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Effect of Pyrolysis Temperature and Feedstock Type on Agricultural Properties and Stability of Biochars

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Abstract

Pyrolysis temperature and feedstock type used to produce biochar influence the physicochemical properties of the obtained product, which in turn display a range of results when used as soil amendment. From soil carbon (C) sequestration strategy to nutrient source, biochar is used to enhance soil properties and to improve agricultural production. However, contrasting effects are observed from biochar application to soil results from a wide range of biochar's properties in combination with specific environmental conditions. Therefore, elucidation on the effect of pyrolysis conditions and feedstock type on biochar properties may provide basic information to the understanding of soil and biochar interactions. In this study, biochar was produced from four different agricultural organic residues: Poultry litter, sugarcane straw, rice hull and sawdust pyrolysed at final temperatures of 350˚C, 450˚C, 550˚C and 650˚C. The effect of temperature and feedstock type on the variability of physicochemical properties of biochars was evaluated through measurements of pH, electrical conductivity, cation exchange capacity, macronutrient content, proximate and elemental analyses, Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analyses. Additionally, an incubation trial was carried under controlled conditions to determine the effect of biochar stability on CO_2-eq emissions. Results showed that increasing pyrolysis temperature supported biochar stability regardless of feedstock, however, agricultural properties varied widely both as an effect of temperature and feedstock. Animal manure biochar showed higher potential as nutrient source rather than a

C sequestration strategy. Improving the knowledge on the influence of pyrolysis temperature and feedstock type on the final properties of biochar will enable the use of better tailored materials that correspond to the expected results while considering its interactions with environmental conditions.

Keywords

Characterization, GHG, C Sequestration, Char, Organic C

1. Introduction

Pyrolysis of organic residues results in a highly stable and carbonaceous material defined as biochar [1]. Pyrolysis reaction in high temperatures and low oxygen concentration produces biochar high C content organized in aromatic and stable structures, defined as fixed C, not available for microorganisms' degradation [2]. Particularly for wood derived biochars, this accumulation of C and release of less stable organic compounds, combined with lower feedstock macronutrient content, produces a highly and stable C containing biochar, ideal for increasing C content of soil [3] [4]. This supports the use of such biochar as a C sequestration strategy rather than a nutrient source. Biochar can contribute to the greenhouse gas (GHG) mitigation not only due to its C sequestration potential [5] but also displacing the use of fossil fuel, producing alternative energy source through pyrolysis process [6]. As a global warming mitigation strategy, application of biochar in soil also showed decreasing N_2O emissions. Evidence found in literature shows more than 14% decrease in N_2O emissions in biochar amended soil compared to soil-only [7]. However, results are inconclusive and display variations and the underlying mechanisms explaining the effect of biochar-soil interaction include biochar properties and soil biotic and abiotic conditions [8].

Biochar produced from different feedstock type may, however, have varied concentrations of nutrients of agricultural interest. In this sense, animal manure derived biochar is shown to accumulate important elements, such as phosphorus (P), calcium (Ca) and magnesium (Mg) [9] [10]. Thus, animal manure derived biochar has higher potential to be used as a nutrient source in agricultural systems [11]. Macronutrients concentration in biochar increase during the pyrolysis process while volatile matter and water is released from biochar structure. These latter compounds are represented by organic acids, and as pyrolysis temperature increases, the release of such molecules and the accumulation of basic elements such as Ca and Mg are the drivers of high pH in biochars. These properties support the use of biochar as soil amendment, as liming agent and nutrient source [12].

Higher soil aggregation was also observed for fine-textured soil where wood and animal derived biochar was added [5], improving soil physical structure, aeration and moisture ratio, consequently an improved environment for root

development. These mechanisms are often related to increased agricultural production; however, results vary due to biochar properties and its interaction with different environmental conditions [13].

It is clear that the use of the biochar can vary according to its properties, which are defined as a function of the origin/type of biomass used and the variables related to the pyrolysis process, such as time and temperature. Several outcomes are observed from the interaction of biochar and soil particles [14]. These contrasting effects are caused by the various physicochemical properties of biochar combined with environmental conditions. Thus, elucidation of the effect of pyrolysis conditions and feedstock type on biochar structure and chemical properties provide basic information to support the understanding of the resultant interactions of biochar with soil. Moreover, this knowledge also enables the selection of feedstock type and production conditions according to the environmental conditions and desired amendments for particular situations.

The purpose of this study is to present potential uses for biochar in cultivated soils considering the variation on biochar agricultural properties and C sequestration potential, as an effect of pyrolysis temperature and feedstock type. In this sense, we specifically aim to 1) evaluate the effect of pyrolysis temperature and feedstock type on relevant agricultural properties and C sequestration potential of biochar and 2) investigate the effect of contrasting biochar on GHG emission applied in tropical soil from Brazil.

2. Materials and Methods

2.1. Biochar Feedstock

Selected feedstock comprised contrasting organic residues derived from agricultural production systems: poultry litter, rice hulls, sugar cane straw and sawdust.

Poultry litter (PL) was donated and collected from the poultry facility within the Department of Genetics at the University of Sao Paulo—"Luiz de Queiroz" College of Agriculture (USP-ESALQ). These poultry are part of a sustainable farming production project developed in the department, and the posture poultry are fed daily with grass. The manure sits on the ground of the facility and it is mixed with sawdust weekly. Clean rice hull (RH) was collected in the same facility where the material is used as bedding for broiler.

Sugarcane straw (SC) was collected from a commercial sugarcane field. The straw was left over the cultivated area after harvesting operation. The Department of Forestry Sciences, in the Wood Technology and Management Laboratory, at USP-ESALQ, provided sawdust (SD). Pre-treatment included drying at 45˚C for 24 h and ground to less than 1 mm particle size, followed by characterization analysis.

2.2. Biochar Production

Prior to pyrolysis, selected feedstocks were dried at 105˚C to approximately 13% moisture (w/w) to improve the reactor efficiency. Biochars were pyrolyzed in a

60 L static reactor in N_2 saturated atmosphere with a heating rate of 10˚C·min^{-1}. The feedstock was placed individually in the reactor chamber and heated by six electrical resistances to the temperatures of 350˚C, 450˚C, 550˚C and 650˚C. Temperature was monitored by three sensors placed in the reactor, reaching its interior atmosphere close to the chamber. The reaction time varied according to each run and feedstock, and the completion was reached when the release of gases from the reactor stopped. The biochars were removed from the chamber 12 h after the reaction time was completed in order to avoid spontaneous combustion. The mass of all materials contained in the chamber reaction was determined in order to obtain biochar yield (Table 1).

2.3. Feedstock and Biochar Analysis

Feedstocks were analyzed accordingly to the same methodologies used for biochar, concerning the determinations of pH, electrical conductivity (EC), cation exchange capacity (CEC), proximate and elemental analysis. Additionally, feedstock samples were evaluated in relation to their devolatization characteristics, through thermogravimetry analysis. Grind samples of 9 mg were placed in a crucible with N_2 gas flow with a heating rate of 10˚C·min^{-1}, from 25˚C to 900˚C (TGA-50, Shimadzu). Weight loss in respect to temperature increase was recorded.

