO₄ or NaOH), and oxidation with 15% H₂O₂ and 0.33 M KMnO₄ (pH 7.2). Results show chemical addition reactions cause underestimation of mass of the labile fraction for chemical extraction and oxidation procedures but not the thermal procedure. Estimates of C and N in labile and recalcitrant fractions were not adversely affected by addition reactions, because solvents were independent of C or N. Results indicate that herbaceous biochars may be a source of N fertility while hardwood biochars may immobilize N during the first few years after biochar application to soils.

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1. Introduction

Biochar has been investigated over the last decade as a carbon sequestration agent and as a soil conditioner. Numerous studies have reported the ability of biochar to sequester carbon (Lehmann, 2007; Laird, 2008) and improve various soil functions (Glaser et al., 2002; Hale et al., 2011; Kookana et al., 2011; Chen et al., 2012; Bakshi et al., 2014), including mitigation of greenhouse gas (GHG) emissions (Mukherjee and Lal, 2013; Spokas, 2013), increase water and nutrient holding capacity (Basso et al., 2013), and reducing herbicide leaching (Hagner et al., 2015).

Knowing the stability of biochar in soils is critical for assessing both carbon sequestration potential and the long-term impact of biochar on soil physical and chemical properties (Lehmann et al., 2009). The stability of biochar in soils is known to depend on various factors such as properties of the biomass feedstock, production technique, maximum heating temperature during production, and soil environmental conditions (Czimeczik and Masiello, 2007; Cheng et al., 2008; Nguyen and Lehmann, 2009; Liang et al., 2010). Because biochars are enriched in condensed aromatic carbon, their decomposition in soils by microorganisms is slow; indeed biochars are much more stable in soils than non-charred biomass materials (Lehmann and Joseph, 2009). Several studies have reviewed the fate of biochars in different environments (Preston and Schmidt, 2006; Knicker, 2011), while others have investigated different approaches for assessing biochar stability. For example, Pereira et al. (2011) showed that dichromate oxidation

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Abbreviations

HS	Hardwood slow
HF	Hardwood fast
GS	Switchgrass slow
SF	Soybean fast
CS	Corn stover slow
CF	Corn stover fast
GG	Switchgrass gasification
MF	Macademia nut shell
HA	Hardwood autothermal
VM	Volatile matter
FC	Fixed carbon
CEC	Cation exchange capacity
AEC	Anion exchange capacity

and thermogravimetric analysis could be effective to estimate the thermally-labile C of biochar. However, no clear scientific consensus has emerged as to the best analytical technique(s) to assess *a priori* the stability of biochar in soil environments.

Most models divide biochar into a labile fraction, which is assumed to be mineralized rapidly in soil environments, and a recalcitrant fraction, which is assumed to be stable for hundreds or even thousands of years (Keiluweit et al., 2010; Lehmann et al., 2011; Mašek et al., 2013). The labile and recalcitrant fractions may influence plant available N in different ways. Because the recalcitrant fraction mineralizes very slowly it will have a negligible direct effect on the soil N cycle, however the recalcitrant fraction of biochar and its aromatic C structure may directly influence N redox reactions in soil (Cayuela et al., 2013; Zhou et al., 2016) and might have an indirect effect on plant available N by influencing both the stabilization and mineralization of biogenic humic substances. On the other hand, if the labile biochar fraction has a high C:N ratio it could immobilize N, or if it has a low C:N ratio it could be a source of plant available N, during the first few years after application as the labile fraction is mineralized. While the C:N ratio of the original biochar can be easily measured, the C:N ratio of the original biochar may not be representative of the C:N ratio of the labile fraction. Here we measure C:N ratios of chemically and thermally labile biochar fractions and determine whether they are different from the C:N ratio of the original biochar.

