UNIVERSIDADE FEDERAL DE LAVRAS

RIMENA RAMOS DOMINGUES

CHARACTERIZATION OF WOOD AND HIGH-ASH BIOCHARS AND THEIR EFFECTS ON THE FERTILITY OF TROPICAL SOILS

LAVRAS – MG
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Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Ciência do Solo, área de concentração em Fertilidade do Solo e Nutrição de Plantas, para a obtenção do título de Doutor.

Prof. Dr. Carlos Alberto Silva
Orientador
Prof. Dr. Leônidas Carrijo Azevedo Melo
Coorientador

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APROVADA em 24 de março de 2017.

Prof. Dr. Leônidas Carrijo Azevedo Melo	UFLA
Prof. Dr. Guilherme Lopes	UFLA
Prof. Dr. Zuy Maria Magriotis	UFLA
Prof. Dr. Paulo Fernando Trugilho	UFLA
Dr. Tatiana Francischinelli Rittl	ESALQ

Prof. Dr. Carlos Alberto Silva

Orientador

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Ao Pedro e à Regina, com muito orgulho
pai e mãe, que me mostraram o caminho
correto e me ensinaram a fazer as
melhores escolhas.
Dedico.

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ensinamentos budistas transmitidos, os
quais são a base da minha conduta.
Ofereço.

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.

RESUMO GERAL

Biocarvão se apresenta como uma tecnologia emergente e tem demonstrado grande versatilidade de uso. Além de ser uma alternativa para o gerenciamento de resíduos de biomassas agrícolas, a adição do biocarvão pode contribuir de diferentes maneiras para a melhoria da fertilidade dos solos. Em função de seu elevado teor de carbono (C) pirogênico, a aplicação de biocarvão em solos intemperizados é fortemente desejável, visto que estes solos apresentam, devido às condições climáticas, baixos teores de matéria orgânica (MO) e, consequentemente, baixa capacidade de troca de cátions (CTC). Combinando biomassas com temperaturas de pirólise é possível obter uma série de materiais com propriedades distintas e capacidades diferenciadas de uso. Os objetivos foram: (i) caracterizar química e fisicamente os biocarvões produzidos a partir das diferentes biomassas e temperaturas de pirólise, (ii) avaliar a fertilidade de solos com texturas contrastantes após a aplicação de diferentes biocarvões, (iii) avaliar a efetividade dos biocarvões quanto à duração de seus efeitos nos solos, e (iv) avaliar a CTC de solos com texturas contrastantes tratados com doses de diferentes biocarvões. Quinze biocarvões originados após a pirólise de cinco biomassas (esterco de galinha, serragem de eucalipto, casca de café, bagaço de cana-de-açúcar e casca de pinus) em três diferentes temperaturas (350, 450 e 750 ºC) foram caracterizados por análise imediata, análise elementar, difração de raios-X, espectroscopia de infravermelho com transformada de Fourier, pH, condutividade elétrica, CTC, carbono solúvel e poder alcalinizante. O teor de Ca e K das biomassas, o elevado pH e poder alcalinizante, bem como a presença de carbonatos nos biocarvões de casca de café e esterco de galinha indicam o potencial destes biocarvões como fontes de nutrientes e corretivo de acidez. Biocarvões derivados de madeira e bagaço de cana-de-açúcar possuem potencial para elevar o estoque de C em solos tropicais devido aos parâmetros que indicam maior aromaticidade. Na segunda etapa, no decorrer de 1 ano, pH, CTC, P e K disponível e Al trocável foram determinados em Latossolo e Neossolo tratados com dose de 2% de biocarvões de casca de café e casca de pinus. Biocarvão rico em cinzas, tal como a casca de café, reduziu a acidez dos solos e elevou excessivamente a disponibilidade de K, sendo estes resultados observados desde o início da incubação. O efeito da casca de café na disponibilidade de P se mostrou dependente da temperatura de pirólise. Biocarvão de casca de pinus, rico em C, não foi efetivo em alterar a fertilidade dos solos. Por último, testou-se o efeito de doses de doze biocarvões (esterco de galinha, serragem de eucalipto, casca de café e bagaço de cana pirolisados a 350, 450 e 750 ºC) como materiais para o aumento da CTC de solos com texturas contrastantes. A CTC dos solos foi positivamente afetada pelo alto valor de CTC dos biocarvões e pelo efeito indireto desses no pH dos solos, os quais foram associados aos biocarvões ricos em cinza (casca de café e esterco de galinha) produzidos a 350 ºC.

Palavras-chave: C pirogênico. CTC. Casca de café. Esterco de galinha. Fertilidade do solo. Solos tropicais.

GENERAL ABSTRACT

Biochars presents itself as an emerging technology and has demonstrated great use versatility. In addition to being an alternative for the management of agricultural biomass, the addition of biochars can contribute in different ways to the improvement of soil fertility status. Due to the high content of pyrogenic C, the application of biochar in weathered soils is strongly desirable, since these soils present, due to climatic conditions, low levels of organic matter (OM) and, consequently, low capacity to retain nutrient – low CEC. By combining biomass with pyrolysis temperatures, it is possible to obtain a series of charred matrices with properties capable to change soil properties. The aims of this study were: (i) to characterize chemically and physically the biochars produced from five biomasses massively found in Brazil in in different pyrolysis temperatures, (ii) to evaluate the fertility of soils of contrasting texture and organic matter (OM) amended with contrasting biochar samples and incubated during 1 year; (iii) to investigate the effectiveness of biochars in changing soil properties considering the dynamics of soil fertility attributes; (iv) to evaluate the CEC of soils with contrasting textures and OM and treated with increasing rates of wood and high-derived biochars. Fifteen biochars originated from five biomasses (chicken manure, eucalyptus sawdust, coffee husks, sugarcane bagasse and pinus bark) pyrolyzed at three different temperatures (350, 450 and 750 ºC) were characterized by proximate analysis, elemental composition, X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), pH, electrical conductivity (EC), CEC, soluble carbon and liming value. The Ca and K content of the biomasses, the high pH and liming value as well as the presence of carbonates in the biochars of coffee husk and chicken manure indicate the potential of these charred matrices to act as liming materials and to supply nutrients (K and P) in tropical acidic soils. Biochars derived from wood and sugarcane have greater potential for improving C storage in tropical soils tha high-nutrient derived biochars due to a higher aromatic character of lignified biochars. In the second experiment, pH, CEC, available P and K and exchangeable Al were determined in Latosol and Neosol treated with coffee bark and pine bark biochars at a rate of 2% (w/w). High-ash biochar, such as coffee husk, reduced the acidity of the soils and increased the availability of K excessively at the beginning and during the one-year basis soil-biochar incubation. The effect of the coffee husk on the availability of P was dependent on the pyrolysis temperature employed during high-nutrient biochars. Biochars from pinus bark, rich in condensed and aromatic C, was not effective in changing the soil fertility status, but was very effective in increased the C stored in soils. Finally, it was investigated the effect of increasing rates twelve biochars (derived from chicken manure, eucalyptus sawdust, coffee husks and sugarcane bagasse and pyrolysed at 350, 450 and 750 ºC) on the changes of CEC of contrasting textural and OM tropical soils. CH and CM biochars are very effective in change soil CEC, but increased in negative charge density is soil-dependent. In fact, increase in soil CEC rely on the biomass, pyrolysis temperature, biochar CEC, changes in soil pH of soil biochar treated soil and also depends on the soil investigated and its interaction with the biochar applied. The positive effects of biochar on soil CEC was predominantly affected by high CEC-biochar and its capacity do neutralize soil acidity, which are positively linked to high-ash biochars produced at low-temperatures (350 ºC).

Key Words: Pyrogenic C. CEC. Coffee husk. Chicken manure. Tropical soil. Soil fertility.

SUMÁRIO

1 INTRODUÇÃO

Na última década, a produção de biocarvão, cada vez mais, tem sido alvo de interesse científico e público, fato verificado pelo aumento abrupto de estudos a partir de 2007 (NOVOTNY et al., 2015). Embora aparentemente recente, o uso de biocarvão como condicionador de solos não é um conceito novo (LEHMANN et al., 2006). A partir de constatações feitas nas *Terras Pretas de Índio* (formadas pela população pré-colombiana) de que o C pirogênico é o elemento chave para a elevada fertilidade desses solos (CUNHA et al., 2009; FALCÃO et al., 2009), surgiu a ideia de transformar resíduos orgânicos, por meio dos métodos de pirólise, em formas mais estáveis de carbono (C), ou seja, em biocarvões. (GLASER et al., 2001; STEINER, 2007). Particularmente para os solos tropicais, predominantemente intemperizados (LOPES; GUIMARÃES GUILHERME, 2016), essa característica é fortemente desejável, visto que os teores de matéria orgânica (MO) são baixos e a capacidade de troca de cátions (CTC) é extremamente dependente da MO (MADARI et al., 2009). Além do acúmulo de C e dos benefícios associados ao C, tais como aumento da CTC e da capacidade de retenção de água (CRA), o fornecimento de nutrientes (P, K, Ca e micronutrientes) (CANTRELL et al., 2012; NOVAK et al., 2009), e a correção da acidez de solos (SIGUA et al., 2016; WANG et al., 2014; YUAN et al., 2011) são exemplos de outros benefícios relatados com a aplicação de biocarvão no solo.

Diante o cenário mundial de geração de resíduos de biomassa agrícolas, onde o Brasil se destaca com sua elevada produção (IPEA, 2012), e à busca por alternativas adequadas de destinação, o uso dessa biocarvão se mostrou ainda mais promissor e recomendável. Segundo o Relatório de Pesquisa “Diagnóstico dos Resíduos Orgânicos do Setor Agrossilvopastoril e Agroindústrias Associadas” (IPEA, 2012) foram contabilizados, somente no ano de 2009, aproximadamente a produção de 291 milhões de toneladas de resíduos oriundos das principais culturas do Brasil. Desse montante, a cana-de-açúcar foi a cultura que mais gerou resíduos, com 201 milhões de toneladas (torta de filtro e bagaço).

Entretanto, embora exista um consenso quanto a importância do biocarvão como uma tecnologia emergente, em função da particularidade de cada resíduo e dos inúmeros processos de produção, é possível obter uma série de biocarvões com propriedades distintas e capacidades diferenciadas de uso. Isso aponta para a necessidade constante de se averiguar as características dos biocarvões, bem como as propriedades do solo e suas interações, haja vista que ignorá-los pode implicar na obtenção de efeitos não desejados, tanto em relação às mudanças, que podem comprometer a qualidade do solo, quanto pelo aumento de custo, já que produzir é tarefa que ainda não ganhou escala comercial, portanto, que ainda de custo elevado.

Nos estudos que avaliam o papel do biocarvão em suprir nutrientes e condicionar o solo, o primeiro passo é a caracterização dos biocarvão e sua incubação em solos, para compreender a relação das caraterísticas do biocarvão com seu desempenho em diferentes solos, bem como a persistência dos efeitos no decorrer no tempo. Os objetivos do presente trabalho foram: (i) caracterizar química e fisicamente os biocarvões produzidos a partir das diferentes biomassas e temperaturas de pirólise, (ii) avaliar a fertilidade de solos com texturas contrastantes após a aplicação de diferentes biocarvões, (iii) avaliar a efetividade dos biocarvões quanto à duração e dinâmica de seus efeitos nos solos, e (iv) avaliar a CTC de solos com texturas contrastantes tratados com doses de diferentes biocarvões.

A tese está dividida em três capítulos apresentados na forma de artigos para a publicação em revistas científicas. O primeiro capítulo, intitulado *Properties of biochar derived from wood and high-nutrient biomasses with the aim of agronomic and environmental benefits*, envolveu a caracterização de quinze biocarvões originados após a pirólise de cinco biomassas (esterco de galinha, serragem de eucalipto, casca de café, bagaço de cana-de-açúcar e casca de pinus) em três diferentes temperaturas (350, 450 e 750 ºC). O estudo identifica parâmetros fundamentais para a recomendação de uso e orientações de experimentos futuros. No segundo capítulo, com o título *Fertility status related to benefits and drawbacks from coffee husk and pine biochar application to weathered soils*, é descrito um estudo de incubação de biocarvões de casca de café e casca de pinus em dois solos de texturas contrastantes. Neste trabalho, são investigados os benefícios desses materiais para a fertilidade em função de coletas periódicas de solo durante 1 ano. O último capítulo (*Ameliorating Cation Exchange Capacity of Highly Weathered Soils with Tailored Biochars*) refere-se à avaliação de doze biocarvões (esterco de galinha, serragem de eucalipto, casca de café e bagaço de cana pirolisados a 350, 450 e 750 ºC) como materiais para o aumento da capacidade de troca de cátions (CTC) de solos com texturas contrastantes.

2 CONSIDERAÇÕES GERAIS

Embora haja um grande volume de estudos com biocarvões publicados na última década, são poucas as informações sobre os potenciais agronômicos e ambientais dos biocarvões produzidos a partir de esterco de galinha, casca de café, bagaço de cana, serragem de eucalipto e casca de pinus – resíduos produzidos em grande quantidade no Brasil. Isto aponta para a necessidade de, ao menos, utilizar informações de caracterização antes de direcionar a aplicação desses materiais no solo para um determinado fim. Este estudo é, portanto, uma análise criteriosa de informações de caracterização, a qual permitiu compreender satisfatoriamente as relações da condições de *produção de biocarvão e suas propriedades*, tornando-se indispensável para uma primeira triagem antes da aplicação no solo.

De posse das informações levantadas na fase de caracterização, a realização de ensaios simples de incubação em solos indicaram com maior precisão se um determinado biocarvão é o mais indicado em cenário específico, como por exemplo, em solos contrastantes quanto à textura e teor de matéria orgânica. Neste sentido, este estudo pode eleger alguns parâmetros, tanto do biocarvão como do solo, como decisórios para a aplicação de biocarvão no solo. Por exemplo, parâmetros como o teor de cinzas e a capacidade de neutralização da acidez (*liming value*) do biocarvão são determinações básicas que devem ser consideradas quando objetiva-se corrigir solos ácidos, ou mesmo reduzir os riscos de alcalinização. Verificou-se que os biocarvões de esterco de galinha e casca de café, cujos teores de cinzas foram os maiores em relação aos demais biocarvões, apresentaram também os maiores valores de poder de neutralização. Para apoiar os resultados de caracterização, esses mesmos biocarvões quando aplicados em solos apresentaram os maiores valores de pH. É possível afirmar ainda que os resultados obtidos nos dois estudos de incubação de biocarvões em solos contrastantes permitem concluir que a dose de biocarvão deve ser modulada com base nas propriedades do solo, tais como textura e teor de matéria orgânica. Este exemplo ilustra como os dados de caracterização e incubação são complementares e indispensáveis.

Ensaios de incubação são testes simples e relativamente rápidos. No entanto, averiguar os efeitos destes biocarvões em estudos com plantas é uma forma mais realista de obter informações dos benefícios dos biocarvões, ou mesmo os possíveis riscos de toxicidade de biocarvões, tornando o uso destes biocarvões agronomicamente eficiente.

