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Characterization of organic compounds in a mixed feedstock biochar generated from Australian agricultural residues

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ABSTRACT

Biochar application into soil has been considered as an effective strategy to improve soil fertility. It has been recognised that biochar, produced from a single feedstock at a particular highest heating temperature (HTT), may not optimise plant yield. A mixture of selected biomass feedstocks, together with appropriate pyrolysis conditions, is suggested as a means to optimise biochar properties and its subsequent effectiveness on soil. However, in order to match selective biochar with specific soil requirements and to maximise its effect on plant growth, it is essential to characterise the biochar, especially the organic components, that can affect soil organic matter and nutrient availability once the biochar is applied. Therefore, the objective of this present work is to characterise the properties of organic compounds in a mixed feedstock biochar produced from two Australian agricultural residues, wheat straw and chicken litter (WsCl), at three pyrolysis temperatures (450 °C, 550 °C and 650 °C) using advanced microscopic, spectroscopic and chromatographic techniques. The results showed that organic compounds are significantly controlled by the pyrolysis temperature. The biochars obtained at 650 °C had a high pH value, C and ash contents, but low O, N and H contents, whereas WsCl450 contained the highest N content. Nitrogen was either removed as a volatile matter or condensed during heat treatment to form aromatic structures, which were less soluble. WsCl biochar produced at 550 °C, with the highest concentration of fixed carbon and aromatic C structure, will presumably be more stable once it is applied. Increases in the pyrolysis temperature also developed pores, which promoted mineral attachment, that arose from the chicken litter particles, inside the pores (mainly Ca and P rich phases) and on the surface (predominantly Si rich phases) of wheat straw particles. Moreover, increasing pyrolysis temperature resulted in a much lower DOC content in the higher temperature biochars, where low molecular fractions were dominant. These results indicate that it is possible to influence biochar properties and develop value-added biochar with unique characteristics tailored for specific agricultural applications.

1. Introduction

Over the last half century, many agricultural soils have been degraded due to rapid population growth, poor management strategies and continuous cultivation, which have resulted in reduced levels of soil fertility. Biochar application to agricultural soils has been proposed as a soil amendment in order to improve soil fertility and crop yield, as well as a means of sequestering carbon, reducing the emission of greenhouse gases and nutrient run off from soils. Biochar can be defined as a charred carbon-rich material produced from thermochemical decomposition (pyrolysis) of waste biomass under limited supply of oxygen [1].

Several studies have shown the significant agronomic benefits of biochar application, mainly due to the presence of recalcitrant carbon, labile organic molecules (LOMs) and inorganic components, which have provided soil with both macro- and micro-nutrients and therefore, improved crop productivity and plant growth [1–3]. However, the agronomic benefits of biochar can significantly vary depending on both feedstock composition and pyrolysis conditions, most importantly the pyrolysis temperature. In short, while cation exchange capacity (CEC) and available nutrient elements for crop yields were promoted in lower temperature biochars [4], high-temperature biochars were more effective in the sorption of organic contaminants due to their high surface area, micro-porosity and hydrophobicity [4,5]. These biochars, with a higher proportion of stable carbon, also demonstrated beneficial properties for soils by increasing stable-C yield and soil alkalinity [2].

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Regarding feedstock compositions, it is now accepted that if biochars are to be adopted by farmers, they need to be produced from readily available biomass resources. In order to optimise feedstock selection, one of the approaches to produce effective biochar products that can be applied at lower application rates and costs [6], as well as meeting soil constraints and plant nutrient requirements, is by combining selected feedstocks, such that a tuned composition, together with appropriate pyrolysis conditions, can be used to optimise biochar properties. In fact, increased nutrient availability and C stabilization are two of the principal roles for biochar application into the soil and producing biochars from blending low-quality biomass feedstock is suggested as a viable solution, which will likely result in a value-added biochar with desirable physical, chemical and biological properties for application into a specific soil [7].

Wheat straw and chicken litter are two Australian agricultural residues, where their positive impacts on agricultural soils have been individually documented [2,3,8–11]. Soils incorporated with wheat straw biochar were found to have a higher water holding capacity (up to 18% after 24 h), with higher microbial C and N, but less soluble organic N [10]. Wheat straw biochar produced at approximately 350–550 °C was observed to increase yields of maize (up to 15%) and rice (up to 20–30%), soil pH, soil organic carbon, total nitrogen and increase methane emission, but reduce nitrous oxide emission [12]. Crombie et al. evaluated the properties of biochars produced from pine wood chips and wheat straw at pyrolysis temperatures ranging from 350 to 650 °C. Wheat straw biochar, produced at 450 °C, was observed to have much higher concentrations of extractable nutrients, such as Ca, K, P, Mg, Na, with a higher CEC than pine wood chips [2]. It is interesting to note that straw-based biochars, especially wheat straw biochars, have been also used as a silica source into agricultural soils because of their high silica content, which has improved soil Si availability [9].