After pyrolysis of feedstock, biochars were maintained within plastic bags tightly sealed. Prior to the analyses, air-dried biochars were ground with mortar and pestle and sieved to achieve particle size of 150 - 850 μm. Proximate and elemental analyses as well as pH and EC measurements were performed following the methods recommended by the International Biochar Initiative Guideline [15]. Measurements of pH and EC were performed in 20 ml of deionized water mixed for 90 min with 1.0 g of sample [16]. pH-meter (Digimed DM-23) and conductivity-meter (Digimed DM-32) were both previously calibrated with standard solutions. CEC was determined using 0.5 g of biochar and 1 g of feedstock. Samples were mixed with 100 ml of HCl (0.5 mol·L^{-1}) in an orbital mixer for 30 min. Samples were filtered in vacuum, while washed with 300 ml of deionized water divided in 10 aliquots of 30 ml each. The residual solution was discarded. Calcium acetate (0.5 mol·L^{-1}, pH = 7.0) was added to the solid sam-

Table 1. Biochar yield after pyrolysis.

Biochar	Yield (%)			
	Temperature (˚C)			
	350	450	550	650
Sugarcane Straw (SC)	41.5	37.6	34.6	32.8
Rice Hull (RH)	49.6	49.2	46.5	46.6
Poultry Litter (PL)	59.6	47.1	42.0	40.2
Sawdust (SD)	42.6	42.4	36.4	33.3

ples retained in the filter paper (Whatman 42) in 10 aliquots of 10 ml each. The washing procedure using deionized water was repeated and the resultant solution was titrated using NaOH (0.1 mol·L^{-1}) to determine the amount of H^+ present in the solution.

Proximate analysis methods were conducted to calculate fixed C content [17] [18]. Elemental analyses for determination of C, N and H contents were assessed by dry combustion using a Perkin Elmer CNH 2400; Oxygen (O) content was obtained by subtraction [19].

The nutrient content was analyzed only for the bio-carbon samples and the procedure was based on the incineration of the samples in muffle, followed by suspension in acidic solution and determination by Inductively Coupled Plasma (ICP OES–Thermo Scientific iCAP 6300 series). Approximately 200 mg of biochar samples were placed in crucibles and ashed in a muffle furnace for 8 h at 500˚C. The samples were transferred to borosilicate tubes and added 5.0 ml of HNO_3, then placed on a digestion bloc to reach temperature of 120˚C. After evaporation was complete and samples were cooled, 1.0 ml of HNO_3 plus 4 ml of 30% H_2O_2 were added and heated at 120˚C to complete dryness. When cooled, concentrated 1.43 ml HNO_3 was added and vortexed, then deionized water was added to complete 20 ml. The resultant solution was used for the determination of total P, K, Mg, S, Ca, Fe, Cu, Mn, B, Zn contents through ICP [20].

Fourier-transform infrared spectroscopy (FTIR) analysis was performed in feedstock using ground material mixed with KBr in a 1:500 ratio (w/w) and in biochars with 1:1000. The mixture was compacted at 5 Mg to form pellets of 1.0 cm of diameter. Pellets were analyzed in a spectrometer (Perkin Elmer Spectrum 100) with 4 cm^{-1} resolution, measuring the absorbance from 400 to 4000 cm^{-1}. Samples were corrected against a pure KBr pellet and the air as background spectrum [21].

2.4. Incubation Experiment

Following characterization, sugarcane straw (SC) and poultry litter (PL) biochar produced at 650˚C and 350˚C (SC350, SC650, PL350 and PL650) were selected to conduct an incubation trial in biochar-treated soils. Based on the results from the proximate analysis, these biochars presented higher and lower stability (SC650, PL650 and SC350, PL350 respectively) [9]. This incubation trial was performed to evaluate whether CO_2-eq emission from biochar-treated soil follow trends according to biochar stability properties.

Additionally, two contrasting tropical soils were selected to investigate the effect of contrasting soil texture on biochar stability: Quartzipsament and typic Hapludox (**Table 2**).

Each soil respectively was collected from two different native vegetation areas located near Anhembi, Brazil (22˚43'31.1"S and 48˚1'20.2"W) and in Piracicaba, Brazil (22˚42'5.1"S and 47˚37'45.2"W). The soils were sampled at the 0 - 20 cm layer, air-dried, homogenized, and sieved to 2 mm. Contrasting biochars were

Table 2. Soil properties for incubation experiment.

Soil type	Quatzipsamment	Hapludox typic
Sand (%)	90	40.6
Silt (%)	2.2	27.7
Clay (%)	7.8	31.7
pH ($CaCl_2$)	4.0 ± 0.1	6.2 ± 0.1
C (%)	0.9 ± 0.1	1.9 ± 0.1
N (%)	0.1 ± 0.1	0.2 ± 0.1
P ($mmol_c \cdot dm^{-3}$)	28.0 ± 1.4	4.0 ± 0.0
S ($mmol_c \cdot dm^{-3}$)	9.5 ± 0.7	5.3 ± 0.6
K ($mmol_c \cdot dm^{-3}$)	4.05 ± 0.1	<0.7
Ca ($mmol_c \cdot dm^{-3}$)	96.5 ± 2.1	5.3 ±0.6
Mg ($mmol_c \cdot dm^{-3}$)	20.0 ± 0.0	<1
Al ($mmol_c \cdot dm^{-3}$)	0.0[(1)]	5.7 ± 0.6
CEC ($mmol_c \cdot dm^{-3}$)	138.5 ± 2.2	69.0 ± 4.0

[(1)]Values of 0.0 were near the instrument detection.

applied in each soil. The selected materials were: sugarcane and poultry litter biochars pyrolysed at 350˚C and 650˚C. Both were added at a dose equivalent to 50 $t \cdot ha^{-1}$ of C [6] in 100 g of soil into a 500-ml jar with sealed lids and rubber stopper where the syringe (50 ml) was used to removed gas samples. The sampling was performed every day for the first 10 days and in intervals of 1, 2, 3 and 4 days after the 11th, 27th and 48th day; respectively until 56 days, during an interval of 60 min. Moisture was maintained at 60% WHC and temperature at 25˚C, jars were placed inside an incubator without the lids. After collecting gas samples, the CO_2 and N_2O concentrations were measured by gas chromatograph (SRI 8610, SRI Instruments, Torrance USA) equipped in with an electron capture detector (ECD) for N_2O and a flame ionization detector (FID) for CO_2 detection. These results were used to estimate the fluxes calculated using the equation proposed in [3]. N_2O emissions were expressed in "carbon dioxide equivalent", considering the global warming potential (GWP) of 298 for N_2O, compared with the GWP of carbon dioxide [22]. Total GHG (N_2O + CO_2, in $mg \cdot kg^{-1}$ soil) emission was represented in terms of carbon dioxide equivalent (CO_2-eq). After incubation period, the mixture soil and biochar were evaluated for pH, EC, total C and N according to [23]. Briefly, soil samples were dried at 40˚C, ground to 1 mm sieve and mixed in water at 1:2.5 (w/w), shaken for 5 min and resting for 1 h, followed by determination of pH with previously calibrated pH-meter (Digimed DM-23) and soil samples were added in water in proportion of 1:2 (w/w), shaken for 1 hour and resting for 24 hours. The EC was determined with an EC-meter (Digimed DM-32) previously calibrated. Total C and N were determined in samples dried and sieved to 100 mesh by using an elemental analyzer (LECO-CN2000).