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SEGUNDA PARTE – ARTIGOS

Properties of biochar derived from wood and high-nutrient biomasses with the aim of agronomic and environmental benefits[1]

Rimena R. Domingues [1*], Paulo F. Trugilho [2], Carlos A. Silva [1], Isabel Cristina N. A. de Melo [2], Leônidas C. A. Melo[1], Zuy M. Magriotis [3], Miguel A. Sánchez-Monedero[4]

[1] Department of Soil Science, Universidade Federal de Lavras, UFLA, Caixa Postal 3037, CEP 37200-000, Lavras, Minas Gerais, Brazil

[2] Forest Sciences Department, Universidade Federal de Lavras, UFLA. Caixa Postal 3037, CEP 37200-000, Lavras, Minas Gerais, Brazil

[3] Chemistry Department, Universidade Federal de Lavras, UFLA. Caixa Postal 3037, CEP 37200-000, Lavras, Minas Gerais, Brazil

[4] Centro de Edafología y Biología Aplicada del Segura (CEBAS-CSIC), Departmento de Conservación de Suelos y Agua y Manejo de Residuos Orgánicos, Campus Universitario de Espinardo, 30100. Murcia, Spain.

*Corresponding author

E-mail address: rimena_r@yahoo.com.br (RRD).

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Abstract

Biochar production and use are part of the modern agenda to recycle wastes and, to retain nutrients, pollutants, and heavy metals in the soil and to offset some greenhouse gas emissions. Biochars from wood (eucalyptus sawdust, pine bark), sugarcane bagasse, and substances rich in nutrients (coffee husk, chicken manure) produced at 350, 450 and 750 ºC were characterized to identify agronomic and environmental benefits, which may enhance soil quality. Biochars derived from wood and sugarcane have greater potential for improving C storage in tropical soils due to a higher aromatic character, high C concentration, low H/C ratio, and FTIR spectra features as compared to nutrient-rich biochars. The high ash content associated with alkaline chemical species such as $KHCO_3$ and $CaCO_3$, verified by XRD analysis, made chicken manure and coffee husk biochars potential liming agents for remediating acidic soils. High Ca and K contents in chicken manure and coffee husk biomass can significantly replace conventional sources of K (mostly imported in Brazil) and Ca, suggesting ahigh agronomic value for these biochars. High-ash biochars, such as chicken manure and coffee husk, produced at low-temperatures (350 and 450 ºC) exhibited high CEC values, which can be considered as a potential applicable material to increase nutrient retention in soil. Therefore, the agronomic value of the biochars in this study is predominantly regulated by the nutrient richness of the biomass, but an increase in pyrolysis temperature to 750 ºC can strongly decrease the adsorptive capacities of chicken manure and coffee husk biochars. A diagram of the agronomic potential and environmental benefits is presented, along with some guidelines to relate biochar properties with potential agronomic and environmental uses. Based on biochar properties, research needs are identified and directions for future trials are delineated.

Introduction

Large amounts of crop residues are generated worldwide and they are not always properly disposed of or recycled. Wood log production in Brazil generates about 50.8 million m^3 of lignocellulosic residue yearly [1], while nearly 200 million tons/year of sugarcane bagasse is generated [2]. In 2016, 49 million bags of coffee [3] were harvested and almost the same amount (by weight) of coffee husk was produced. Based on the Brazilian chicken flock and on the average amount of manure produced per animal, about 12 million t $year^{-1}$ of manure were generated in Brazil in 2009 [1]. Chicken manure is characterized by high N, P, Ca, and micronutrient contents, while coffee husk contains the highest K concentration [4]. Sugarcane bagasse and wood-derived wastes have low amounts of nutrients and high lignin and cellulose content.

In humid tropical areas, the application of raw residues on soils is the main management practice, but this has limited impact on increasing C in soils due to high organic matter decomposition rates [5]. *In natura* disposal of coffee husk in crop fields may lead to an increased population of *Stomoxys calcitrans*, a pest that may cause damages to dairy cattle and feedlots [6]. Conversion of wastes into biochar increases the recalcitrance of C due to increased proportions of condensed aromatic compounds in the biochar, which ensures higher persistence of C in the soil compared to the C from raw biomass [7]. In addition, conversion of wastes into biochar reduces residue volume, generates energy, improves the efficiency of nutrient use by crops, eliminates pathogens, and generates products with high agronomic value [8 – 10].

Characterization of biochars generated from the main Brazilian organic wastes is the first step in identifying agronomic and environmental applications and guiding future research trials. Plant-derived biochars have high aromatic C content due to the greater amount of lignin and cellulose present, which gives the biochar high stability and resistance to microbial decomposition [11]. Animal manures have high contents of labile organic and inorganic compounds, resulting in biochars with high ash content, which is positively related to the nutrient and chemical composition of the biomass [8, 12]. Higher ash, N, S, Na, and P concentration have been observed in poultry litter biochar than in peanut hull and pecan shell biochars [13]. High nutrient concentrations in the biomass can generate biochars with more ash content and alkalizing capacity [14]. Thus, biochar can be used in soils to correct acidity [12], increase soil cation exchange capacity (CEC), retain water [15 – 16, 12], and regulate C and N dynamics [17]. In addition, researchers have pointed out positive effects of biochar on soil remediation due to its adsorption of pesticides or metals [18 – 20].

We characterized biochars derived from wood, sugarcane bagasse, and nutrient-rich residues (coffee husk, chicken manure) aiming to identify potential agronomic and environmental benefits for fertilizing soil and enhancing soil quality. Our hypothesis is that nutrient-rich biochars derived from waste have fertilization potential, while biochars derived from wood and sugarcane charred at high temperature are potential for increasing C sequestered in soils. We also hypothesized that the liming value of the biochar is primarily regulated by its ash content, regardless of its pH; the mineral phase of chicken manure is effective in protecting the organic compounds from degradation, ensuring production of high CEC biochars even under high temperature (750 ^{o}C). In this study, we aimed to (i) assess the chemical and physicochemical properties of biochars derived from wood and nutrient-rich sources in terms their potential agronomic and environmental benefits, and (ii) identify potential uses and drawbacks in biochar production from contrasting biomass types and suggest guidelines for future research trials in biochar-treated soils.

Materials and methods

Biochar manufacture

Fifteen biochars were produced from five biomass and three pyrolysis temperatures (350, 450, and 750 ºC). The biomasses selected were those with greatest availability in Brazil: i) chicken manure (CM); ii) eucalyptus sawdust (ES); iii) coffee husk (CH); iv) sugarcane bagasse (SB); and v) pine bark (PB). The nutrient concentrations of the biomasses are shown in S1 Table.

The biochars were produced by a slow pyrolysis procedure in an adapted muffle furnace with a sealed chamber to prevent airflow. Prior to pyrolysis, biomass wasoven dried at 105 ºC. The amount of material used in each procedure varied according to the density of each material. A heating rate of 1.67 °C min^{-1} was adopted, and the final temperature reached were 350, 450, and 750 °C. The target temperature was maintained for 30 minutes and the biochar sample was cooled to room temperature. The yield of the biochar mass was calculated as follows:

Yield (%) = [100 × (biochar mass/105 ºC dried biomass)].

Biochar characterization

Yield and ash content

The volatile material, ash, and fixed carbon concentrations were determined according to standard procedure D-1762-84, established by the American Society for

Testing and Materials [21]. The biochar samples (< 0.25 mm) were oven dried at 105 °C and then heated in a covered crucible inside a muffle furnace at 950 °C for 6 minutes. The resulting loss of mass refers to volatile material (VM). The biochar was then returned to the oven and heated in an open crucible at 750 °C for 6 hours. The mass of material remaining after incineration refers to ash. Finally, the fixed carbon (FC) concentration was determined by the following equation:

$$FC\ (\%) = [100 - (VM + Ash)].$$

Thermogravimetric analysis (TGA) was performed using a Shimadzu DTG-60H device. Samples of approximately 5 mg were heated from room temperature to 600 °C at a rate of 10 °C min^{-1} and a nitrogen flow of 50 mL min^{-1}. Then, the first derivative of the TGA curve was calculated, which establishes loss in mass over the temperature range employed.

Biomass and biochar elemental composition

The elemental composition (C, H, N, S) of the biochars was determined on 0.5 g of ground and sieved (200 mesh) material by dry combustion using TOC and CHNS analyzers (Vario TOC cube, Elementar, Germany). Biochar oxygen concentrations were obtained by difference as follows: O (%) = 100 – (% C + H + N + S + Ash). The biochar elemental composition was used to calculate the H/C, O/C, and (O + N)/C ratios [22].

Water-soluble organic carbon (WSOC) and water-soluble inorganic carbon (WSIC) was measured in a 10% (w v^{-1}) biochar-water mixture shaken for 1 h and then filtered through a 0.45 μm membrane filter. In the liquid extracts, WSOC and WSIC were quantified using the liquid mode of a TOC analyzer (Vario TOC cube, Elementar, Germany). Considering that a single 1 h extraction is unlikely to solubilize all water-soluble organic and inorganic C from biochar, it should be take into account that WSOC and WIOC provide an index of part of water soluble C chemical species rather than 100% of all biochar soluble C; however, they were considered suitable for comparisons among biochars.

ATR-FTIR analysis

Fourier transform infrared spectroscopy (FTIR) analysis was performed on a Perkin Elmer Spectrum 1000 device equipped with an attenuated total reflectance (ATR) accessory, in which the powder of each sample was inserted in a diamond crystal gate. All biomass and biochars had been dried at 65 ºC and sieved through a 0.150 mm mesh. FTIR spectra from 32 scans was recorded in the wavenumber range 4000-500 cm^{-1} with 2 cm^{-1} resolution. The broad band chemical group assignments described in Jindo et al. [23] were used to interpret the FTIR-ATR spectra.

X-ray diffraction

The X-ray diffraction (XRD) analysis was carried out at the XRD1 beam-line of the Brazilian Synchrotron Light Laboratory (LNLS), Campinas, SP, Brazil, for detection of all mineral phases present in the biochars. Powdered biochar samples (< 150 mesh) were inserted in glass capillaries and analyzed in the X-Ray diffractometer through the range of 4-60 ° 2 in a transmission mode with steps of 0.2 ° 2 and a wavelength of about 1.0 Å. Minerals found in the biochar structure were identified after calculation of the *d* spacing according to Bragg's law. The peak areas identified for different minerals were compared with XRD patterns of standard minerals compiled by the Mineralogy Database available at "web minerals" (http://webmineral.com/).

Chemical and physicochemical attributes

Biochar pH was measured in deionized water and in a 0.01 mol L^{-1} $CaCl_2$ solution at a 1:10 (w/v) ratio, after shaking the samples for 1h. All measurements were performed in triplicate. Biochar CEC was determined by the modified ammonium acetate compulsory displacement method, adapted to biochars [24]. During CEC determination, a vacuum filtration system was employed, and samples were filtered through a 0.45 um membrane filter. Initially, 0.5 g of biochar sample was leached five times with 20 mL of deionized water to remove excess salts. After that, the samples were washed three times with a 1 mol L^{-1} sodium acetate (pH 8.2) solution, followed by five washes with 20 mL of ethanol to remove free (non-sorbed) Na^+ ions. Samples were then washed four times with 20 mL of 1 mol L^{-1} ammonium acetate to displace the Na^+ from the exchangeable sites of the biochar. The leachates were collected and stored in a 100 mL volumetric flask, and Na contents in the leachates were determined by flame photometry. The CEC corresponds to the amount of Na adsorbed per unit mass of biochar, expressed as $cmol_c$ kg^{-1}.

The biochar liming value (LV) was evaluated by the acid-base titration method [25]. A quantity of 0.5 g of biochar (< 0.25-mm) was placed in a 50 mL plastic bottle, and then 20 mL of distilled water was added. The bottles were stirred for 2 h and then titrated with 0.1 mol L^{-1} of HCl solution to a pH 2.0 end point. To ensure that the biochar pH was stabilized at 2.0, after 12 h of equilibration, the pH was again measured and, if necessary, corrected with the HCl solution already mentioned. Based on the assumption that alkalinity is the capacity of biochar to accept protons from a 0.05 M HCl solution ($1.3 \leq pH \leq 2$) after 72 h of equilibration [26], LV is a partial measurement of biochar total alkalinity. The volume of acid used and its pH value were recorded. These results were used to calculate the LV, here defined as the volume of 0.1 mol L^{-1} HCl necessary to reduce the biochar pH by one unit, according to the following equation:

Liming value (volume of HCl/pH unit) = (total volume of HCl to reach the titration end point/pH interval).

Experimental design and statistical analysis

Biochars are hereby referred by the biomass abbreviation and pyrolysis temperature, for example, CH350 denotes coffee husk pyrolysed at 350 ºC and CH750, coffee husk pyrolysed at 750 ºC. The experimental design used was factorial completely randomized with five biomasses (CM, ES, CH, SB, PB) combined with three pyrolysis temperature (350, 450, 750 ºC).

The data were subjected to analysis of variance (ANOVA) for significant differences between factors as biomasses, pyrolysis temperatures, and their interaction. When significant F-tests were obtained (0.05 probability level), the factors separation was achieved using Tukey's honestly significant difference test. Data were statistically analysed employing SISVAR [27].

Results and discussion

Yield, volatile matter, and ash content

Biochar yields were reduced and ash contents increased with an increase in pyrolysis temperature (Table 1). The CM biochar at three temperatures (350, 450 and 750 ºC) showed higher yield and higher ash content than the other biochars (Table 1), due to large amount of inorganic compounds (K, P, Ca, and Mg) in this biomass (S1 Table), which accumulated after volatilization of C, O, and H compounds. Coffee husk biochar also showed a high ash content, which is probably due to the high K (22 g kg^{-1}) content of the biomass. The ES and SB biochars, regardless of the pyrolysis temperature, showed the lowest ash content (<1.1% and <2.2%, respectively) (Table 1), explained by their low nutrient content (Table S1). According to derivative thermogravimetric (DTG) curves of biomass losses (S1 Fig), ES and SB showed higher mass loss between 250 and 350ºC, which is attributed to high cellulose content in the biomass [28], which is easily degraded during low-temperature pyrolysis. CM, CH and, PB biochars showed lower mass loss between 250 and 350ºC indicating higher thermal stability (S1 Fig).

Table 1. Yield and proximate analysis (volatile matter, ash, carbon fixed) of biochars produced at different pyrolysis temperatures.

Biomass	Temp. (ºC)	Yield (%)	Proximate analysis (wt. %)		
			Volatile Matter	Ash	Carbon Fixed
Chicken manure	350	69.7	36.9 Ab	52.0 Ba	11.1 Cd
	450	63.0	30.6 Ba	55.3 Aa	14.1 Be
	750	55.9	26.5 Ca	56.4 Aa	17.0 Ae
Eucalyptus sawdust	350	42.5	36.9 Ab	0.9 ABe	62.2 Cb
	450	36.0	28.5 Bb	0.7 Be	70.8 Bb
	750	28.2	6.5 Cd	1.1 Ae	92.4 Aa
Coffee husk	350	43.5	34.6 Ac	12.9 Bb	52.5 Cc
	450	37.7	26.2 Bc	12.9 Bb	60.9 Bc
	750	31.6	17.6 Cb	19.6 Ab	62.8 Ad
Sugarcane bagasse	350	37.5	35.0 Ac	1.9 Ad	63.0 Ca
	450	33.2	24.0 Bd	2.1 Ad	73.9 Ba
	750	26.9	7.7 Cc	2.2 Ad	90.1 Ab
Pine bark	350	59.6	38.5 Aa	8.3 Bc	53.2 Cc
	450	49.3	29.3 Ba	7.9 Bc	62.8 Bc
	750	38.9	6.0 Cd	14.5 Ac	79.4 Aa

Uppercase letters compare pyrolysis temperatures within the same biomass and lowercase letters compare biomass at the same temperature. The same letter do not differ by the Tukey test at $p < 0.05$.