Similarly, the production of biochar from animal manure offers several agronomic benefits to farmers by providing nutrients for agricultural crops and increasing soil organic matter [13], as well as reducing costs to dispose of feedstocks [14]. Chicken litter-derived biochar application was observed to significantly increase soil pH, N uptake and available P, Ca, Mg and K contents in plant biomass. Moreover, radish yield was increased from 42% at 10 t ha^{-1} to 96% at an application rate of 50 t ha^{-1} for a poultry litter biochar application, due to both the ability of this biochar to increase N availability [15] and the high inorganic constituents of the feedstock [5].

Interestingly, phosphorus-rich manure-based biochars have the ability to stabilize heavy metal contaminants [16]. Similar results have been also reported for wheat straw biochar application, where Cd and Pb bonded with mineral phases, such as those rich in Al, Fe and P, in the contaminated biochar particles [17]. However, high concentrations of some mineral nutrients in chicken litter biochar can cause a problem if it is applied to soils with high runoff potentials and, further, can pose water quality threats if it is transported into the water system [18]. Thus, a combination of chicken litter with another C-rich feedstock, such as wheat straw [2], which can act as an absorbent to retain nutrients and water and thus, decrease the risks of nutrients runoff, can be envisaged as a promising strategy.

While numerous studies have reported the development of single-feedstock-biochars, very limited literature is available regarding the characterization of mixed-feedstock-biochars derived from available biomass materials. The effect of pyrolysis temperature on the organic components of such biochars, which are the components most affected by pyrolysis temperature, and their interactions with mineral phases is also unclear. Therefore, the present study aims to develop mixed-feedstock-biochars produced from the combination of wheat straw and chicken litter (termed here WsCl), which were provided by a partner organization based in Australia, Renewed Carbon (RC) Pty Ltd. Since several studies have documented the significant effects of biochars obtained at temperatures in the range from 350 to 650 °C, in this study three pyrolysis temperatures, 450 °C, 550 °C and 650 °C, were applied to produce the WsCl biochars. The characteristics of the organic components and their interactions with minerals and inorganic compounds have been investigated using advanced microscopic and spectroscopic methods in order to better understand the effects of biochar on soil properties once it is applied. The results of this study will assist in the development of biochar-based products that can improve soil health and increase yields, as well as reducing the cost of managing waste biomass both in rural and urban areas.

2. Materials and methods

2.1. Biochar production

A mixture of 50% wheat straw and 50% chicken litter, was dried according to the IBI standard of "oven-dry biochar" at 105 °C (termed here WsCl105) for 24 h in order to remove free water until a constant weight was achieved [19]. This mixture would be representative of a mixture used in commercial plants, as specified by our industrial partner. It should be noted that while biochar production on a small-scale allowed for the high level of control required to investigate the changes in organic component as a function of pyrolysis temperature, the same control may not be readily achievable at an industrial-scale level of production. However, it can be assumed that the same type of biochar, with broadly the same properties, can be produced if raw mixed-feedstock is exposed to the same pyrolysis conditions and environment. The dried feedstock mixture was then placed in a stainless steel barrel nipple (grade 316) and sealed with an airtight hexagonal cap to provide a controlled atmosphere.

This assembly was prepared in a muffle furnace by increasing the temperature from 25 °C to 110 °C at a heating rate of 5 °C min^{-1}. This was maintained for 15 min to remove any free water. Then, the temperature was increased from 110 °C to 220 °C at a heating rate of 5 °C min^{-1} and held for 15 min in order to drive off all moisture or impurities. The final temperature was either 450 °C (termed here WsCl450), 550 °C (termed here WsCl550) or 650 °C (termed here WsCl650). This was reached by heating at a rate of 5 °C min^{-1}, holding for 30 min in order to remove volatile compounds that would otherwise have an effect on chemical reactions between different organic matters and mineral phases. The biochar samples were then cooled down to room temperature (i.e 25 °C, at a rate of 5 °C min^{-1}). Both the dried mixed feedstock (WsCl105) and the three WsCl biochar samples were ground into fine particles, using a ring mill, to make them more homogenous for analysis by various microscopic, spectroscopic and chromatographic techniques.

2.2. Characterization methods

2.2.1. Analysis of dried WsCl and WsCl biochars

The mineral composition of both dried feedstocks was measured using x-ray florescence (XRF) with either a Philips PW2400 WDXRF spectrometer or an Axios Advanced WDXRF spectrometer. In addition, proximate, ultimate and ash analyses were conducted on ground WsCl samples according to the relevant ASTM standards by ALS Coal Division in Australia and the mass loss was measured (Fig. S1). Some of the agronomic properties of the WsCl samples (electrical conductivity (EC) and pH values, extractable nitrate (NO_3^-) and extractable ammonium (NH_4^+) concentrations), were also performed by NSW Department of Primary Industries (DPI) Wollongbar Environmental Laboratory in Australia.