2.5. Statistical Analysis

The effects of temperature and feedstock type were compared amongst biochars' properties using a 2-way analysis of variance (ANOVA) in a completely randomized design, with one additional treatment (original biomass). Significant differences in the factors were investigated using a Tukey's test ($p < 0.05$) to compare biochars produced with different feedstock type, and regression analysis to evaluate biochar in different pyrolysis temperature. Each biochar, originated from a single combination of feedstock and temperature, was compared with its original biomass through Dunett's test ($p < 0.05$).

The CO_2-eq results obtained in the incubation experiment were submitted to ANOVA and the mean of each treatment with biochar was compared with the value of the control treatment (soil only) using Dunnett's test ($p < 0.05$). All analyses were performed using R software.

3. Results and Discussion

3.1. Effects of Feedstock Type and Pyrolysis Temperature on Biochar Properties

3.1.1. Relevant Agricultural Properties

Chemical analyses assessed in the present study reflected different rates of transformation for each biochar derived from contrasting feedstock. Electrical conductivity (EC) results varied with greater influence of the type of material rather than the pyrolysis temperature (**Table 3**). Our findings indicated that biochars can preserve the initial nutrient content, as also reported in [14]. Hence poultry litter showed the highest EC values since animal derived feedstock usually contain higher nutrient concentration [24]. In contrast with previous studies [25] [26] [27] there was no increase in EC when increasing pyrolysis temperature. Particularly for poultry litter biochars, the decrease in EC corroborated with literature when compared with its feedstock, which showed much higher values [28].

Increases in pH have been observed in all pyrolyzed materials and this can be explained by the effect of the temperature on the release volatile matter composed by acid functional groups and concentrates ash contents consequently elevating the pH [9]. Nonetheless, pH values followed the trend found in literature and increased with higher pyrolysis temperature (**Table 3**) [14] [29] [30], except for sawdust. Poultry litter biochar exhibited the highest values, corroborating with the higher amount of basic salts found in its feedstock [31]. Values of pH in sugarcane straw biochar were similar the data described by [29] between 8 and 10 and reflect the presence of basic elements concentrated in its composition. Particularly for rice hull, pH results exhibited lower values than what found in the literature [21] and reasons for that could be due to the different methodologies used to assess this property.

As a function of the loss of acidic functional groups by the action of the pyrolysis temperature, it was expected to reduce the CEC [30] [32] in comparison to

Table 3. Basic characteristics of biochar and respective feedstock.

	Feedstock	Temperature of Pyrolysis (˚C)				
		350	450	550	650	
			EC ($mS \cdot m^{-1}$)			
SC[1]	1.8	1.2 b[2]	1.4 b	2.0 b*[3]	1.9 b*	$y = 0.3025 + 0.0027x$ ($r^2 = 0.797$; $p = 0.0003$)
RH	0.8	0.2 a	0.2 a	0.3 a	0.3 a	ns[4]
PL	11.4	4.4 c	3.9 c	3.8 c	4.0 c	$y = 8.4609 - 0.0174x + 1.6 \times 10^{-5}x^2$ ($r^2 = 0.997$; $p = 0.0334$)
SD	0.4	0.1 a	0.1 a	0.1 a	0.1 a	ns
			pH			
SC	7.8	8.7 d*	8.8 c*	9.1 c*	9.2 c*	$y = 8.0200 + 0.0018x$ ($r^2 = 0.907$; $p < 0.0001$)
RH	6.1	8.4 c*	8.3 b*	8.7 b*	8.7 b*	$y = 7.9275 + 0.0012x$ ($r^2 = 0.617$; $p < 0.0001$)
PL	7.3	8.2 b*	9.8 d*	9.8 d*	9.9 d*	$y = -1.5314 + 0.0404x - 3.5 \times 10^{-5}x^2$ ($r^2 = 0.931$; $p < 0.0001$)
SD	4.0	7.6 a*	7.0 a*	7.4 a*	7.5 a*	$y = 11.2748 - 0.0164x - 1.6 \times 10^{-5}x^2$ ($r^2 = 0.625$; $p < 0.0001$)
			CEC ($mmol_c \cdot kg^{-1}$)			
SC	190	280 bc	200 c	166 b	169 b	$y = 878.896 - 2.436x - 0.0021x^2$ ($r^2 = 1.00$; $p = 0.0425$)
RH	77	158 a	166 ab	171 b	165 ab	ns
PL	597	320 c*	203 c*	106 b*	105 ab*	$y = 533.6833 - 0.6604x$ ($r^2 = 0.929$; $p < 0.0001$)
SD	303	207 ab	113 a*	86 a*	91 a*	$y = 901.9854 - 2.8627x - 0.0025x^2$ ($r^2 = 0.994$; $p = 0.0160$)

[1]SC = sugarcane straw, RH = rice husk, PL = poultry litter, SD = sawdust. [2]Means followed by the same letter are not different for biochars in the same pyrolysis temperature by Tukey's test 5%. [3]Means followed by an asterisk refer to differences between each biochar and its respective original biomass by Dunnett's test 5%. [4]Regression analysis was not significant for linear model.

the respective original biomasses and with the increase of the temperature, which was actually observed for poultry litter and sawdust (**Table 3**). The inverse relationship between CEC and pyrolysis temperature was also observed for sugar cane straw. The actual values of CEC are similar to values reported in literature [32], particularly for straw derived biochar, between the ranges of 100 and 230 $mmol_c \cdot kg^{-1}$ and the lowest for wood derived biochars in the range of 13 and 30 $mmol_c \cdot kg^{-1}$. The higher mineral phase found in manure derived biochars promotes the formation of O-containing functional groups on biochar surface generating CEC, varying from 292 to 511 $mmol_c \cdot kg^{-1}$ [27], which can be linked with results from spectroscopic analysis showing the loss of oxygen functional groups.

As regards the application of the biochar in the soil, it can be noticed from the results of Table 3 that lower temperatures provide a higher cation exchange capacity. Nevertheless, CEC develops with surface oxidation [12], and could potentially support CEC increase after application of biochar in the soil.

The sum of macronutrient content of animal derived biochars was higher when compared to crop residues and wood derived materials (Table 4). Poultry

Table 4. Macronutrients contents ($g \cdot kg^{-1}$) in biochars and feedstock samples.