Biochar volatile matter values reduced as the pyrolysis temperature was raised from 450 °C to 750 °C (Table 1). This is explained by an the increase in aromatization and greater losses of gas products, tar oil and low molecular weight hydrocarbons as a result of increasing pyrolysis temperature [28]. CM750 and CH750, however, showed the smallest losses of volatiles (Table 1) in contrast to the other biochars prepared at this same temperature. This was coincident with higher quantities of ash found in these biomasses, which can protect the organic fraction and structures of biochars during pyrolysis [29–31]. Chemical activation of KOH impregnation has a catalytic effect in intensifying hydrolysis reactions, increasing volatile products [32, 33] and the development of pores in the charcoal structure [31], suggesting a role for pores in the adsorption of volatile materials [33]. Fixed C was inversely correlated with the ash contents and was higher in eucalyptus sawdust and sugarcane bagasse biochar compared to other biochars produced (Table 1).

Elemental composition and soluble C fractions

Total C concentrations in plant-derived biochars increased with an increase in pyrolysis temperature (Table 2), whereas the O and H concentrations diminished (Table 2). Biochars derived from plant biomass showed the highest C concentration, up to 90% C for ES and SB pyrolyzed at 750ºC (Table 2). Increase in C concentrations with a rise in pyrolysis temperature occurs due to a higher degree of polymerization, leading to a more condensed carbon structure in the biochar [11]. Similar results were reported for biochars produced from pine straw [22], peanut shells [13], sugarcane bagasse [34], and wheat straw [35]. The greater the degree of formation of aromatic structures is, the higher the resistance of the biochar to microbial degradation [36, 7]. The C concentration in CM biochar reduced with an increase in pyrolysis temperature (Table 2). Such results suggest that the organic compounds found in animal waste are more labile and are rapidly lost as pyrolysis temperature is increased, before the formation of biochar with recalcitrant compounds. A 6% reduction in C concentration in poultry litter biochar was reported when pyrolysis temperature was increased from 350 °C to 700 °C [8], as well as a decrease in sewage sludge biochar C content [37]. The C concentration in CM biochar was lower (≈ 30% C) than wood biochars (Table 2). These results are in agreement with those of Novak et al. [13].

Table 2. Elemental composition (C, H, S, O), and atomic ratios (H/C, O/C) of biochars produced at different pyrolysis temperatures.

Biomass	Temp. (ºC)	Elemental composition (%)				Atomic ratio	
		C	H	S	O	H/C	O/C
Chicken manure	350	31.2 Ad	7 Ac	0.31 Ba	10.9 Bc	0.76 Ba	0.26 Ba
	450	27.2 ABd	1.92 Bc	0.44 Aa	11.4 Bc	0.85 Aa	0.31 Ba
	750	24.7 Bd	0.67 Cc	0.29 Ba	16.3 Aa	0.32 Ca	0.49 Aa
Eucalyptus sawdust	350	70.4 Ca	3.81 Ab	0.02 Ac	24.0 Aab	0.65 Aa	0.26 Ab
	450	78.6 Ba	3.42 Ba	0.01 Ac	16.6 Bab	0.52 Bb	0.16 Bc
	750	90.9 Aa	1.52 Ca	0.04 Ac	5.6 Cc	0.20 Cc	0.05 Cc
Coffee husk	350	60.5 Bc	3.92 Ab	0.09 Bb	19.5 Aab	0.78 Aa	0.24 Aa
	450	61.3 Bc	3.65 Ba	0.10 Bb	19.0 Aa	0.71 Aa	0.23 Ab
	750	66.0 Ac	1.57 Ca	0.23 Ab	9.8 Bb	0.29 Bb	0.11 Bb
Sugarcane bagasse	350	74.7 Ca	4.26 Aa	0.03 Ac	17.9 Ab	0.68 Aa	0.18 Ab
	450	81.6 Ba	3.66 Ba	0.05 Ac	11.3 Bbc	0.54 Bb	0.10 Bc
	750	90.5 Aa	1.64 Ca	0.06 Ac	4.3 Cc	0.22 Cc	0.04 Cc
Pine bark	350	67.6 Cb	3.73 Ab	0.01 Ac	28.7 Aa	0.66 Aa	0.32 Aa
	450	75.2 Ba	2.74 Bb	0.02 Ac	24.7 Ba	0.44 Bb	0.25 Bc
	750	86.3 Aab	1.16 Cb	0.04 Ac	19.1 Ca	0.16 Cc	0.17 Cc

Uppercase letters compare pyrolysis temperatures within the same biomass and lowercase letters compare biomass at the same temperature. The same letter do not differ by the Tukey test at p <0.05.

The H/C and O/C ratios of biochars derived from plant biomass decreased as the pyrolysis temperature was increased (Table 2), indicating increasing aromaticity and a lower hydrophilic tendency, respectively [8, 13]. An increase in the aromatic character of biochars is associated with dehydration reactions and removal of O and H functional groups, as well as the formation of aromatic structures, as charring is intensified [11]. These features are consistent with the van Krevelen diagrams generated in this study, which showed a positive relationship between H/C and the O/C atomic ratios (Supplementary Fig S2). Biochars derived from CM did not change H/C and O/C ratios or the degree of aromaticity as the pyrolysis temperature increased from 350 to 450 ºC (Table 2).

The sugarcane bagasse biomass had the highest WSOC concentration (94.5g kg^{-1}) (Fig 1A). However, with increasing pyrolysis temperature, WSOC concentration in bagasse were significantly reduced (< 0.2g kg^{-1}), suggesting that the water-soluble carbon is degraded or incorporated into the organic compounds of biochar even at a relatively low pyrolysis temperature.

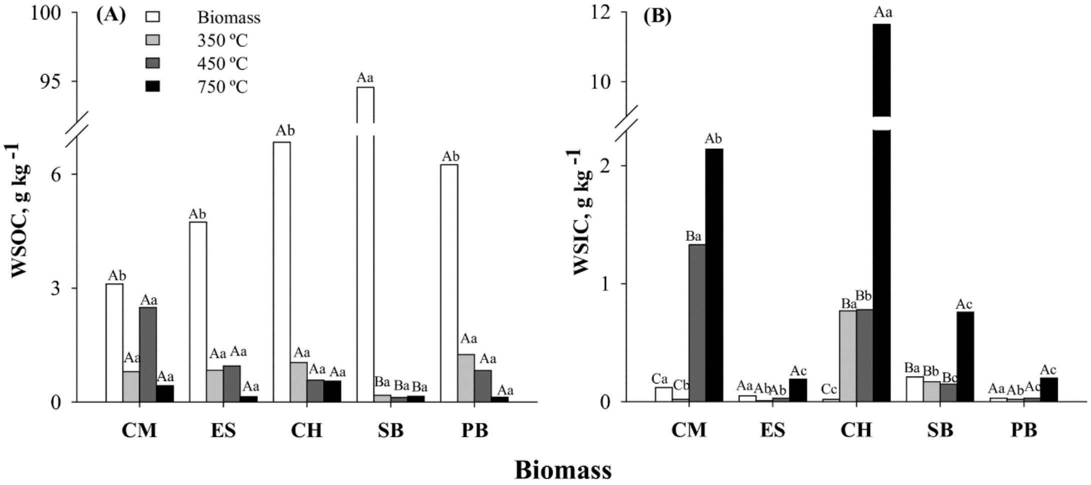

Fig 1. Water-soluble organic carbon – WSOC (A) and water-soluble inorganic carbon – WSIC (B) of biomasses and biochars at different pyrolysis temperatures
Legend: CM = chicken manure, ES = eucalyptus sawdust, CH = coffee husk, SB = sugarcane bagasse, and PB = pine bark.
Uppercase letters compare pyrolysis temperatures within the same biomass and lowercase letters compare biomass at the same temperature. Bar followed by the same letter do not differ by the Tukey test at $p < 0.05$

The biochar WSIC concentration increased with pyrolysis temperature (Fig 1A). The highest WSIC concentration (11.7g kg^{-1}) was verified for CH750. WSIC-coffee biochar was significantly (p<0.05) different from the other biochars produced at other pyrolysis temperatures. The WSIC concentrations of CM and SB biochars were also influenced by the pyrolysis temperature, especially those samples pyrolyzed at 750 ºC, whose WSIC concentration were 2.1 g kg^{-1} and 0.8 g kg^{-1}, respectively (Fig 1B). For the other biochar samples, the WSIC concentration was not significantly (p<0.05) different

(Fig 1B). The higher WSIC concentration found in CH750 in comparison with similar low-temperature biochar is probably due to the presence of the mineral kalicinite (Fig 2), a K inorganic compound with high solubility in water [38].

Spectroscopic characterization

X-ray diffractometry

Mineral components in the crystal form were identified in the CM, CH and PB biochars (Fig 2). No crystal substances were observed in the X-ray diffraction spectra for ES and SB biochars. For CM biochars produced at all temperatures, the presence of calcite ($CaCO_3$) was identified by peaks at 3.85, 3.03, 2.49, 2.28, 2.09, 1.91, and 1.87 Å (Fig 2A). The presence of calcite in CM biochars is consistent with the high Ca content found in the chicken manure biomass (S1 Table). The presence of calcite in this biochar sample is probably due to the addition of phosphogypsum in manure, normally used to stabilize N forms during composting [4], as well as the use of calcium carbonate in chicken diets. Similarly, calcite and dolomite [$CaMg(CO_3)_2$] were identified in sewage sludge biochar at 300–800 ºC [39].

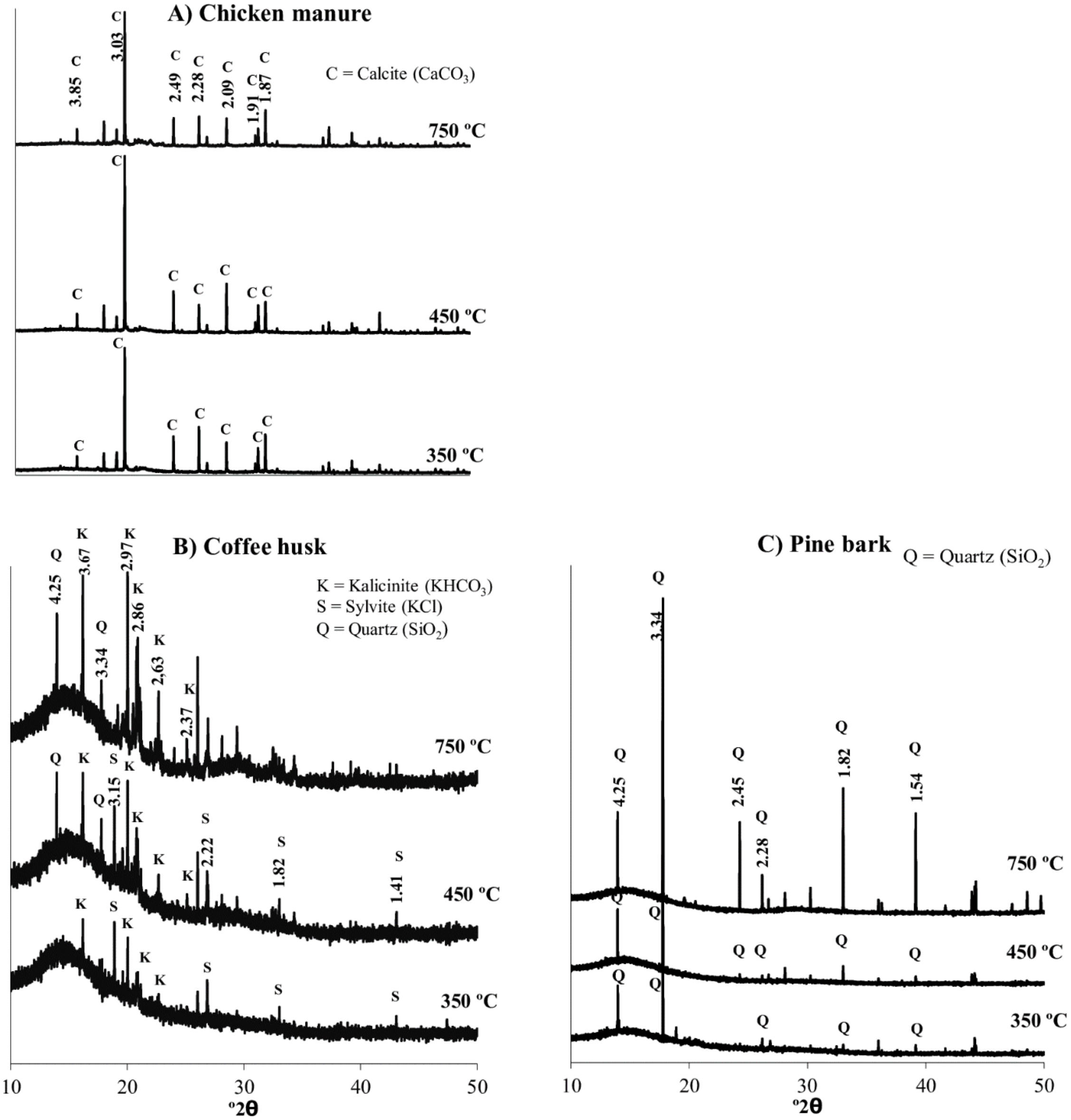

Fig 2. X-ray diffraction spectra of biochars pyrolized at different temperatures (350, 450 and 750 °C).
(A) Chicken manure biochar. (B) Coffee husk biochar. (C) Pine bark biochar.

For all CH biochars, the presence of kalicinite ($KHCO_3$) was observed (Fig 2B). The formation of $KHCO_3$ may have been favored by the reaction of K with CO_2 released during thermal decomposition of hemicellulose and cellulose [32]. An increase in the amounts of $KHCO_3$ may also explain the high WSIC contents found in CH biochars (Fig 1). The peak intensity at 3.67 Å increased with increasing pyrolysis temperature, indicating relative accumulation of kalicinite in CH biochars. The peaks at 3.15, 2.22, 1.82, and 1.41 Å were found in CH350 and CH450 were attributed to the presence of sylvite (KCl) (Fig 2B). In durian shell biochar, kalicinite was also the dominant mineral [38]. The presence of quartz (SiO_2) was also confirmed in CH450 and CH750 from peaks at 3.34 and 4.25 Å in the X-ray spectra. Identification of SiO_2 was also noted in the biochars produced from PB biochar at the three pyrolysis temperatures (Fig 2B). Yuan et al. [25] also identified the presence of sylvite and calcite in biochars from canola straw pyrolyzed at 300, 500, and 700 ºC.