Several chemical and/or physical analysis techniques have been proposed for *a priori* measuring the size of the labile fraction of biochar. For example, McBeath and Smernik (2009) used ^{13}C nuclear magnetic resonance spectroscopy to distinguish the chemical shift of $^{13}\text{C}_6$ benzene from the diamagnetic ring currents due to the fused aromatic condensation of C in biochars. Michel et al. (2009) used near-infrared or mid-infrared spectroscopy to predict char-derived C from different sources in soils; and De la Rosa et al. (2008) and Kaal et al. (2009) used thermogravimetric and pyrolysis-gas chromatography-mass spectrometry analysis to detect black C that formed during artificial smoldering and natural combustion processes. Other researchers have measured the labile C pool in biochar using benzene polycarboxylic acids (Brodowski et al., 2005), potassium dichromate oxidation (Knicker et al., 2007), and nitric acid extraction (Trompowsky et al., 2005). However, the relevance of these chemically labile/recalcitrant fractions to the biologically labile/recalcitrant fraction is not clear. Biologically labile C in biochars is typically measured by quantifying CO_2 emissions coming from biochar in long-term soil incubations (Kimetu and Lehmann, 2010; Bruun et al., 2011). In some studies,

^{13}C enriched biochars are used in soil incubations so that CO_2 coming from the biochar can be distinguished from CO_2 coming from biogenic soil organic matter (Kuzyakov et al., 2009; Zimmerman et al., 2011).

Our long-term goal is to develop rapid analytical techniques that can be used to assess the size, stability, and properties (such as C:N ratio) of the biologically labile and biologically recalcitrant biochar fractions, as this information is needed to accurately model agronomic and environmental impacts of soil biochar applications (Archontoulis et al., 2016). In this study, we compare both the size and the C:N ratios of the thermally-labile and chemically-labile fractions for diverse biochars. Our first objective was to determine whether various chemical (acid and base extractions and chemical oxidation) and thermal (proximate analysis) methods yield similar or different estimates for the size and the C:N ratios of the labile and recalcitrant fractions. Our second objective was to evaluate the various chemical methods for assessing labile and recalcitrant biochar C to determine which method(s) may be suitable for subsequent comparison with results of biological incubations. And, our third objective was to assess the influence of production technique and feedstock on the relative amounts of labile and recalcitrant C in biochars.

2. Materials and methods

2.1. Source and basic characteristics of the studied biochars

A total of nine biochars prepared using fast (F) pyrolysis, slow (S) pyrolysis, gasification (G), and autothermal fast pyrolysis (A) techniques were utilized in this study. Biochars were produced by fast pyrolysis from hardwood (HF), soybean stover (SF), corn stover (CF), and macademia nut shell (MF) feedstocks. The slow pyrolysis biochars were produced using hardwood (HS), switchgrass (GS), and corn stover (CS) feedstocks. The gasification and autothermal fast pyrolysis biochars were produced from switchgrass (GG) and hardwood (HA) feedstocks, respectively.

All biochars were initially ground using a mortar and pestle and passed through a 0.5-mm sieve before being used. Moisture content, volatile matter (VM), fixed carbon (FC) and ash content of the biochars were measured using the modified proximate analysis procedure (Aller et al., 2017). Basic chemical characterization of the biochar samples, pH, EC, elemental C, H, N, and S, inorganic elements content, anion exchange capacity (AEC) and cation exchange capacities (CEC), were determined using methods detailed by Bakshi et al. (2016). Inorganic C content (CO_3^{2-}) was determined by stirring the biochar in 0.05 M HCl (biochar/0.05 M HCl = 1/50 w/v) overnight in a closed mason jar containing a NaOH trap, and back titrating the NaOH with 0.05 M HCl (Fidel et al., 2017). Mineral phases associated with the ash in the biochar samples were identified using X-ray diffraction (XRD) also following procedures described by Bakshi et al. (2016). Specific surface area of biochar was measured using both the BET- N_2 (Chun et al., 2004) and EGME methods (Cerato and Luttenegger, 2002).

2.2. Determination of chemically and thermally labile and recalcitrant biochar fractions

Chemically labile biochar fractions were extracted from the nine biochars using hot water and various acid (0.05, 0.5, 1, 2, 3, and 6 M H_2SO_4) and base (0.05, 0.5, 1, 2, 3, and 6 M NaOH) solutions. For the hot water extraction, biochar was heated to 80–85 °C in milli-Q water (biochar/water = 1/80 m/m) for 16–18 h, cooled, and then filtered through 0.45 μm membrane filters and the residue was retained. The residue was collected after filtration, dried at 80–85 °C for 4 d and the mass lost due to hot water treatment was

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