Material	Temperature of Pyrolysis (˚C)				
	350	450	550	650	
			P		
SC[1]	0.94 b[2]	1.67 c	1.99 c	2.73 c	$y = -1.0175 + 0.0057x$ ($r^2 = 0.979$; $p < 0.0001$)
RH	0.00[4] a	0.00 a	0.00 a	0.00 a	ns[3]
PL	3.72 c	2.13 c	3.51 d	4.28 d	$y = 15.8519 - 0.0558x + 5.9 \times 10^{-5}x^2$ ($r^2 = 0.742$; $p < 0.0001$)
SD	1.10 b	1.06 b	1.03 b	1.06 b	ns
			K		
SC	6.75 c	9.87 c	10.58 c	13.65 c	$y = -0.4950 + 0.0214x$ ($r^2 = 0.953$; $p < 0.0001$)
RH	0.94 a	0.75 a	0.81 a	0.88 a	ns
PL	3.13 b	1.78 b	2.48 b	3.05 b	$y = 13.7939 - 0.0476x + 4.8 \times 10^{-5}x^2$ ($r^2 = 0.796$; $p < 0.0001$)
SD	0.25 a	0.25 a	0.26 a	0.27 a	ns
			Mg		
SC	2.28 d	3.01 c	3.38 d	3.66 d	$y = -1.7685 + 0.0154x - 1.1 \times 10^{-5}x^2$ ($r^2 = 0.997$; $p = 0.0005$)
RH	0.22 a	0.18 a	0.19 a	0.21 a	ns
PL	1.16 c	0.74 b	1.03 c	1.28 c	$y = 4.7262 - 0.0162x + 1.7 \times 10^{-5}x^2$ ($r^2 = 0.838$; $p < 0.0001$)
SD	0.65 b	0.60 b	0.80 b	0.84 b	$y = 0.3300 + 7.7 \times 10^{-4}x$ ($r^2 = 0.756$; $p = 0.0043$)
			S		
SC	0.60 c	0.92 d	0.87 d	1.09 d	$y = 0.1542 + 0.0014x$ ($r^2 = 0.810$; $p < 0.0001$)
RH	0.10 a	0.06 a	0.09 a	0.09 a	ns
PL	0.76 d	0.39 c	0.60 c	0.65 c	$y = 3.1042 - 0.0104x + 1.0 \times 10^{-5}x^2$ ($r^2 = 0.608$; $p < 0.0001$)
SD	0.29 b	0.26 b	0.26 b	0.26 b	ns

[1]SC = sugarcane straw, RH = rice husk, PL = poultry litter, SD = sawdust. [2]Means followed by the same letter are not different for biochars in the same pyrolysis temperature by Tukey's test 5%. [3]Regression analysis was not significant for linear and quadratic models. [4]Values of 0.00 were near the instrument detection.

litter biochar showed the greatest values for macronutrients especially due to high content of Ca, which explains the higher pH determined for this material [25]. Contents of P and K found in the present study were lower than other results found in the literature, which could be due to differences in methodology to determine concentration of elements, and heterogeneity of poultry litter feedstock [10] [27]. Even though the concentrations dropped with temperature increase, poultry litter biochar conserved higher amounts of the analyzed elements, when compared to the other materials studied, indicating its potential use as fertilizer [28].

Sugarcane straw biochars showed intermediate concentration of macronutrient, and consistent increase in these elements when pyrolysis temperature rose (**Table 4**). This material is characterized by higher content of K when compared to the other macronutrients due to the higher concentration of such element in its feedstock [29].

By contrast, rice hull and sawdust biochars showed very low concentration of macronutrients, and little to no variability in the concentration of the elements, when pyrolysis temperature rose (**Table 4**). Lower contents of nutrients in plant straw and wood derived materials when compared to animal manure biochars, regardless of pyrolysis temperature are showed in literature [30].

Nevertheless, the total amount of macronutrient determined has no relation to the supply of available nutrients [12] when biochar is added in the soil. Similarly, the initial concentration of nutrients in biochars feedstock did not secured the concentration in its biochars after the pyrolysis process. Thus, neither feedstock material nor pyrolysis temperature are good indicators of the final nutrient concentration in the biochars [10].

Micronutrients contents showed little to no variability in relation to temperature increase, for the majority of biochar samples (**Table 5**), only differences for the metallic micronutrients Fe, Mn and Zn.

Sugarcane straw biochar exhibited the highest concentration of micronutrients, especially due to the high amount of iron (Fe), that could be explained by contamination with soil, since the straw was removed from the field and was not washed before being placed inside the reactor chamber. Other element concentrated in sugarcane biochar was manganese (Mn), with linear increase as a function of temperature, reaching a maximum of 0.11 ppm when pyrolyzed at 650˚C.

Poultry litter exhibited the highest concentration of zinc (Zn) reaching 0.09 ppm, which is reflecting the common addition of Zn as a supplement in poultry diet [33]. These results represent the potential use of biochars as soil amendment.

3.1.2. Stability Indicators

Proximate analysis (**Table 6**) is an approach to evaluate recalcitrance of biochars, and its components vary mostly between different feedstocks than due to temperature increase [9]. For instance, large proportions of ash content are ex-

Table 5. Micronutrients contents (mg·kg^{-1}) in biochars and feedstock samples.

Material	Temperature of Pyrolysis (˚C)				
	350	450	550	650	
			Fe		
SC[(1)]	10.15 b[(2)]	5.88 b	6.24 b	3.68 b	$y = 26.0954 - 0.0615x + 4.3 \times 10^{-5}x^2$ ($r^2 = 0.869$; $p < 0.0001$)
RH	0.08 a	0.06 a	0.02 a	0.06 a	ns[(3)]
PL	0.44 a	0.34 a	0.45 a	0.56 a	ns
SD	0.49 a	0.49 a	0.44 a	0.51 a	ns
			Mn		
SC	0.07 b	0.08 b	0.08 c	0.11 c	$y = 0.0242 + 0.001x$ ($r^2 = 0.778$; $p < 0.0001$)
RH	0.04 a	0.04 a	0.02 a	0.04 a	ns
PL	0.05 a	0.04 a	0.05 b	0.07 b	$y = 0.1939 - 0.0007x + 10^{-6}x^2$ ($r^2 = 0.940$; $p = 0.0011$)
SD	0.05 a	0.04 a	0.05 b	0.06 b	$y = 0.0267 - 4.0 \times 10^{-5}x$ ($r^2 = 0.720$; $p < 0.0395$)
			Zn		
SC	0.03 a	0.03 bc	0.03 a	0.04 b	ns
RH	0.01 a	0.01 a	0.01 a	0.02 a	ns
PL	0.09 b	0.05 c	0.08 b	0.08 c	$y = 0.3421 - 0.0011x + 10^{-6}x^2$ ($r^2 = 0.493$; $p = 0.0001$)
SD	0.03 a	0.02 ab	0.01 a	0.02 a	ns

[(1)]SC = sugarcane straw, RH = rice husk, PL = poultry litter, SD = sawdust. [(2)]Means followed by the same letter are not different for biochars in the same pyrolysis temperature by Tukey's test 5%. [(3)]Regression analysis was not significant for linear and quadratic models.

Table 6. Proximate analysis if biochar and feedstock samples.