FTIR analysis

The FTIR-ATR biomass and biochar spectra are shown in Fig 3. The spectra of the all biomass samples showed a broad band at 3200-3400 cm^{-1}, which is attributed to -OH from H_2O or phenolic groups [22, 40, 11]. For all biomass sources, absorption in the region between 2920 and 2885 cm^{-1} (C-H stretching) was assigned to aliphatic functional groups [8, 40, 11], and the strong band at 1030 cm^{-1} is due to the C-O stretching and associated with oxygenated functional groups of cellulose, hemicellulose, and methoxyl groups of lignin [8, 35, 41] [3–5]. The intense bands at 1270 cm ^{1} were assigned to phenolic –OH groups [22].

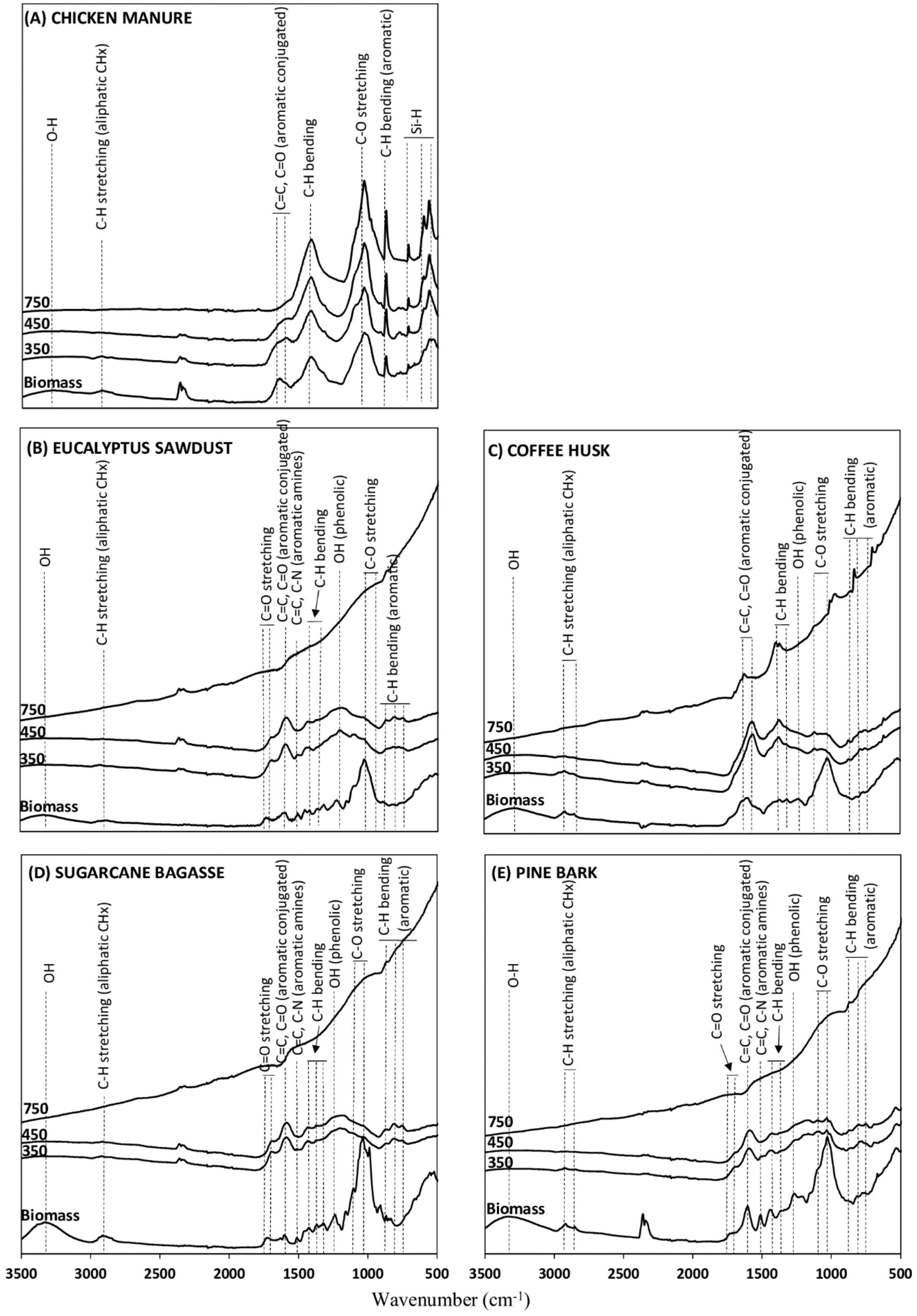

Fig 3. FTIR-ATR spectra of biomasses and their respective biochars pyrolyzed at 350, 450, and 750 °C

Legend: (A) Chicken manure. (B) Eucalyptus sawdust. (C) Coffee husk. (D) Sugarcane bagasse. (E) Pine bark.

Changes in biochar organic structure were apparent when biomass was pyrolyzed at 350 ºC, except for the CM biochars (Fig 3). The intensities of bands of -OH (3200 – 3400 cm^{-1}), aliphatic C-H stretching (2920 and 2885 cm^{-1}), -OH phenolic (1270 cm^{-1}), and C-O stretching region (1030 cm^{-1}) decreased sharply due to degradation and dehydration of cellulosic and ligneous components, even at low temperatures (350 °C) [35, 22]. An increase in band intensity in the 1600 cm^{-1} region (C=C, C=O of conjugated ketones and quinones) and the appearance of weak bands between 885 and 750 cm^{-1} (aromatic CH out-of-plane) were attributed to an increasing degree of condensation of the biochar organic compounds. An increase in the degree of biochar condensation as pyrolysis temperature increases is in agreement with the results reported by Keiluweit et al. [35], Jindo et al. [23], and Melo et al. [40]. In the FTIR spectra of ES750, SB750, and PB750 biochars most of the organic functional groups present in the biochar structure were lost (Fig 3B, 3D, and 3E). For CH biochars, weak bands remaining at the highest pyrolysis temperature were identified, which were assigned to aromatic C=C stretching (at about 1600 cm^{-1}), $-C-H_2$ bending (1400 cm^{-1}), and aromatic C-H bending (885 cm^{-1}). Losses of chemical groups in CH750 could explain the sharp decrease in CEC of this biochar in comparison to CH350 and CH450. In the CM biochars, the intensity of all organic functional bands remained largely unchanged after the biomasses were subjected to the charring process, regardless of the pyrolysis temperature used (Fig 3A). Protection of organic groups, even at high pyrolysis temperature, may be associated with the high ash content found in coffee husk and chicken manure (Fig 3). Ash acts as a heat resistant component, which may protect organic compounds against degradation and may hinder the formation of aromatic structures as charring intensity advances [42].

Physicochemical properties

The pH in water of the biochars ranged from slightly acidic to alkaline (Fig 4A). Overall, the pH values of biochars were higher than 6.0 units. Compared to the biomass pH, the charring process increased pH in water and, in some cases, differences were up to 4 pH units for some of the biomasses pyrolyzed at 750 °C (Fig 4A). An increase in biochar pH with pyrolysis temperature has been reported for corn straw [25], sewage sludge [36], pine [43], poultry litter [44], and sugarcane straw [40] biochars. With increasing temperature, there is an enrichment of basic cations in the ashes, which may be associated with alkaline species, such as carbonates, oxides and hydroxides [25, 45], and a reduction in the concentration of acidic surface functional groups [16]. Among biochars, the highest pH values were recorded for the CM biochars, which exhibited a pH of 9.7 (at 350 ºC), 10.2 (at 450 ºC), and 11.7 (at 750 ºC) (Fig 4A). In general, all biochars pyrolyzed at 750 ºC showed pH values higher than 8.0.

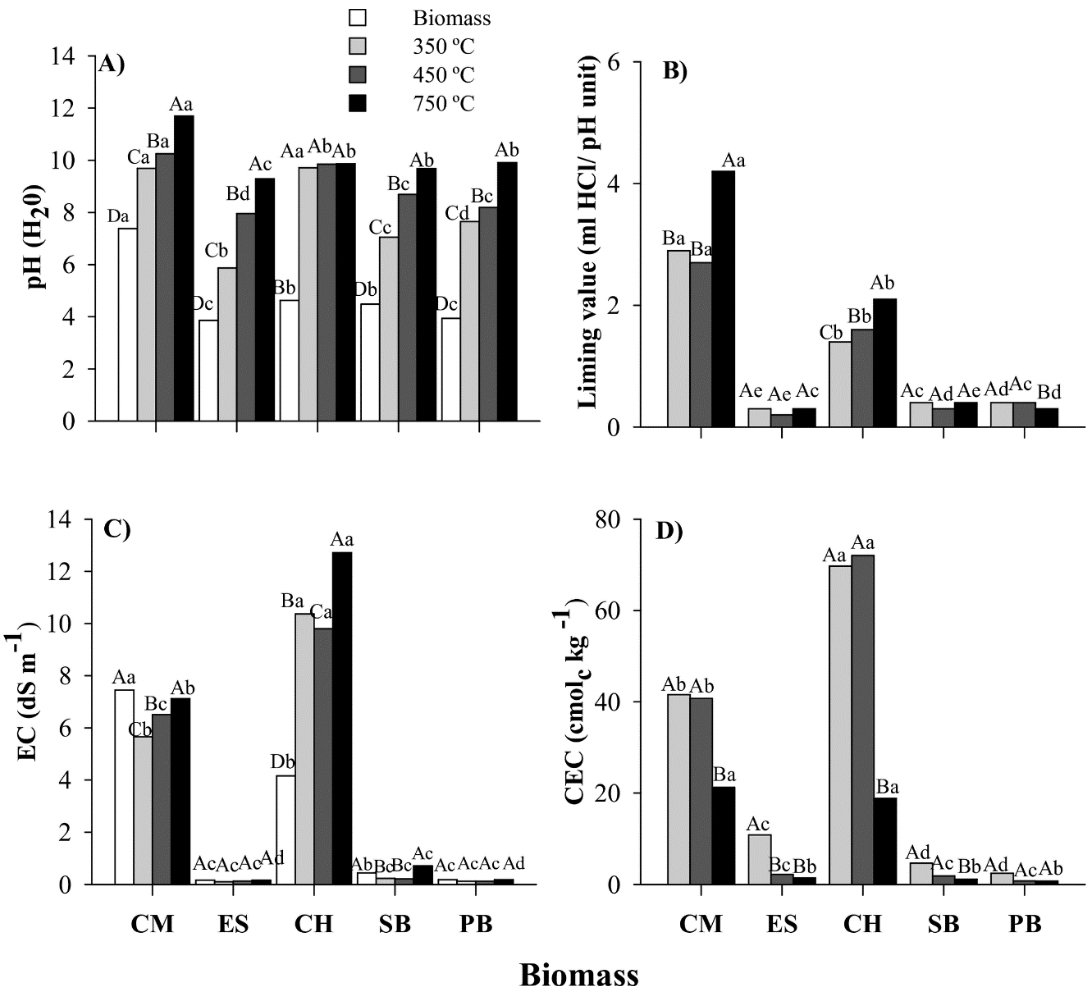

Fig 4. Values of pH-H₂0 (A), liming value (B), EC – electrical conductivity (C), and CEC – cation exchange capacity (D) as related to biomass and biochars.
Legend: CM = chicken manure, ES = eucalyptus sawdust, CH = coffee husk, SB = sugarcane bagasse, and PB = pine bark.
Uppercase letters compare pyrolysis temperatures within the same biomass and lowercase letters compare biomass at the same temperature. Bar followed by the same letter do not differ by the Tukey test at $p < 0.05$

Biochars of ES, SB, and PB produced at all pyrolysis temperatures used in this study showed reduced liming values (capacity to neutralize acidity) (Fig 4B), i.e, the ability to correct soil acidity should not only be evaluated by the pH value. CM and CH biochars, regardless of the pyrolysis temperature, showed higher liming values compared to the other biochars (4B), which were related to the high mineral concentration in chicken manure and coffee biochars, specifically to the calcium and potassium carbonates found in their respective X-ray diffraction spectra (Fig 2A and 2B). The presence of carbonates has been previously reported as the main alkaline components of the biochars [25]. Biochars produced from tomato [46] and paper sludge [16] showed high liming value, which was attributed to the presence of calcite and other carbonate minerals in these biochars. Thus, the biochar liming value is mainly regulated by the biochar ash content and chemical composition (especially of basic cations) and, to a much lesser extent, by the biochar pH. This characteristic should be considered when biochar is added to soils to correct soil acidity.

Electrical conductivity (EC) was mainly influenced by the biomass used in biochar production (Fig 4C). At all pyrolysis temperatures, the CH biochar showed the highest EC value, followed by the CM biochar (Fig 4C). These results, among other factors, may be due to the presence of soluble minerals, i.e., kalicinite and sylvite, in CH biochar (Fig 2B) and calcite in CM biochar (Fig 2A), and may be related to the high levels of WSIC in both biochars, as well (Fig 1B).

Biochar cation exchange capacity (CEC) values varied greatly, and are mainly dependent on the biomasses and the temperature used in the pyrolysis process (Fig 4D). CH350 and CH450 stood out from the other biochars due to the high CEC values (means of 69.7 $\text{cmol}_c\ \text{kg}^{-1}$ at 350 ºC and 72.0 $\text{cmol}_c\ \text{kg}^{-1}$ at 450 ºC) (Fig 4D). CM biochars produced at low temperatures (350 ºC and 450 ºC) also showed high CEC values (21.3 $\text{cmol}_c\ \text{kg}^{-1}$) (Fig 4D). Negative charge density on biochar surfaces produced at low temperatures is attributed to the exposure of functional groups, such as carboxylic acids, ketones, and aldehydes released by depolymerization of cellulose and lignin [47, 22, 35]. CH and CM biomasses also exhibited high K concentration, which can intercalate and cause the separation of carbon lamellae by the oxidation of cross-linking carbon atoms, resulting in formation of surface groups at the edge of the carbon lamellae [32]. ES, SB, and PB biochars shown low CEC, with mean values for biochar pyrolyzed at 350 ºC of

10.8, 4.6, and 2.4 $\mathrm{cmol_c\ kg^{-1}}$, respectively (Fig 4D). An increase in pyrolysis temperature from 450 ºC to 750 ºC reduced the biochar CEC values, except for PB biochar (Fig 4D). These results were supported by the FTIR spectra shown in Fig 3, in which most of the organic group assignments and bands responsible for generating negative charges were lost, indicating the removal of oxygen-containing functional groups at most of the biochar at high temperature (750 ºC). Song and Guo [44] also verified that as carboxylic and phenolic group assignments disappear, the biochar CEC is lower; consequently, depending on the biomass charred, CEC is inversely correlated with pyrolysis temperature. In conclusion, biochar CEC is mainly regulated by the biomass rather than by pyrolysis temperature; however, the increase in temperature from 450 ºC to 750 ºC leads to a drastic reduction in the CEC of some biochars.

Biochar properties related to potential environmental benefits

Carbon concentration, atomic ratios, and biochar FTIR fingerprints can be used as predictors of C persistence in biochars in soils. High C content, low H/C ratio, and FTIR spectrum features recorded for biochars derived from high temperatures are key indices of the aromatic character, stability against degradation in soils, and, consequently, high C residence time in biochar-treated soils [34, 6, 48]. Considering these, it is expected greater aromatic character for ES750, SB750, and PB750 than nutrient-rich biochars (S1 Table). As pointed out by Bruun et al. [34], the use of these biochars with a possible high residence time may be an important strategy to increase C sequestration in Brazilian soils, acting to offset greenhouse gas emissions.