Material	Temperature of Pyrolysis (˚C)					
	Feedstock	350	450	550	650	
			Volatile Matter (%)			
SC[(1)]	90.6	50.1 b[(2)]*	45.2 b*[(3)]	44.0 c*	43.8 b*	$y = 55.8667 - 0.0201x$ ($r^2 = 0.772$; $p = 0.0010$)
RH	77.0	25.8 a*	26.5 a*	24.2 a*	28.0 a*	ns[(4)]
PL	69.7	60.8 c*	46.9 bc*	45.7 c*	42.1 b*	$y = 139.0231 - 0.3163x + 2.6 \times 10^{-4}x^2$ ($r^2 = 0.944$; $p = 0.0002$)
SD	93.6	54.0 b*	50.0 c*	35.3 b*	29.1 a*	$y = 86.8058 - 0.0894x$ ($r^2 = 0.953$; $p < 0.0001$)
			Ash (%)			
SC	8.5	24.2 b*	16.0 b*	17.0 b*	13.3 b*	$y = 60.2596 - 0.1447x + 1.1 \times 10^{-4}x^2$ ($r^2 = 0.848$; $p = 0.0055$)
RH	19.5	40.4 c*	40.5 c*	42.0 c*	42.0 c*	ns

Continued

PL	29.7	38.2 c*	51.0 d*	50.3 d*	48.8 d*	$y = -53.5375 + 0.3893x + 3.7 \times 10^{-4}x^2$ ($r^2 = 0.927$; $p < 0.0001$)
SD	1.2	1.2 a	0.9 a	1.0 a	1.2 a	ns
			Fixed Carbon (%)			
SC	0.0[5]	21.9 b*	35.2 c*	35.2 b*	38.7 c*	$y = -51.1921 + 0.2976x + 2.5 \times 10^{-4}x^2$ ($r^2 = 0.915$; $p = 0.0005$)
RH	0.0	31.0 c*	29.5 b*	30.8 b*	27.2 b*	ns
PL	0.0	0.0 a	1.0 a	2.8 a	7.5 a*	$y = -12.6417 + 0.0300x$ ($r^2 = 0.967$; $p < 0.0001$)
SD	0.0	41.5 d*	45.6 d*	60.3 c*	66.5 d*	$y = 8.5892 - 0.0897x$ ($r^2 = 0.954$; $p < 0.0001$)

[1]SC = sugarcane straw, RH = rice husk, PL = poultry litter, SD = sawdust. [2]Means followed by the same letter are not different for biochars in the same pyrolysis temperature by Tukey's test 5%. [3]Means followed by an asterisk refer to differences between each biochar and its respective original biomass by Dunnett test 5%. [4]Regression analysis was not significant for linear and quadratic models. [5]Values of 0.00 were near the instrument detection.

hibited by poultry litter biochar, which corroborates with literature [9]. Animal derived biochar composition reached approximately 50% of ash content and between 45% and 60% of volatile matter similar to the results reported by [27] [28].

Larger proportions of ash are found in crop residues than in wood derived biochar due to higher nutrient concentration on the former feedstock [9]. Values from 24% to 34% were found for rice straw decreasing with higher temperature [21] and around 37% were also reported for rice husk biochar produced at 500˚C [32]. For sugarcane straw biochar, ash values found in the literature are scarce but fall in the range of 11% to 13% increasing with temperature [29].

The unexpected decrease in ash content for this material might be explained by the volatilization of elements such as P, K and S, which can occur at lower temperatures as 500˚C [9]. The values reported for sawdust varied from more than 10% to 1% according to the type of wood and the particle size of the materials [30] [34] [35]. Ash content increases in higher temperatures, due to the release of labile components, enhancing the mineral phase proportion. Fixed C is regarded as the recalcitrant C remaining within biochar composition after thermal degradation caused by pyrolysis [1]. Fixed C content is mostly influenced by the type of feedstock than by pyrolysis temperature in the production process, even though all materials showed increase in content of fixed C while temperature increased [30]. In this sense, the content of fixed C in biochar derived from wood materials is relatively higher when compared to the different biochars, particularly when compared to poultry manure (**Table 6**). The higher ash content in the feedstock, the less effect of increasing fixed C in higher temperature [9]. Therefore, wood derived biochars produced at higher temperature have increased potential to sequester C in soil by adding organic C in stable forms.

Increasing pyrolysis temperature decreased the concentration of O and H and increased C of all materials. This reflects the decrease in surface reactivity and thus higher stability of biochars. Although C content (Table 7) was initially similar among feedstocks, the difference in concentration for each material became larger after pyrolysis [9].

This is due to the fact that each material accumulates C at different rates with increasing temperature, and most of plant based biochar show high quantities of C in relation to other nutrients, which is the opposite trend found in biochars derived from manures [12]. For instance, poultry litter (30% to 40%) showed slightly decreasing content with increasing temperature. High ash materials, such as animal manure biochar, have high inorganic C content bound to carbo-

Table 7. Elemental composition of biochar and feedstock samples.

Material		Temperature of Pyrolysis				
Feedstock		350˚C	450˚C	550˚C	650˚C	
			Carbon (%)			
SC[(1)]	42.4	60.1 b[(2)]*	65.6 c*[(3)]	67.6 c*	69.4 c*	y = 50.8267 + 0.0297x (r^2 = 0.917; p = 0.0001)
RH	36.1	32.8 a	48.6 b*	49.1 b*	49.5 b*	y = −71.8981 + 0.4236x + 3.9 × $10^{-4}x^2$ (r^2 = 0.941; p < 0.0001)
PL	30.4	38.1 a*	29.8 a	35.3 a	32.6 a	ns[(4)]
SD	45.6	71.6 c*	72.4 d*	79.8 d*	84.6 d*	y = 53.9725 + 0.0463x (r^2 = 0.929; p < 0.0001)
			Oxygen (%)			
SC	50.5	35.8 b*	30.0 b*	29.2 b*	26.7 b*	y = 44.4900 − 0.0281x (r^2 = 0.892; p = 0.0009)
RH	58.6	66.1 d*	49.4 c*	49.4 c*	49.0 c*	y = 79.0567 − 0.0512x (r^2 = 0.617; p < 0.0001)
PL	62.0	55.9 c	68.5 d*	61.5 d	65.1 d	y = −1.0937 + 0.2462x + 2.3 × $10^{-4}x^2$ (r^2 = 0.471; p = 0.0129)
SD	48.4	24.3 a*	22.9 a*	16.6 a*	12.4 a*	y = 40.2542 − 0.0424x (r^2 = 0.951; p < 0.0001)
			Hydrogen (%)			
SC	6.1	2.4 b*	2.8 a*	2.2 b*	2.5 b*	ns
RH	5.1	1.1 a*	2.0 c*	1.5 a*	1.5 a*	y = −4.3064 + 0.0237x + 2.3 × $10^{-5}x^2$ (r^2 = 0.595; p = 0.0043)
PL	4.5	3.4 c*	1.7 a*	1.4 a*	0.9 a*	y = 12.9610 − 0.0383x + 3.1 × $10^{-5}x^2$ (r^2 = 0.953; p = 0.0003)
SD	6.0	3.9 c*	4.1 b*	3.2 c*	2.8 b*	y = 5.6183 − 0.0042x (r^2 = 0.815; p < 0.0001)

[(1)]SC = sugarcane straw, RH = rice husk, PL = poultry litter, SD = sawdust. [(2)]Means followed by the same letter are not different for biochars in the same pyrolysis temperature by Tukey's test 5%. [(3)]Means followed by an asterisk refer to differences between each biochar and its respective original biomass by Dunnett test 5%. [(4)]Regression analysis was not significant for linear and quadratic models.

nates, which can decrease the C by 24% [9] [36]. Biochars derived from sugarcane straw exhibited total C values ranging from 67% to 73% [29] while for rice hull biochar results varied from 36% to 39% [32]. For wood derived biochars, as sawdust feedstock, total C content showed largest variation with increasing temperature, ranging from 51% to 77%. Nitrogen content varied within feedstock, exhibiting highest values for sugarcane straw (1.43%) and poultry litter biochars (1.46%), and the lowest for sawdust (0.3%) and rice hull biochars (0.02%). However, contrary to literature [9], N regression analysis was not significant for linear and quadratic models, showing no variability with temperature increase. Hydrogen and oxygen contents decreased in all biochars. This is an indication of carbonization and aromatization of carbon structures during pyrolysis reaction, and it is reflected in the lower reactivity of biochars as temperature increases [37].