In Brazil, agriculture is the main source of greenhouse gas (GHG) emissions. Most of the N_2O emissions originate from rice fields fertilized with N and from manure deposition by cattle grazing in low and intensively managed animal production systems.

Feedstock type, production temperature and process, soil properties, biochar rate, and biochar N-source interactions are the dominant factors that contribute to reductions in N_2O emissions from biochar-treated soils [49]. In fact, Cayuela et al. [49] reported that biochar can still effective at mitigating N_2O emissions even at pyrolysis temperatures of 400-600°C (in addition to >600°C), in application rates of 1-5%, and in coarse-textured soils with water filled pore space of <80%. In addition to the already mentioned factors, the H:Corg ratio is a suitable factor to infer the capacity of biochar in reducing N_2O emissions [50]. According to Cayuela et al. [50], biochar with H:Corg ratio <0.3 (i.e., biochar with high degree of polymerization and aromaticity) decreased N2O emissions by 73% while biochars with H:Corg ratio >0.5 only diminished N_2O emissions by 40%. Considering only the technical aspects, most of the 750 ^{o}C biochars, and especially the wood biochars produced in this study, are potential inputs for decreasing N_2O emissions in crop fields, but, due to the high application rates required, biochar use to offset N_2O emissions should be focused on more profitable processes (e.g., composting) instead of use in soil.

For the purpose of reducing CO_2 emissions, the use of low labile C biomass pyrolyzed at >550 ^{o}C is recommended [50, 51]. Based on these assumptions, sugarcane bagasse, pine bark, and eucalyptus biochars pyrolyzed at 750 ^{o}C are suitable for reducing CO_2 emissions. Nevertheless, it has been suggested that the application of biochar can increase CH_4 emissions [52, 53]. However, these studies were carried out in paddy soil, where species of methanogenic bacteria predominate and, thus, the addition of some biochars to the substrate creates a favorable environment for methanogenic microbial activity [52]. Therefore, it is very difficult to anticipate the role that may be played by the biochars characterized in this study in decreasing CH_4 fluxes from soil to air, but wood and high-surface area biochars are potential inputs for use in soil to reduce CH_4 emissions.

The labile C fraction in biochars can be easily decomposed and, in some cases, can stimulate the mineralization of native soil organic matter, through a positive priming effect [54, 33, 55, 50]. In general, these events occurred in soils treated with biochar produced at low temperature, but this condition may not be generalized. An increase in the biochar mineralization rate can be explained by the volatile material contained in the biochar, which may also be present in high concentrations in biochars produced at high temperatures [55]. Under these assumptions, chicken manure and coffee husk biochars both pyrolyzed at 750 ºC are not expected to increase C storage in soils due to their possible rapid decomposition in treated soils. The magnitude of volatile matter content in biochar is an important attribute to evaluate in C bioavailability and N cycling in biochar in the soil ecosystem. High aliphatic character (high O/C ratios and more intense FTIR peak) observed at low temperature (350 and 450 ºC) can be considered an index of biochar susceptibility to degradation by soil microorganisms, causing short-term immobilization of inorganic N in soil [33, 14]. This N immobilization may hamper the supply of N to plants in biochar-treated soils [56, 14]. Nevertheless, N immobilization can be seen as a beneficial mechanism for mitigating N_2O emissions and for reducing inorganic-N leaching from soils [57, 16].

Biochar properties related to potential agronomic benefits

Differentiation of biochars was established by the parameters evaluated, which allowed the identification and discussion of agronomic benefits. Characterization by proximate analysis (Table 1) showed clear differentiation in ash contents among the biochar samples. In many cases, high ash content ensures biochars rich in nutrients with high alkalizing capacity [14, 58]. The high ash content was associated with alkaline chemical species, such as $KHCO_3$ and $CaCO_3$, as verified by XRD analysis (Fig 2). Such characteristics make chicken manure and coffee husk biochars potential materials to increase soil acidity buffering capacity and to neutralize soil acidity, which may partially replace the large amounts of limestone used to correct soil acidity in crop fields in Brazil (Fig 5). The solubilization of these alkaline chemical species can increase soil pH, decrease Al^{3+} toxicity, reduce Fe and Mn availability, and increase soil CEC [59, 25, 60], which may decrease the precipitation and adsorption of P [61, 62], as well as enhance the supply of Ca and K to plants. The high Ca and K contents in chicken manure and coffee husk biomass (S1 Table) can significantly replace conventional sources of K (mostly imported in Brazil) and Ca, which suggests the high agronomic value of these biochars (Fig 5). However, despite the high total concentration of these chemical elements, the availability of nutrient forms in biochars should not be neglected, since an increase in pyrolysis temperature can drastically reduce the labile P forms in biochars according to [39]. Other uses of these biochars could be for remediation of some cationic trace element found in contaminated soils due to their alkalinity and high CEC (Fig 5) [63, 45, 49].

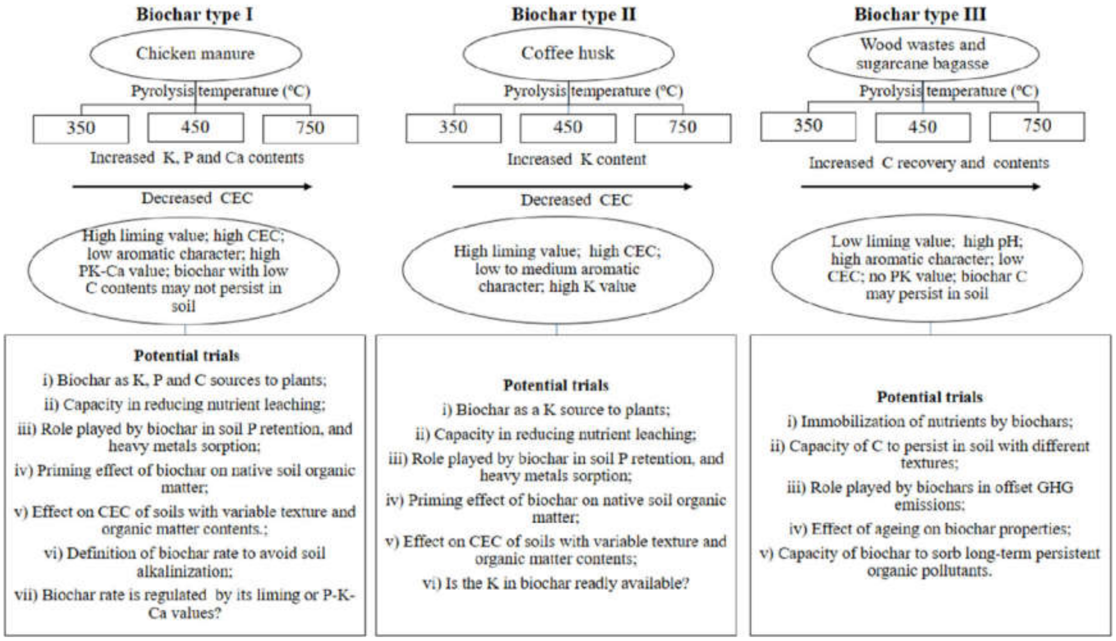

Fig 5. Simplified schematic representation in which wood, sugarcane, coffee husk, and chicken manure biochars are typified according to chemical and physiochemical properties

and potential for carrying out trials on weathered soils in regard to their potential agronomic or environmental services.

Low–temperature biochars provided the largest CEC (chicken manure and coffee husk pyrolyzed at 350-450 ºC), which can make them possible to adsorb N-NH_4^+ up to 2.3 mg g^{-1} and to reduce N leaching rates [64]. Although high-surface-area biochars generated at high temperature (>600 ºC) usually generate low CEC biochars, the aging effect may come into play, oxidizing the organic biochar , increasing the negative charge density and increasing the formation of biochar-mineral complexes [33].

Recommendations and suggestions for future trials

Wood- and sugarcane-derived biochars, regardless of the charring conditions, can potentially improve C storage in tropical soils (Fig 5). The agronomic value of biochars from wastes poor in nutrients is questionable since they have low CEC, and low ash contents. Charring intensity improved the potential capacity of wood and sugarcane biochars to offset GHG emissions due to their C-fixing and aromatic character. The potential of these aromatic biochars for increasing C sequestration is probably mediated by soil texture and organic matter contents. It is more plausible to use low nutrient and high C content biochars to decrease emissions of CO_2 rather than N_2O, due to the high biochar rates required to offset N gas emissions from soil. The potential of biochars from wood and sugarcane bagasse for remediating contaminated soils and/or increasing water retention capacity should not be overlooked. In this case, supplementary fertilization, especially with N, should be used to avoid immobilization and maintain soil fertility [65]. In Brazil, the cost associated with the use of biochars to sequester C in soils may be offset by governmental incentives such as that offered by the Brazilian government through the Low-Carbon Agriculture (Agricultura de Baixa Emissão de Carbono - ABC) Program.

The agronomic value of the biochars generated in this study is predominantly regulated by the nutrient richness of the biomass. CM and CH biochars have high agronomic value and they should be tested in crop fields in order to identify their potential for supplying K (CH and CM) and Ca (CM) to plants and for correcting soil acidity. Several experiments have been performed trying to enrich biochars with clays and minerals to modify the final characteristics of the biochars [29, 66]. With the use of chicken manure or other nutrient-rich biomasses like coffee husk, it may be possible to create biochars to reach similar results in a natural way. Among the potential uses of biochars discussed in this study, the K content in coffee husk biochars enables them to act as a slow-release K fertilizer. Considering the average coffee husk biochar yield of 63% and a mean K_2O content of 16% in the final coffee husk biochars, each ton of the potential organo-mineral K biochar fertilizer produced may be sold for < US$100 per ton, considering the current cost of K_2O in Brazil (US$ 0.625/kg). In short, all the aspects and possible functions of biochars in soil emphasize the fact that the "one biochar fits all approach" [65] is not an option for the main organic wastes available in Brazil and for the biochars produced in the charring conditions of this study. Following Yargicoglu et al. [67], whatever the potential agronomic or environmental use, screening of biochars is highly recommended, given the range of variability that biomass and the extent of thermal degradation may cause in the chemical and physicochemical properties of the chars produced.

Conclusions

In this study, the biomass source, rather than pyrolysis temperature, is the primary factor conditioning the biochar characteristics and the agronomic and environmental value of the biochar. However, pyrolysis temperature acts as a modify, changing the chemical nature and increasing the aromatic character of the organic compounds of most of the biochars investigated. In this study, characterization of the biochars was used to identify the main differences and similarities between them, offering guidelines for selecting a biomass and charring conditions to biochar end-users according to their specific soil and environmental requeriments. Biochars manufactured from ES, PB, and SB, regardless of the pyrolysis temperature employed, have potential for increasing C storage in soils, as the biochar aromatic character increases along with pyrolysis temperature. Both CH and CM biochars were also characterized by their high liming value, which make them potential materials for correcting soil acidity in crop fields. Both CH and CM biochars have a role as P and K sources for plants. High-ash biochars, such as CM and CH, produced at low-temperatures (350 and 450 ºC) exhibited high CEC values, which can be considered as a potential applicable material to retain nutrients. . Inorganic components found in CM biochar can protect its organic compounds from degradation or hinder the charring process at 750ºC. A diagram with the potential agronomic and environmental benefits of biochars is presented, and some guidelines are shown to relate the properties of biochars with their possible use. Research needs are identified and suggestions for future trials are also made.

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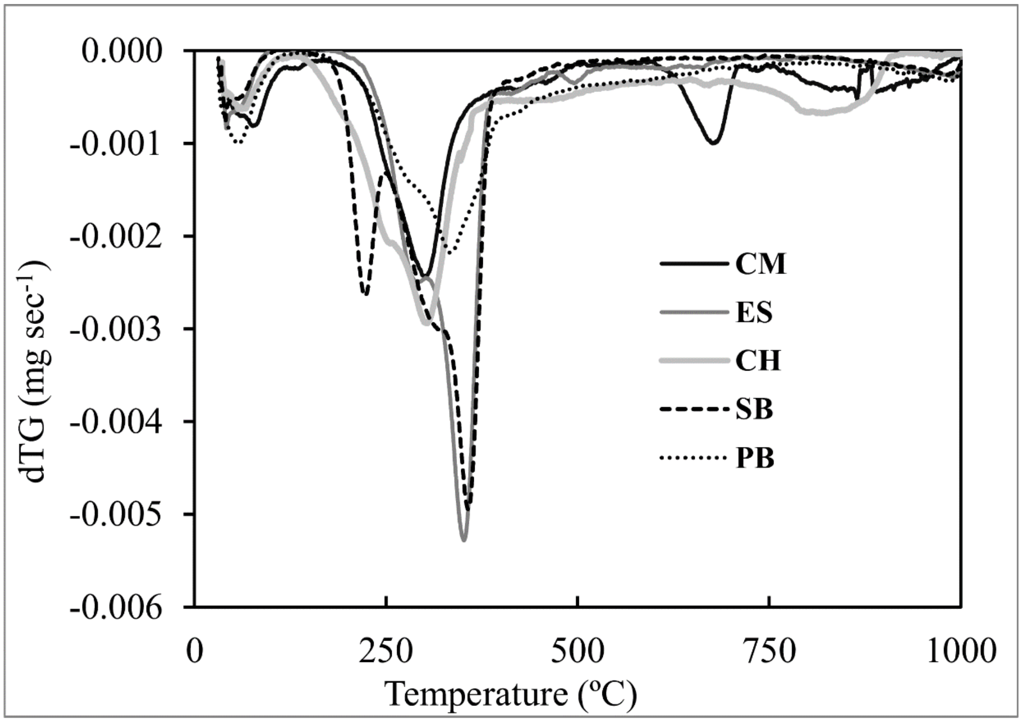
Supporting Information

S1 Table. Total nutrient contents in the biomasses investigated.

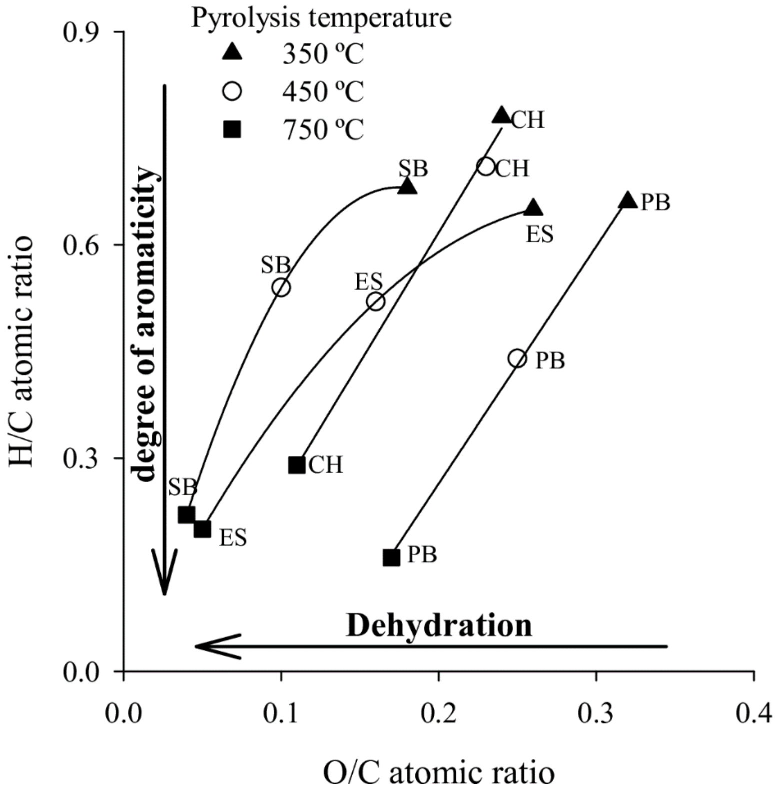
Biomass	C	N	P[1]	K	Ca	Mg	B[2]	Cu	Fe	Mn	Zn
	------%-------		——— g kg^{-1}———				——— mg kg^{-1} ———				
Chicken manure	25.2	4.9	25.9	19.3	117	4.6	38	61.8	3066	685	415
Eucalyptus sawdust	45.3	0.2	0.01	0.01	0.1	0.01	2.6	1	23.3	28.4	2.3
Coffee husk	43.3	2.9	1.1	22	1.9	0.2	17.9	16.2	222	47.7	5.5
Sugarcane bagasse	43.7	0.5	0.1	1.6	0.05	0.01	1.5	2.6	59.4	13.0	3.8
Pine bark	47.9	0.3	0.1	1.0	0.2	0.01	11.0	3.5	567	68.1	12.5

[1] The contents of P, K, Ca, Mg, Cu, Fe, Mn, and Zn were determined in extracts from the nitric-perchloric digestion procedure. [2] Total content of B extracted with hot water



S1 Fig. dTG curves of biomass.

Legend: CM = chicken manure, SE = eucalyptus sawdust, CH = coffee husk, SB = sugarcane bagasse, and PB = pine bark.



S2 Fig. van Krevelen diagram.
Legend: SE = eucalyptus sawdust, CH = coffee husk, SB = sugarcane bagasse, and PB = pine bark.

FERTILITY STATUS RELATED TO BENEFITS AND DRAWBACKS FROM COFFEE HUSK AND PINE BIOCHAR APPLICATION TO TROPICAL SOILS[2]

Rimena R. Domingues [1*], Carlos A. Silva[1], Paulo F. Trugilho [2], Leônidas C. A. Melo[1], Isabel Cristina N. A. de Melo [2], Miguel A. Sánchez-Monedero[3]

[1] Department of Soil Science, Universidade Federal de Lavras, UFLA, Caixa Postal 3037, CEP 37200-000, Lavras, Minas Gerais, Brazil

[2] Department of Forest Sciences, Universidade Federal de Lavras, UFLA. Caixa Postal 3037, CEP 37200-000, Lavras, Minas Gerais, Brazil

[3] Centro de Edafología y Biología Aplicada del Segura (CEBAS-CSIC), Departmento de Conservación de Suelos y Agua y Manejo de Residuos Orgánicos, Campus Universitario de Espinardo, 30100. Murcia, Spain.

*Corresponding author

E-mail address: rimena_r@yahoo.com.br (RRD).

Abstract

Biochar production by pyrolysis of locally available organic wastes is an environmentally friendly strategy to improve waste disposal as well as to benefit the soil fertility and C storage in tropical soils. Feedstocks and pyrolysis temperature are the main regulators on biochar characteristics and their effect in soils. However, long-term incubation studies to determine the dynamics of fertility in biochar-treated soils are lacking. This study aimed at evaluating the effects of coffee husk (CH) and pine bark (PB) biochars pyrolyzed at 350, 450 and 750 ºC on the dynamics of properties of an Oxisol (clayey) and of an Entisol (sandy). Soil pH, CEC, P and K availability, exchangeable acidity (Al^{3+}), electrical conductivity (EC), and C contents were determined in biochar-amended soils (at a 2% rate, w/w) incubated during 1, 7, 14, 28, 56, 180, and 365 days. In the evaluated times measured, the effect of biochar application on soil properties occurs immediately after its

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[2] Artigo nas normas da revista CATENA, versão preliminar.

incubation, valuable insight to measure both the long and short-term impact of biochars on soil fertility. CH biochar decreased soil acidity and increased soil pH above optimum level for growing most crops in the Entisol, which is a low buffered soil. Pyrolysis temperature is the driving force controlling the effect of CH biochar on the available P levels on both clayey and sandy soils. Potassium availability was increased excessively by CH biochars at the rate of 2%, regardless of the pyrolysis temperature and soil type. Thus, CH application rate must be adjusted based on the amount of K^+ added to the soil, to avoid over application and potential K leaching. PB biochars are not effective in changing the soil fertility status, though the wood biochar is suitable to increase C storage in sandy and clayey soils. Changes in fertility status and C storage intended in the tropical soils studied must be priority defined to tailor biochar production and its rate based on feedstock and pyrolysis temperature.

Key words: biochar agronomic value, tropical soils, K fertilizer, P availability, soil acidity neutralization.

1. Introduction

Brazil is among the largest producers of agricultural residues in the world, which has increased demand for safe and environmentally friendly disposal. Among the wastes, the production of wood logs in Brazil generates about 50.8 million m^{-3} of lignocellulosic residue yearly (IPEA, 2012), while the Brazilian coffee production (~49 million of coffee bags $year^{-1}$) represents 1/3 of the coffee grain globally harvested (CONAB, 2016). Each coffee grain bag processed generates at least one bag of coffee husk (IPEA, 2012), which is mostly produced in the state of Minas Gerais. In the last decade, the use of biochar technology as a soil amendment has attracted increased attention (Novotny et al., 2015). Motivation for producing biochar was stimulated by the high fertility status of the *Terra Preta de Índios* (Amazonian Dark Earth), where the pyrogenic carbon (C) is the primary reason for the dark, and fertile weathered soils in a moist and warm environment that favors decomposition of non-charred residues (Lehmann and Joseph, 2009). Biochar as a soil amendment is of particular interest for Brazilian weathered soils, which are characterized by the low fertility status: low pH, high exchangeable (Al^{3+}) and potential acidity (H+Al), severe deficiencies of P, Zn and B and presence of low chemical activity minerals on the clay fraction, which cause in the soil an extremely low cation exchange capacity (CEC at pH 7 < 5 $cmol_c$ dm^{-3}) (Lopes and Guimarães Guilherme, 2016).

Variations in biochar chemical and physicochemical characteristics are mainly due to feedstock type and the temperatures achieved during pyrolysis (Atkinson et al., 2010). The variability in elemental composition and in organic substances found in the biomasses are expected to lead to differences in biochars properties, as well as variations in the fertility status and crop yield responses in biochar-amended soils (Cantrell et al., 2012; Lehmann and Joseph, 2009; Novak et al., 2009). Wood biomass, a lignin-rich material, is considered suitable to increase soil C storage (Murray et al., 2015), usually showing high biochar yield with high recalcitrant C content, though it may have low potential to ameliorate tropical acidic soils in comparison to biochar produced from high-ash wastes (Bougnom et al., 2010). Conversely, high-ash biochars are potential sources of nutrients along with high liming value (Bougnom et al., 2010; Deenik et al., 2011; Smider and Singh, 2014), although it may increase soil EC (Kloss et al., 2012), especially when applied at high rates (Zhai et al., 2015). Moreover, such high-ash biochars may stimulate native C mineralization and increase the availability of N, P, S in mineral forms (Zimmerman et al., 2011). Increased mineralization o native organic matter in labile biochar-treated soils is not discharged along with subsequent increase in soil acidity indices.

In K-rich feedstocks, like coffee husk, K chemical species are, in general, soluble and readily available in biochar-treated soils (Prakongkep et al., 2014). Phosphorus, on the other hand, can be transformed from water soluble forms in the biomass into less soluble forms in the biochar (Liang et al., 2006). In addition, the complex interactions between biochar and soil type also need be investigated, since highly variable responses can be observed in soils of contrasting properties, even in situations where biochar rate applied is equal (Smider and Singh, 2014). In less buffered soils, depending on the rate ant type of biochar added to soil, pH may be drastically increased in a short time by chemical species and ions found on the biochar ash. In fact, variations of soil fertility status rely on the fertility attribute analyzed ad type of soil treated. According to the nutrient chemical species found on biochar, the effects on soil could be verified in a short time for soluble nutrient species but may last a much longer time to show up for recalcitrant C substances which need to be reprocessed by soil decomposers. Effect of biochar on soil acidity propertied may happen in a short time since most lime materials found in biochars tend to be soluble in water (Lehmann and Joseph, 2009)

We hypothesized that: (i) biochar effects on soil fertility vary across soils with contrasting properties; (ii) biochar made from high-ash biomass, such as coffee husk, is effective in correcting soil acidity and supply K and P, however the magnitude of changes in fertility status is soil-dependent; (iii) regardless of the pyrolysis temperature employed, pine bark biochars are suitable to improve C storage in tropical soils. This study aimed at evaluating: i) the dynamics of fertility status of tropical soils in a 365-day incubation experiment; ii) changes in P and K availability, CEC, EC and acidity attributes as related to the use of coffee husk and pine biochars charred in temperatures up to 750 °C in low and high buffered soil (high levels of OM and clay); iii) to verify if the use of biochars at the rate of 2% causes in tropical contrasting soils excessive application of nutrient and overlimig.

2. Material and Methods

2.1 Biochars and soils

Six biochars were produced from coffee husk (CH) and pine bark (PB) pyrolyzed at 350, 450 and 750 ºC. The pyrolysis procedure (slow process) was carried out in an electrical muffle furnace with temperature control and condensers for cooling the condensable gases derived from the pyroligneous liquid. The amount of material used in each procedure varied according to the density of each biomass. The samples were previously oven-dried at 105 ºC, until constant weight. Each sample was heated up to the desired temperature (350, 450 and 750 °C), at constant heating rate of 1.67 °C/ min, and kept for 30 min at the final temperatures.

Some selected chemical and physicochemical properties of biochars are shown in Table 1. The ash concentrations were determined according to standard procedure D-1762-84, established by the American Society for Testing and Materials (ASTM, 1990). The total C was determined by dry combustion using a TOC analyzer (Vario TOC cube, Elementar, Germany). The semi-total P and K was determined by digesting the biochar samples in concentrated nitric-acid, using microwave heating, according to the EPA 3015A analytical procedure (USEPA, 1995). Biochar pH and electrical conductivity (EC) was measured in deionized water at a 1:10 (w/v) ratio; and biochar CEC was determined by the modified ammonium acetate compulsory displacement method, adapted to biochars (Gaskin et al., 2008). The liming value was determined by the acid-base titration method (Yuan et al., 2011), and defined as the volume of 0.1 mol L^{-1} HCl necessary to reduce the biochar pH in one unit.

Table 1. Chemical and physicochemical properties of the biochars produced from coffee husk and pine bark pyrolyzed at 350, 450 and 750 ºC.

Property	Coffee husk biochar			Pine bark biochar		
	350 ºC	450 ºC	750 ºC	350 ºC	450 ºC	750 ºC
Ash (%)	12.9 ± 0.09	12.7 ± 0.09	19.7 ± 0.04	8.3 ± 0.04	8.3 ± 0.06	15.5 ± 0.09
C (%)	60.5 ± 1.69	61.3 ± 0.46	66.0 ± 2.19	67.6 ± 2.01	75.2 ± 2.52	86.3 ± 0.82
P (g kg^{-1})	3.3 ± 0.04	3.0 ± 0.10	3.5 ± 0.15	0.1 ± 0.03	0.1 ± 0.02	0.0 ± 0.01
K (g kg^{-1})	125 ± 2.28	138 ± 3.78	145 ± 3.94	2.9 ± 0.26	3.5 ± 0.18	5.4 ± 0.08
pH (H_2O)	9.7 ± 0.00	9.8 ± 0.00	9.8 ± 0.00	7.6 ± 0.03	8.2 ± 0.01	9.9 ± 0.01
EC (dS m^{-1})	10.4 ± 0.18	9.8 ± 0.09	12.7 ± 0.11	0.1 ± 0.00	0.1 ± 0.00	0.2 ± 0.00
CEC ($cmol_c$ kg^{-1})	69.7 ± 2.27	70.0 ± 3.00	18.9 ± 0.97	2.4 ± 0.57	0.8 ± 0.07	0.7 ± 0.14
Liming value (mL HCl/ pH unit)	1.4 ± 0.02	1.6 ± 0.01	2.1 ± 0.01	0.4 ± 0.00	0.4 ± 0.01	0.3 ± 0.02

C: total C; P: total phosphorus; K: total potassium; EC: electrical conductivity; CEC: cation exchange capacity at pH 8.2.

Two soils were chosen for the one-year incubation study, based on their main contrasting properties, including clay and organic C content. Samples of surface soil layer (0-0.2 m) were collected from a dystrophic Red Latosol (RL) and a Quartzarenic Neosol (QN) (EMBRAPA, 2006) located in Lavras, MG, Brazil (21º14’S, 45º00’W) and in Itutinga, MG, Brazil (21º17’S, 49º39’W), respectively. The RL and QN soils can be classified as Oxisol and Entisol, respectively, according to the Soil Taxonomy (USDA, 1998). Soil samples were air-dried and sieved to obtain fraction of < 2 mm for the incubation experiment. Soil properties were determined following analytical procedures described in Silva et al. (2009) and the mean values of soil fertility attributes are shown in Table 2.

Table 2. Basic fertility properties and clay content of the Oxisol (Red Latosol) and the Entisol (Quartzarenic Neosol) samples.

Soil attribute	Oxisol[a]	Entisol[a]
pH (1:2.5 soil:H_2O ratio)	4.3	5.3
H+Al / $cmol_c$ dm^{-3}	11.8	2.9
CEC / $cmol_c$ dm^{-3}	16	2.4
Total carbon / %	5.2	0.5
K available / mg dm^{-3}	61	60
P available/ mg dm^{-3}	4.8	15
Ca^{2+} / $cmol_c$ dm^{-3}	0.6	1.9
Al^{3+} / $cmol_c$ dm^{-3}	0.6	0.3
Clay / %	75	23

[a]According to Soil Taxonomy (USDA 1998). CEC, cation exchange capacity.

2.2 Laboratory incubation and experimental design

Biochars samples (<0.25 mm) were homogenously mixed with each soil type (100 g) at the rate of 2% (w/w). Control treatments (soil only) were also included. Biochar-amended soils were placed into 250 mL plastic containers with lid and small sized holes to permit aeration. Three replicates of each treatment and incubation time were prepared, placed randomly and incubated under laboratory conditions at 25(±4) ºC for one year. The water content of the treatments was maintained constant close to 70% of maximum water-holding capacity (good ratio between the liquid and gaseous phase) by replacing water twice a week by weight. Soil sampling was performed at 1, 7, 14, 28, 56, 180 and 365 days to evaluate the effect of biochar application over time. Treatments investigated consisted of the combination of three pyrolysis temperature (350, 450, 750 ºC) with seven incubation time (1, 7, 14, 28, 56, 180 and 365 days).Therefore, no statistical comparison between biochar (CH and PB) or soil type (Oxisol and Entisol) was performed.