FTIR spectroscopy results of all biochars exhibited flattening of bands located between 3200 and 3400 cm^{-1} with increasing temperature (**Figure 1**), indicating less intensity of the O-H stretching due to dehydration [38].

All biochar samples showed decrease in the intensity of the band at 1700 cm^{-1} after pyrolysis process, which indicates the release of carbonyl and carboxyl organic groups, and is also associated to CEC reduction. Moreover, FTIR spectroscopy showed that with higher temperature the broadening and flattening for all biochar spectra indicates loss of labile aliphatic compounds [25] and maintenance of more recalcitrant compounds, such as aromatic chains. Specifically to the stretching at 2900 cm^{-1}, all samples showed flattening representing the loss of aliphatic C-H bond [21]. The pyrolysis of cellulose, hemicellulose and lignin was indicated by the absence of functional groups, which was more noticeable for the sugarcane straw and sawdust biochars, around 1030 cm^{-1} [10] [39].

The three main components of biomass; hemicellulose, cellulose and lignin have different chemical structures and thus, correspondingly thermal stability [40]. Thermogravimetric analysis (**Figure 2**) indicated the thermal decomposi-

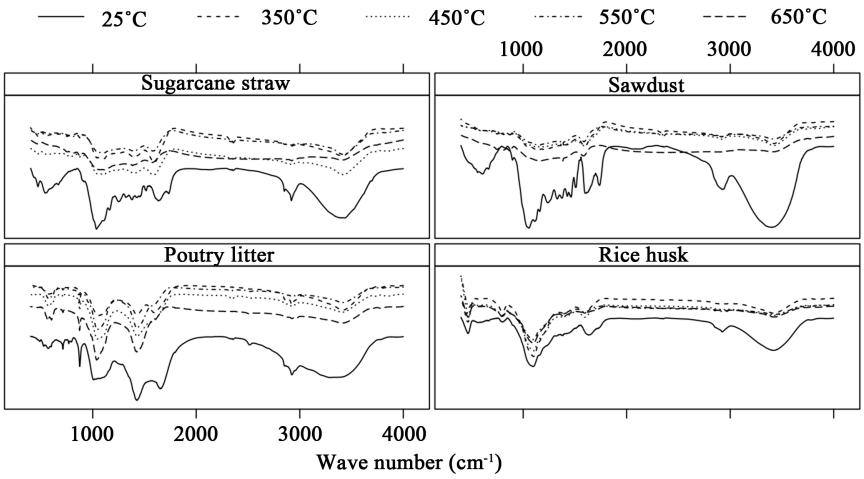

Figure 1. FTIR spectra displayed for all treatments of all biochar samples and feedstock.

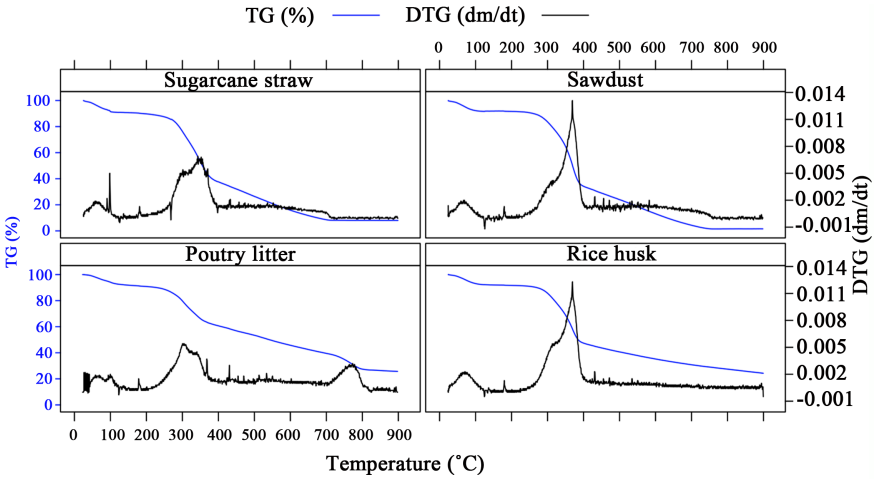

Figure 2. Results from thermogravimetric analysis in all treatments. TG (%) is the cumulative mass loss in temperature increase, and DTG (dm/dt) is the derivative of the TG curve.

tion behavior of lignocellulosic component for each biomass [39]. In all materials, the mass loss within the first stage of temperature increased, up to 105˚C, indicating water release. The peaks observed between temperatures of 200˚C to 300˚C and 300˚C to 400˚C relate to the release of hemicellulose and cellulose, respectively [34]. Lignin has a much higher molecular weight and during pyrolysis it decomposes over a wider range of temperature, contributing for the formation of condensed aromatic carbon in biochar's structure [40]. The interval between 300˚C and 400˚C is the highest for all samples from 20% to 50% mass loss, the highest value exhibited by sawdust and the lowest by poultry litter. Sugarcane straw and rice hull lost about 38% of its mass in the same range of temperature.

This corroborates with high cellulose contents in wood materials and low in animal manure. The cumulative mass loss was the lowest in poultry manure and rice hull within the temperature range analyzed (from 25˚C to 900˚C), which was also found by [11] [34].

3.1.3. Biochar Amended Soils and CO_2-Eq Emission

In both soil types, the cumulative CO_2-eq emissions in sugarcane straw and poultry litter biochar amended soils presented similar results when each treatment was compared to control (**Table 8**) excluding poultry litter biochar pyrolysed at 350˚C. As shown previously, biochar from poultry litter has higher ash content and volatile matter in comparison with sugarcane straw biochars in both pyrolysis temperatures (**Table 6**).

The higher proportion of volatile matter determined in the poultry litter biochar (**Table 6**) indicates higher amount of easily degradable source of C, enabling its use by the microorganisms, which in turn cause soil respiration to spike when comparing to control treatment. In sandy soils, lower initial C content was incremented, amongst other elements that were also added to the soil with poul-

Table 8. Cumulative CO_2-eq emissions, total C and N and EC from clayey soil incubated with sugarcane and poultry litter biochars pyrolysed at 350˚C and 650˚C.