Biochars are thereby referred by the biomass abbreviation and pyrolysis temperature, for example, CH350 denotes coffee husk pyrolyzed at 350 ºC and CH750, coffee husk pyrolyzed at 750 ºC.

2.3 Soil analyses

At each incubation sampling time (1, 14, 28, 56, 180 and 365 days), the biochar-amended and non-amended soils were oven-dried immediately at 65 ºC and then analyzed for: pH in water, exchangeable acidity (Al^{3+}), available P, available K, electrical conductivity (EC), CEC, oxidizable C and total C. The soil pH and EC were measured in deionized water at the ratio of 1:2.5 (soil: water), after shaking samples for 5 minutes, followed by 30 min of equilibration. Soil exchangeable acidity (Al^{3+}) was extracted by a 1 mol L^{-1} KCl solution and determined by titration with 0.025 mol L^{-1} NaOH solution. Available P and K were extracted using the Mehlich-1 soil test procedure (dilute HCl + H_2SO_4) and determined by the colorimetric method (P), and K, by flame photometry. Soil CEC was determined by a modified ammonium acetate compulsory displacement method (Gaskin et al., 2008). This method was chosen for being appropriate for CEC determination in biochar or biochar-treated soils. During the whole process of the CEC determination, it was employed a vacuum filtration system, and samples were filtered in a 0.45 µm pore size membrane. Initially, 2 g of soil sample were leached with 20 mL of deionized water for five times to remove excess of salts. In sequence, samples were washed with a 1 mol L^{-1} of sodium acetate (pH 8.2) three times, followed by five washes with 20 mL of ethanol to remove free (not sorbed) Na^+ ions. Samples were then washed with 20 mL of 1 mol L^{-1} ammonium acetate for four times to displace the Na^+ on the exchangeable sites of the biochar-soil mixture. The leachates were collected and stored in a 100 mL volumetric flask and Na contents in the leachates were determined by a flame photometer. The CEC corresponds to the amount of Na^+ adsorbed per unit mass of the biochar-soil mixture, expressed as $cmol_c\ kg^{-1}$. The total C of the soils was determined in 0.2 g of ground and sieved (200 mesh) samples by dry combustion, using a TOC Elementar Vario Cube analyzer (vario TOC cube, Elementar, Germany).

The equivalent amount of calcium carbonate (in t ha^{-1}) was calculated to reach the same pH values of treatments with CH biochars. The amounts were calculated through soil acidity neutralization curves generated in a previous study carried out by Carmo (2015), using the same soils (Oxisol and Entisol) where soil pH increase were displaced over pure calcium carbonate

($CaCO_3$) rates. The mathematical equations relating soil pH and $CaCO_3$ rate are described as follows: (i) pH = 4.9517 + 0.0754 ($CaCO_3$, g kg^{-1}), $R^2 = 0.98$ (Oxisol); and (ii) pH = 5.3217 + 0.3673 ($CaCO_3$, g kg^{-1}), $R^2 = 0.96$ (Entisol).

2.4 Statistical analysis

The data set was submitted to analysis of variance (ANOVA) for significant differences of pyrolysis temperatures and soil incubation time, and their interactions on the soil fertility attributes analyzed. Significant differences among the treatment means were verified by the F-test ($p<0.05$). The Tukey test ($p<0.05$) was used for multiple comparison of means. Regression analyses were also performed to study the variation of soil fertility attributes over soil incubation time. The ANOVA was performed for each soil and biochar tested. The statistical software SISVAR (Ferreira, 2011) was used to test the significance of treatment means investigated.

3. Results and Discussion

3.1 Biochars and soil acidity amelioration

Soil acidity attributes over incubation time are shown in Figure 1 (Oxisol and Entisol). In the Oxisol, there was a marked linear reduction of pH values (Figures 1A and 1B), while exchangeable (Al^{3+}) (Figures 1E and 1F) acidity increased linearly over time, regardless of the treatmentinvestigated. Probably, the organic matter (OM) mineralization in Oxisol increased over time after biochar addition to Oxisol samples, causing soil acidification due to increased nitrification rates. The evidence of the OM mineralization is confirmed by the six-fold increase in the NO_3^- content in Oxisol biochar treated samples after 365 days of incubation (Figure S1). Other studies also found correlation of increased mineral N availability with an increase in soil acidity in biochar-treated soils (Ritchie and Dolling, 1985; Maluf et al., 2015). Therefore, the pH reduction favors the increase of Al^{3+} exchangeable contents (Figure 1E and 1F), since, in low pH values (<5.5), the hydrogen (H^+) acts on the mineral soil phase, releasing exchangeable Al^{3+} ions to soil solution (Bohnen, 1995), hampering growth of most crops.

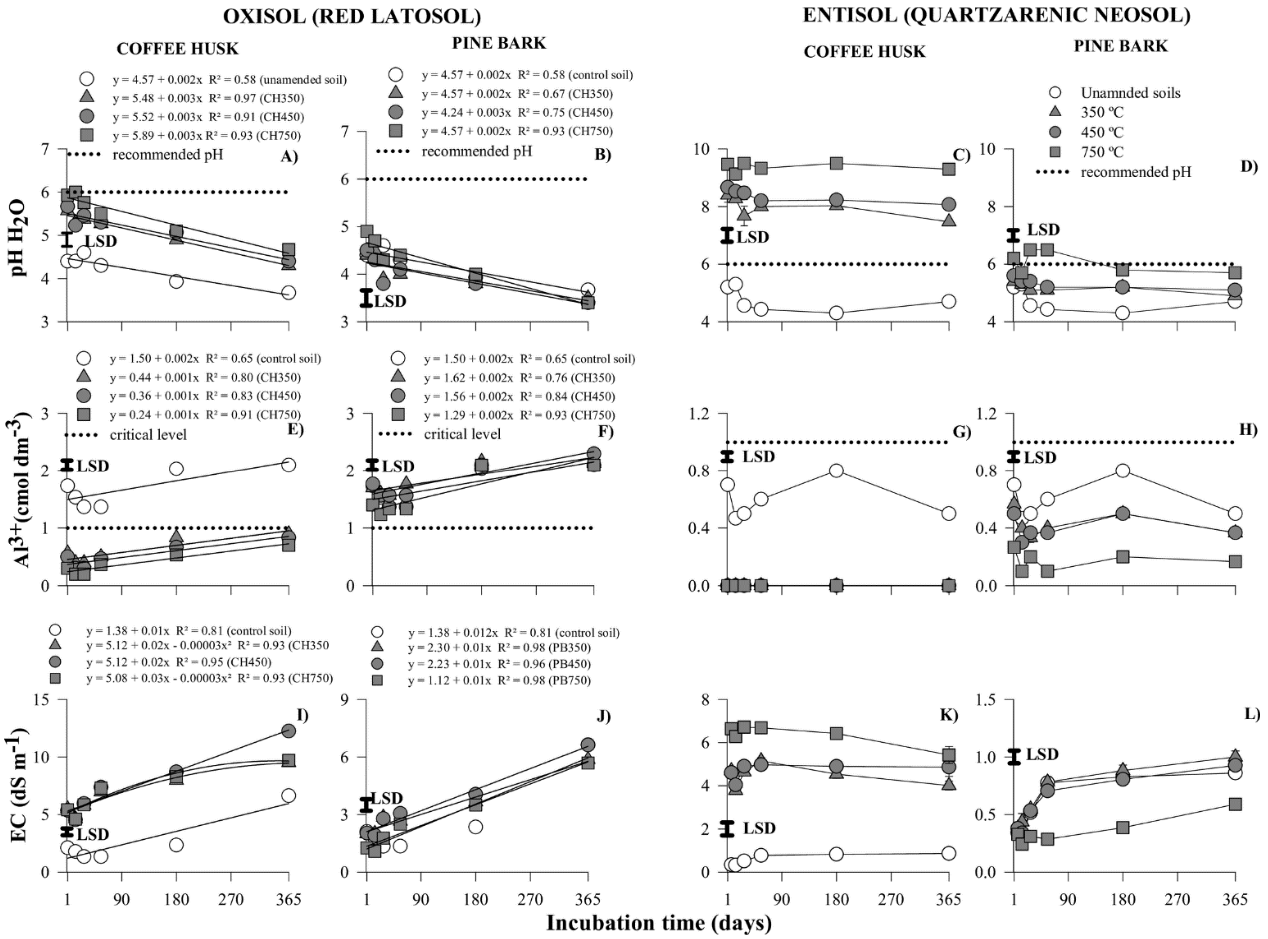

Figure 1. Dynamics of soil properties of the amended Oxisol and Entisol with coffee husk and pine bark biochars produced at three pyrolysis temperatures (350, 450 and 750 ºC), during 365 days of incubation: (A, B, C, D) pH; (E, F, G, H) and exchangeable acidity - Al^3; (I, J, K, L) electrical conductivity-EC. Bold

bar on the y-axis refer to Tukey's LSD (*P* < 0.05). Dashed line refers to recommended value or critical level of the fertility attribute, considering the requirement of most crops cultivated.

The soil pH of Oxisol responds positively to CH biochar for all pyrolysis temperature employed (Figure 1A), reducing the acidity produced probably by N transformation processes in this clayey soil. Among pyrolysis temperature, it was observed in soil amended with CH750 the highest increase in soil pH, with pH values up to 1.5 unit higher than pH values measured in the biochar not-treated soil (Figure 1A). Consistently with the effect on pH, the application of CH biochar significantly decreased soil exchangeable Al^{3+} as compared to the control soil, whose Al^{3+} values were below the level considered critical for the plants (1 $cmol_c$ dm^{-3}). These contributions of CH biochars occurred just after one day of incubation and remained over the whole incubation period (365 days) (Figures 1A and 1E). After 28 days of incubation, the pH of the amended soils with PB350 and PB450 significantly decreased about 0.6 unit, while PB750 did not have a significant effect on soil pH (Figure 1B). PB biochar, on the other hand, showed no effect on the neutralization of the soil acidity, as measured by soil pH and exchangeable Al^{3+} in the Oxisol (Figure 1F).

Increase in the pH of the Oxisol and reduction of Al^{3+} after application of CH biochars is in line with their high pH and high liming values, which are associated with alkaline chemical species found in the ash of CH biochar, such as $KHCO_3$, detected by the XRD analysis (Domingues et al., 2017). Solubilization of these substances give to CH biochar about 4 to 6 times higher liming values as compared to PB biochar (Table 1). Increase in soil pH was also observed in an Ultisol in China after 65 days of incubation with 1% (m/m) peanut biochar with the highest ash content amongst the tested biochars (Wang et al., 2014). Over time, Oxisol EC increases linearly in all treatments (Figures 1I and 1J), which may be associated with higher OM mineralization rates in the Oxisol in comparison to sandy soils (Table 1). Oxisol treated with CH showed greater EC in relation to the non-amended soil during incubation time (Figure 1I), while PB increased EC up to 180 days (Figure 1J).

For the Entisol samples, there were some fluctuations in soils properties and no mathematical model applied to the analysis was capable to illustrate the effect of incubation time on the dynamic of the fertility attributes investigated (Figure 2). This effect can be explained due to the lower organic matter content in the Entisol as compared to the Oxisol (Table 2). The soil pH was also significantly ($P < 0.05$) increased by the CH biochar addition throughout all incubation experiment as compared to the control soil (Figure 1C), causing alkalization of this soil. The magnitude of soil pH increase ranged from 2.8 (CH350) up to 4.7 (CH750) units in comparison to the pH value of the control soil (Figure 1C). Exchangeable acidity (Al^{3+}) was not verified in the Entisol in treatments with CH biochar addition (Figure 1G), probably, due to the high increase in the pH, which caused its precipitation as $Al(OH)_3$ (Bohnen, 1995). Application of PB biochar to the Entisol slightly increased the pH (Figure 1D). However, the increments were not enough to reach the pH recommended for most crops. Since pH was not changed by PB biochar use, regardless of pyrolysis temperature, PB biochar was also not effective in reducing exchangeable acidity (Figure 1H). In the Entisol, there was no effect of incubation time on EC (Figures 1K and 1L), however, it was observed that the same behavior for the CH-treated samples (Figure 1K). Use of b PB750 reduced the soil EC, though no change in EC was verified for other treatments (Figure 1L).

The magnitude of soil acidity attributes changes was larger for the Entisol in comparison to Oxisol samples. As example, CH750 increased soil pH above the pH of biochar not treated soil by about 1.5 unit for the Oxisol and in 4.7 pH units for the Entisol. The Oxisol is a high-buffered soil (750 g kg^{-1} of clay; 6.6% of organic matter) and, consequently, lime rate required to neutralize acidity is higher than those applied to low-buffered sandy soils (e.g. Entisol).

3.2 CEC, C and changes in P and K availability

The dynamic changes on nutrient availability, CEC, and total C did not follow a trend that could be modelled over time (Figure 2).

Availability of P was significantly higher ($p < 0.05$) in all CH biochar treatments and was influenced by mostly by CH biochar pyrolysis temperature both in the Oxisol (Figure 2A) and in the Entisol samples (Figure 2C), as compared to the control. In the Entisol, the effect of increasing available P was more pronounced in the Oxisol than in the Entisol, due to the much higher sorption capacity of the clayey soil as compared to the sandy soil. After 365 days of incubation, the increase in available P in the Entisol (Figure 2C) was from 17.2 mg dm^{-3} to 52.5 (350 ºC), 57.4 (450 ºC) and 29.8 mg dm^{-3} (750 ºC). Correspondingly for Oxisol (Figure 2A), it was observed increase of available P from 3.9 mg dm^{-3} to 8.2, 8.6 and 4.7 mg dm^{-3}. Thus, CH biochar can be considered a suitable P source when pyrolyzed at temperatures ≤450ºC, due to its relatively high total P content (3.0 – 3.5 g kg^{-1}) (Table 1). The PB biochar, on the other hand, did not influence the P availability in both soils (Figures 2B and 2D).

An interesting result found was that at high pyrolysis temperature (750 °C) of CH, there was a lower increase in available P in treated soils as compared to 350 ºC and 450 ºC biochars (Figures 2A and 2C). There are two likely explanations for this effect. One is that phosphorus species are dependent on the pyrolysis temperature, which leads to the formation of compounds with different stability and low solubility as the pyrolysis temperature increases (Uchimyia and Hiradate, 2014; Zhao et al., 2014). Uchimiya and Hiradate (2014) indicated that pyrophosphate ($P_2O_7^{4}$) is the stable P species that persisted in plant biochars generated at 650 °C. Another aspect is that due to the high ash content and liming value of the CH biochar prepared at 750 °C (Table 1), the Mehlich-1 soil test components (0.05 M HCl + 0.025 M H_2SO_4; pH 1.2) may be neutralized, exhausting its capacity to extracts available P forms from tropical soils (Bahia Filho et al., 1983). Gaskin et al. (2008) observed lower available P chemical species in poultry litter and peanut hulls biochars when the pyrolysis temperature was increased from 400 °C to 500 °C. According to results already published, the pyrolysis temperature for high-nutrient biomasses like coffee husk is likely to be a driving-force controlling the P chemical species and their solubility in the biochar produced. Biochar lime value, its rate added to soils, and the soil acidity buffering capacity and all the effects of these factors on the capacity of soil test procedures in extracting soil P should be verified in future trials.