Feedstock	Pyrolysis Temp.	CO_2 eq cumulative ($mg \cdot kg \cdot soil^{-1}$)	Total N (%)	Total C (%)	EC ($mS \cdot m^{-1}$)
		Typic Hapludox			
SC[(1)]	350˚C	153.94 ± 16.1	0.43 ± 0.01*[(1)]	5.38 ± 0.04*	134.70 ± 4.12*
	650˚C	153.52 ± 24.55	0.40 ± 0.03*	5.40 ± 0.18*	114.30 ± 4.43
PL	350˚C	251.01 ± 43.89*	0.51 ± 0.02*	4.76 ± 0.09*	242.61 ± 19.37*
	650 ˚C	163.12 ± 29.62	0.39 ± 0.01*	4.90 ± 0.09*	236.07 ± 18.40*
Control		185.55 ± 35.7	0.29 ± 0.01	2.92 ± 0.06	106.08 ± 19.42
		Quartzipsament			
SC	350˚C	163.45 ± 34.94	0.19 ± 0.01*	3.09 ± 0.21*	82.42 ± 2.31*
	650˚C	129.82 ± 13.22	0.14 ± 0.03*	2.74 ± 0.06*	94.91 ± 1.40*
PL	350˚C	348.95 ± 47.49*	0.24 ± 0.01*	2.41 ± 0.11*	231.17 ± 11.44*
	650˚C	103.05 ± 38.79	0.13 ± 0.01*	2.58 ± 0.14*	253.48 ± 6.87*
Control		136.01 ± 22.81	0.09 ± 0.01	0.74 ± 0.08	28.20 ± 5.16

[(1)]SC = sugarcane straw, PL = poultry litter. [(2)]Means followed by an asterisk refer to differences between each biochar and its respective original biomass by Dunnett test 5%.

try litter biochar application, enabling microbial degradation which reflected in higher CO_2-eq emission. The lower reactivity of sandy soils, demonstrated by lower CEC (**Table 2**), is unable to buffer the addition of biochar in the soil [41]. The higher CO_2-eq emissions in poultry litter biochar amended soils is also reflected in the lower total C determined in the samples at the end of the incubation period. These aforementioned treatments showed the lowest levels of total C, indicating that the C added with biochar was metabolized and emitted, while the higher values, presented by sugarcane straw biochar treated soil corroborate the persistence of highly stable C structures. As the less recalcitrant material, poultry litter biochar at 350˚C, was a readily available C and N source for soil microorganisms to perform mineralization.

4. Conclusions

This study demonstrated how pyrolysis reaction affects biochar properties depending on the temperature range and the feedstock type. During pyrolysis, contrasting feedstock showed similar trends, such as the increase in pH values, and the concentration of macronutrients such as P, K, Ca and Mg. The extent of these trends however, occurred differently. Stability indicators showed same results, where release of O and H, while accumulation of C were influenced by the initial contents of such elements in each of the feedstocks.

It is essential to note that agricultural properties, that support the use of biochar as nutrient source, were improved in manure derived biochars, while C sta-

bility was lower. Contrastingly, wood derived biochars developed higher stability and have potential to be applied as C sequestration strategy; however, did not exhibit properties of agricultural interest. Biochars produced from crop residues showed intermediary properties and have the potential to fulfill both functions in soil. Specifically, the use of sugarcane straw biochar as C sequestration strategy is encouraged in this study, considering that CO_2-eq emissions of biochar treated soils were similar to soil-only treatments. Further analysis should be carried to investigate the potential of sugarcane biochar as a nutrient source in cropping systems.

Overall these results demonstrate the potential of biochar as soil amendment, the selection of biochar for agricultural purposes or as a C sequestration strategy, however, must consider the biochar's chemical properties along with the environmental conditions and expected results after application.

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References

[1] Lehmann, J. and Joseph, S. (2009) Biochar for Environmental Management: An Introduction. In: Lehmann, J. and Joseph, S., Eds., *Biochar for Environmental Management: Science and Technology*, Routledge, Abingdon, 416.

[2] Luo, L., Xu, C., Chen, Z. and Zhang, S. (2015) Properties of Biomass-Derived Biochars: Combined Effects of Operating Conditions and Biomass Types. *Bioresource Technology*, **192**, 83-89. https://doi.org/10.1016/j.biortech.2015.05.054

[3] Mukome, F.N.D., Zhang, X., Silva, L.C.R., Six, J. and Parikh, S.J. (2013) Use of Chemical and Physical Characteristics to Investigate Trends in Biochar Feedstocks. *Journal of Agricultural and Food Chemistry*, **61**, 2196-2204. https://doi.org/10.1021/jf3049142

[4] Wang, J., Xiong, Z. and Kuzyakov, Y. (2016) Biochar Stability in Soil: Meta-Analysis of Decomposition and Priming Effects. *GCB Bioenergy*, **8**, 512-523. https://doi.org/10.1111/gcbb.12266

[5] Wang, D., Fonte, S.J., Parikh, S.J., Six, J. and Scow, K.M. (2017) Biochar Additions Can Enhance Soil Structure and the Physical Stabilization of C in Aggregates. *Geoderma*, **303**, 110-117. https://doi.org/10.1016/j.geoderma.2017.05.027

[6] Woolf, D., Amonette, J.E., Street-Perrott, F.A., Lehmann, J. and Joseph, S.D. (2010) Biochar as Carbon Negative in Carbon Credit under Changing Climate. *Nature Communications*, 1-56.

[7] Singh, B.P., Hatton, B.J., Singh, B., Cowie, A.L. and Kathuria, A. (2010) Influence of Biochars on Nitrous Oxide Emission and Nitrogen Leaching from Two Contrasting Soils. *Journal of Environmental Quality*, **39**, 1224-1235. https://doi.org/10.2134/jeq2009.0138

[8] Van Zwieten, L., *et al*. (2014) An Incubation Study Investigating the Mechanisms that Impact N_2O Flux from Soil Following Biochar Application. *Agriculture*, *Ecosystems* & *Environment*, **191**, 53-62. https://doi.org/10.1016/j.agee.2014.02.030

[9] Enders, A., Hanley, K., Whitman, T., Joseph, S.D. and Lehmann, J. (2012) Characterization of Biochars to Evaluate Recalcitrance and Agronomic Performance. *Bioresource Technology*, **114**, 644-653. https://doi.org/10.1016/j.biortech.2012.03.022

[10] Cantrell, K.B., Hunt, P.G., Uchimiya, M., Novak, J.M. and Ro, K.S. (2012) Impact of Pyrolysis Temperature and Manure Source on Physicochemical Characteristics of Biochar. *Bioresource Technology*, **107**, 419-428. https://doi.org/10.1016/j.biortech.2011.11.084

[11] Azargohar, R., Nanda, S., Kozinski, J.A., Dalai, A.K. and Sutarto, R. (2014) Effects of Temperature on the Physicochemical Characteristics of Fast Pyrolysis Bio-Chars Derived from Canadian Waste Biomass. *Fuel*, **125**, 90-100. https://doi.org/10.1016/j.fuel.2014.01.083

[12] Ippolito, J.A., Spokas, K.A., Novak, J.M., Lentz, R.D. and Cantrell, K.B. (2015) Biochar Elemental Composition and Factors Influencing Nutrient Retention. In: Lehmann, J. and Joseph, S.D., Eds., *Biochar for Environmental Management*: *Science*, *Technology and Implementation*, Earthscan, 137-162.

[13] Lorenz, K. and Lal, R. (2014) Biochar Application to Soil for Climate Change Mitigation by Soil Organic Carbon Sequestration. *Journal of Plant Nutrition and Soil Science*, **177**, 651-670. https://doi.org/10.1002/jpln.201400058

[14] Joseph, S.D., *et al*. (2010) An Investigation into the Reactions of Biochar in Soil. *Australian Journal of Soil Research*, **48**, 501-515. https://doi.org/10.1071/SR10009

[15] IBI (2015) Standardized Product Definition and Product Testing Guidelines for Biochar that Is Used in Soil, International Biochar Initiative. http://www.biochar-international.org/characterizationstandard

[16] Rajkovich, S., *et al*. (2012) Corn Growth and Nitrogen Nutrition after Additions of Biochars with Varying Properties to a Temperate Soil. *Biology and Fertility of Soils*, **48**, 271-284. https://doi.org/10.1007/s00374-011-0624-7

[17] ASTM International ASTM D1762-84. (2007) Standard Test Method for Chemical Analysis of Wood Charcoal. *ASTM International* 1-2, West Conshohocken.

[18] ASTM International. ASTMD 3172-13. (2013) Standard Practice for Proximate Analysis of Coal and Coke. *ASTM International* 1-2, West Conshohocken.

[19] Kim, K.H., Kim, J.Y., Cho, T.S. and Choi, J.W. (2012) Influence of Pyrolysis Temperature on Physicochemical Properties of Biochar Obtained from the Fast Pyrolysis of Pitch Pine (*Pinus rigida*). *Bioresource Technology*, **118**, 158-162. https://doi.org/10.1016/j.biortech.2012.04.094

[20] Enders, A. and Lehmann, J. (2012) Comparison of Wet-Digestion and Dry-Ashing Methods for Total Elemental Analysis of Biochar. *Communications in Soil Science and Plant Analysis*, **43**, 1042-1052. https://doi.org/10.1080/00103624.2012.656167

[21] Wu, W., *et al*. (2012) Chemical Characterization of Rice Straw-Derived Biochar for Soil Amendment. *Biomass and Bioenergy*, **47**, 268-276.

[22] Myhre, G., *et al*. (2013) Anthropogenic and Natural Radiative Forcing. In: Stocker, T.F., *et al*., Eds., *Climate Change* 2013: *The Physical Science Basis*. *Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge.

[23] Embrapa (1997) Manual de Metodos de Analise de Solo. 2nd Edition.

[24] Singh, B., Singh, B.P. and Cowie, A.L. (2010) Characterisation and Evaluation of Biochars for Their Application as a Soil Amendment. *Australian Journal of Soil Research*, **48**, 516-525. https://doi.org/10.1071/SR10058

[25] Kloss, S., *et al*. (2012) Characterization of Slow Pyrolysis Biochars: Effects of Feedstocks and Pyrolysis Temperature on Biochar Properties. *Journal of Environmental Quality*, **41**, 990-1000. https://doi.org/10.2134/jeq2011.0070

[26] Oh, T.-K., Choi, B., Shinogi, Y. and Chikushi, J. (2012) Characterization of Biochar Derived from Three Types of Biomass. *Journal of the Faculty of Agriculture*, **57**, 61-66.

[27] Song, W. and Guo, M. (2012) Quality Variations of Poultry Litter Biochar Generated at Different Pyrolysis Temperatures. *Journal of Analytical and Applied Pyrolysis*, **94**, 138-145. https://doi.org/10.1016/j.jaap.2011.11.018

[28] Meng, J., *et al*. (2013) Physicochemical Properties of Biochar Produced from Aerobically Composted Swine Manure and Its Potential Use as an Environmental Amendment. *Bioresource Technology*, **142**, 641-646. https://doi.org/10.1016/j.biortech.2013.05.086

[29] Melo, L.C.A., Coscione, A.R., Abreu, C.A., Puga, A.P. and Camargo, O.A. (2013) Influence of Pyrolysis Temperature on Cadmium and Zinc Sorption Capacity of Sugar Cane Straw—Derived Biochar. *BioResource*, **8**, 4992-5004. https://doi.org/10.15376/biores.8.4.4992-5004

[30] Zhao, L., Cao, X., Mašek, O. and Zimmerman, A.R. (2013) Heterogeneity of Biochar Properties as a Function of Feedstock Sources and Production Temperatures. *Journal of Hazardous Materials*, **256-257**, 1-9. https://doi.org/10.1016/j.jhazmat.2013.04.015

[31] Lehmann, J., *et al*. (2011) Biochar Effects on Soil Biota-A Review. *Soil Biology and Biochemistry*, **43**, 1812-1836. https://doi.org/10.1016/j.soilbio.2011.04.022

[32] Wang, Y., Hu, Y., Zhao, X., Wang, S. and Xing, G. (2013) Comparisons of Biochar Properties from Wood Material and Crop Residues at Different Temperatures and Residence Times. *Energy and Fuels*, **27**, 5890-5899. https://doi.org/10.1021/ef400972z

[33] Park, S., Birkhold, S., Kubena, L., Nisbet, D. and Ricke, S. (2004) Review on the Role of Dietary Zinc in Poultry Nutrition, Immunity, and Reproduction. *Biological Trace Element Research*, **101**, 147-163. https://doi.org/10.1385/BTER:101:2:147

[34] Ghani, W.A.K., *et al*. (2013) Biochar Production from Waste Rubber-Wood-Sawdust and Its Potential Use in C Sequestration: Chemical and Physical Characterization. *Industrial Crops and Products Journal*, **44**, 18-24.

[35] Mukherjee, A., Zimmerman, A.R. and Harris, W. (2011) Surface Chemistry Variations among a Series of Laboratory-Produced Biochars. *Geoderma*, **163**, 247-255. https://doi.org/10.1016/j.geoderma.2011.04.021

[36] Cimo, G., *et al*. (2014) Effect of Heating Time and Temperature on the Chemical Characteristics of Biochar from Poultry Manure. *Journal of Agricultural and Food Chemistry*, **62**, 1912-1918. https://doi.org/10.1021/jf405549z

[37] Chan, K.Y. and Xu, Z. (2009) Biochar: Nutrient Properties and Their Enhancement. In: Lehmann, J. and Joseph, S.D., Eds., *Biochar for Environmental Management. Science and Technology* 2009, Earthscan, 416.

[38] Mimmo, T., Panzacchi, P., Baratieri, M., Davies, C.A. and Tonon, G. (2014) Effect of Pyrolysis Temperature on Miscanthus (Miscanthus × Giganteus) Biochar Physical, Chemical and Functional Properties. *Biomass and Bioenergy*, **62**, 149-157.

https://doi.org/10.1016/j.biombioe.2014.01.004

[39] Nanda, S., Azargohar, R., Kozinski, J.A. and Dalai, A.K. (2014) Characteristic Studies on the Pyrolysis Products from Hydrolyzed Canadian Lignocellulosic Feedstocks. *Bioenergy Research*, **7**, 174-191. https://doi.org/10.1007/s12155-013-9359-7

[40] Lee, Y., *et al*. (2013) Comparison of Biochar Properties from Biomass Residues Produced by Slow Pyrolysis at 500°C. *Bioresource Technology*, **148**, 196-201. https://doi.org/10.1016/j.biortech.2013.08.135

[41] Mukherjee, A., Lal, R. and Zimmerman, A.R. (2014) Effects of Biochar and Other Amendments on the Physical Properties and Greenhouse Gas Emissions of an Artificially Degraded Soil. *Science of the Total Environment*, **487**, 26-36. https://doi.org/10.1016/j.scitotenv.2014.03.141