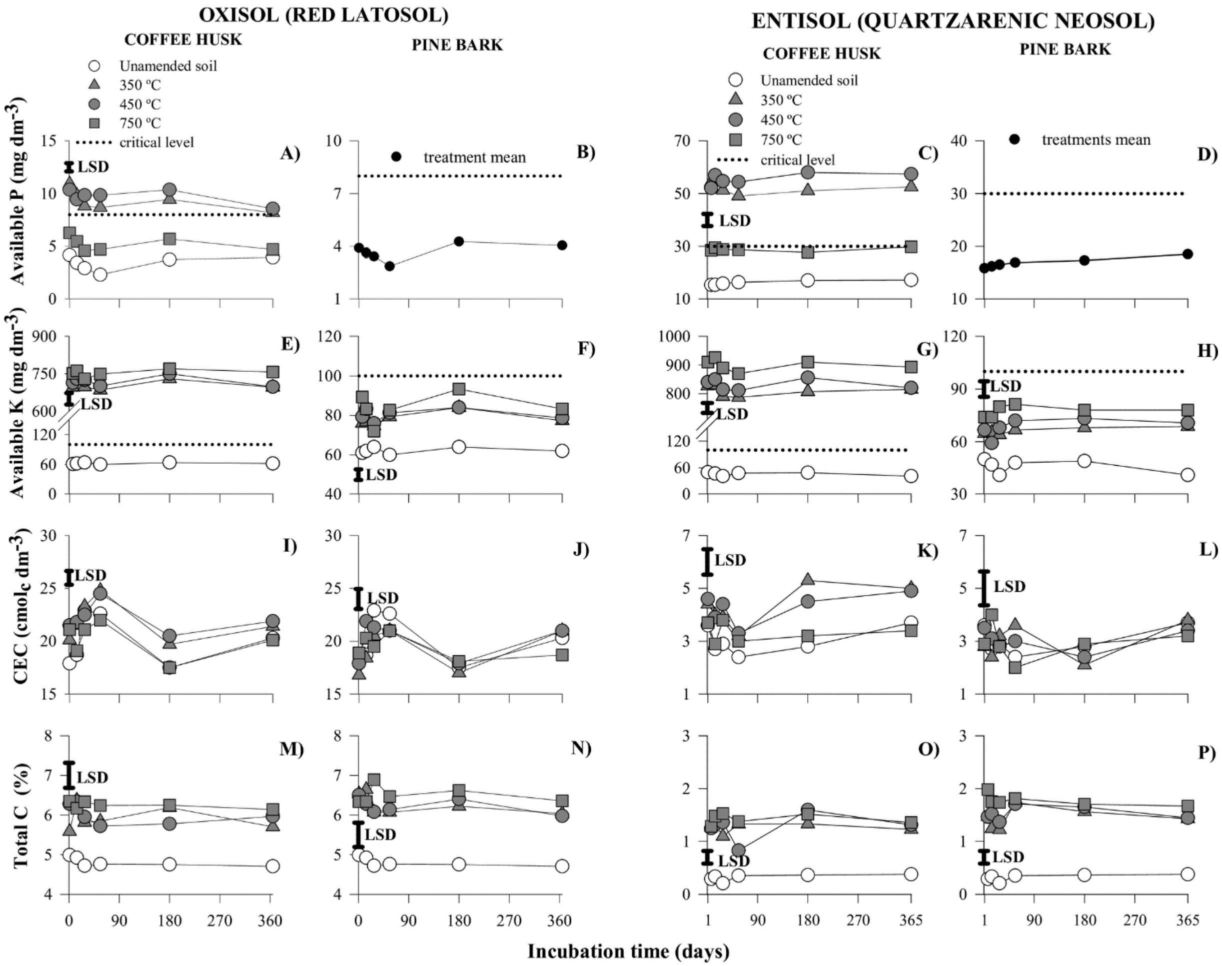

Figure 2. Dynamics of soil fertility of the amended Oxisol and Entisol with coffee husk and pine bark biochar at three pyrolysis temperature (350, 450 and 750 ºC), in incubation times up to 365 days of incubation: (A, B, C, D) available P; (E, F, G, H) available K; (I, J, K, L) cation exchange capacity-CEC; (M, N, O, P) total C. Bold bar on the y-axis refer to Tukey's LSD ($P < 0.05$). Dashed line refers to critical level.

The CH biochar application to soil (regardless of the pyrolysis temperature) resulted in higher K availability in both the Oxisol (Figure 2E) and the Entisol (Figure 2G), as compared to the control soils. Contents of available K in CH biochar-treated soils were much higher than the critical level (100 mg dm^{-3}) recommended for most crops in both soils. After 365 days of incubation, the mean concentration of available K varied between 696 (350 ºC) to 757 mg dm^{-3} (750 ºC) in the Oxisol and from 815 (350 ºC) to 893 mg dm^{-3} (750 ºC) in the Entisol, which are far higher than 62 and 41 mg dm^{-3} of available K verified in the controls of the Oxisol and Entisol, respectively. Coffee husk biomass has high levels of P and K, which are accumulated in the ash during pyrolysis, resulting in relative enrichment of total P and K in biochars (Table 2), which is readily available in the case of K. On the other hand, PB biomass is poor in nutrients (e.g. K) and only caused a slight increase in available K on both soils (Figures 2F and 2H), which was still below the soil critical levels of K (100 mg dm^{-3}) for plants, despite the high application rate (2%, w/w). Similarly, the high ash biochar (≈ 56%, w/w) from tomato green waste, comprising leaf and stem material, revealed high concentrations of K, P, and other nutrients and significant amounts of K in sylvite mineral forms (Smider and Singh, 2014). Several studies were carried out focusing on improving soil fertility status after biochar use (Hansen et al., 2016; Liu et al., 2014; Wan et al., 2014), exhibiting positive effects on nutrient availability and potential for increasing crop yields (Pandey et al., 2016; Zhang et al., 2016). In addition to fertilizer use strategy, biochars can also be used as liming materials for correcting soil acidity (Wan et al., 2014). Thus, the influence of biochar on nutrient availability can have a direct and indirect (by changing soil properties) effect on soil fertility status, conditioning the levels of available nutrients, CEC, C stocks and changes in the SOM native decomposition rate and, as a consequence, in its soil acidity degree.

High increase in available K is probably related to the increase in EC values in Oxisol (Figure 1I and 1J) samples, since most of the K content is present in biochars in the ionic form (Alfaro et al., 2004), causing an increase in soil solution ionic strength, thus, in EC (Reis et al., 1999). Moreover, higher mineralization rate in the Oxisol over time increased markedly soil levels of N in NH_4^+ and NO_3^- forms (FigS. 1) in this soil, which may also help to explain the increase in EC over time, even in the control plot (Figure 1K). Similar results were verified in soils amended with poultry litter biochar (Sigua et al., 2016).

The CEC dynamics in the Oxisol following CH or PB biochar application (Figures 2F and 2J) had a small impact over time, with a decrease in the two last sampling times, most likely caused by the acidification due to native OM mineralization as discussed previously. In the Oxisol there was, a slight change in CEC after the CH350 and CH450 addition, which increased from 20.1 up to 21.4 cmolc kg^{-1} and 21.9 cmol$_c$ kg^{-1}, respectively, at the end of experiment. Such changes in the CEC of biochar-treated Oxisol are low, since they only correspond to 5% and 8% increase as compared to the control Oxisol (Figure 2I). On contrary, CEC was markedly increased by the use of CH350 and CH450 application in the Entisol samples, which increased over time (Figure 2K) in 1.3 cmol$_c$ kg^{-1} (CH350) and 1.2 cmol$_c$ kg^{-1} (CH450) after 180 days of incubation, representing, respectively, 37% and 32% increase as compared to the control sandy sample(Figure 2K). The CEC of both the Oxisol and the Entisol was not affected by PB biochar use, regardless of the pyrolysis temperatures, as compared to the control soil samples (Figures 2J and 2L). Several studies have demonstrated that soil CEC was not affected by wood biochar addition (Basso et al., 2013; Nagodavithane et al., 2014; Oguntunde et al., 2004; Schulz and Glaser, 2012; Steiner et al., 2007). The positive effect of the addition of CH biochar produced at low temperatures (350 and 450 ºC) on soil CEC is linked to the high CEC of these biochars, which is 2.5 times higher than the CEC determined in the CH750 (Table 1). Decrease in biochar CEC with the increase of the pyrolysis temperature is explained by the loss of oxygenated functional groups as pyrolysis temperature increases (Chen et al., 2008; Novak et al., 2009; Zimmerman, 2010; Bruun et al., 2011). Therefore, in this study, the CEC of biochars was the main factor governing the increase in the sandy soil CEC, which also rely on the feedstock type and pyrolysis temperature employed during biochar production.

During the incubation, total C in Oxisol significantly increased at the beginning and remained stable over time following both CH and PB biochars application in both soils (Figures 2M; 2O and 2N; 3P). Application of biochars to the Oxisol samples increased the total C from 4.7% up to 6.1% (CH750) and 6.4% (PB750). Such changes in soil C are directly linked to content and load charges of C added to soils by the biochars (Table 1). High persistence in the environment of the recalcitrant C found in biochars is an important factor governing the residence time of C from biochar in soils, which may help to offset GHG emissions (Zhang et al., 2016), as well as determines the longevity of other benefits, such as the increase in CEC, enhances water-holding capacity, etc. The molecular recalcitrance and the biochar-organo-mineral associations with clay or the biochar C occlusion in soil aggregates can contribute to greater stabilization of soil C over time in the Oxisol (Lehmann and Joseph, 2009; Fang et al., 2014). However, with the techniques used, it was not possible to state if soil decomposers were or not capable to oxidize the organic compounds in the biochars tested. Potentially, the priming effect of the coffee husky biochars in increasing the decomposition rate of the Oxisol native OM is a topic to be investigated in future trials.

3.3 Biochar agronomic value

Coffee husk is best suited for biochar production, due to the parameters that guide the high agronomic value of this feedstock, i.e. high liming value and high K content. CH biochars were more effective than PB biochars in correcting soil acidity and, thus, can mirror lime materials in increasing soil pH as well as decreasing the toxicity of Al^{3+} chemical species. Despite the agronomic significance of biochar addition on soil attributes, the high increase of soil pH caused by CH biochar addition may represent a risk of alkalinity in low-buffered soils. The unfavorable effect of overliming verified in Entisol after the addition of CH biochar, leads to the conclusion that the rate of 2% (w/w) of CH biochar needs to be revised. It should be noted that overliming reduces the soil micronutrients availability, affect the soil structure, precipitates soluble P forms, and increase NH_3 volatilization, thus, excessive soil pH may hamper crop growth (Fageria et al., 1995). Considering these assumptions, it was calculated new rates of CH biochar based on the acidity neutralization curves already shown and available in Carmo (2015). These curves allows calculating the required amount of limestone to achieve a given soil pH. Therefore, to reach the same pH values of the Entisol amended with CH biochars (at 2%, w/w/) will be needed 6.5 (CH350), 8.6 (CH450) and 11.4 (CH750) t ha^{-1} of the $CaCO_3$+ $MgCO_3$. On the other hand, to raise the pH of the Entisol to 6.0 with CH biochar it would be necessary to apply 0.6%, 0.4% and

0.3% of CH350, CH450 and CH750, respectively. For the Oxisol, the rates of $CaCO_3$+ $MgCO_3$ to reach the pH 6.0 are 4.7, 3.8 and 2.5% of CH350, CH450, CH750, respectively.

Potassium released was about 25 % (Oxisol) and 30% (Entisol) of K charge added by CH biochar, considering the rate of 2% (Table 1), though, CH can be considered a valuable source of K to plants. Since the availability of K far exceeds the critical level of K (100 mg dm^{-3}) in both Oxisol and Entisol treated samples, definition of CH biochar rate must be based exclusively on the amounts of K liberated in soil to avoid K leaching due over application of K in soils. In the Entisol, the K saturated up to 67% of the CEC. Thus, addition of biochar at the 2% rate in the low CEC Entisol may increase K leaching, mainly in soil under tropical conditions with high rainfall. Besides, excess of K in soil leads to imbalance of Ca: Mg: K ratios, which can result in reduced uptake of Ca and Mg by plants (Andreotti et al., 2000). In addition, high EC values probably caused by excessive levels of K in soil may affect several soil processes, such as respiration, nitrification, infiltration or drainage and water and nutrient uptake by plants (Marschner, 2012). Therefore, considering the concentration of 100 mg dm^{-3} as a critical level to be reached in most soils, the CH biochar rate could be reduced to only 0.28-0.38%, according to soil type and pyrolysis temperature employed in the biochar manufacture. The amount of P released by biochar was lower compared to K released and available in soils. However, in a soil-plant system where the plant constantly changes the physical-chemical conditions of the root environment, either plant alternating the pH or exuding chelating agents (acid citric, acid malic, etc.), the residual P liberated by biochars may continue over several crop growing seasons (Angst and Sohi, 2013).

However, results obtained in this study showed that biochar rates necessary to increase CEC of clayey and sandy Brazilian soils is not feasible due to the high rates required, which increases costs, and may alkalanize soil. According to Gai et al. (2014), low–temperature biochars (corn-straw and peanut-shell pyrolysed at 400 ºC) provided the highest CEC (up to 38.8 $cmol_c$ kg^{-1}), enabling these matrices to adsorb N-NH_4^+ up to 2.3 mg g^{-1} and to reduce N leaching. Besides, only CH biochars showed potential to increase CEC, but these biochars must be used preferentially as a K source to plants. Changes in soil C did not explain alone changes in soil CEC, mainly for the PB-treated soils. Changes in soil CEC predominantly rely on the negative charge density per biochar unit of C, and in the magnitude of pH changes in the biochar-treated soils.

4. Conclusions

Fertility status dynamics is markedly dependent on the soil type. Over time, regardless of the biochar used to treat Oxisol, soil pH is decreased and exchangeable Al and electrical conductivity are sharply increased. Changes in soil fertility already highlighted is associated to a higher decomposition rate of native organic matter of the clayey than in the sandy samples. At the rate of 2% (w/w), the addition of coffee husk biochars increased pH and soil EC to level far beyond those considered optimal to plant growth. Pine bark biochar, mainly the matrix pyrolyzed at 750ºC are effective in correcting soil acidity and increase C stored in soil, without increase electrical conductivity above the average threshold limit to plants. Instead of the liming value, the levels of available K reached in both soils investigated should be taken into account to modulate the agronomic rate of coffee husk biochar. Low rates of coffee husk biochar required to add adequate levels of K^+ in both soils make this charred matrix a suitable source of the nutrient to plants. Coffee husk are very effective in increase the availability of P , however the amount of biochar applied overlimed the sandy Entisol. Despite the negative side effects in soil pH, the most effective coffee biochar samples in increasing P availability are those charred in temperatures ≤450ºC. The driving force controlling the positive effect of coffee husk biochar on the sandy soil CEC is also the pyrolysis temperature. Changes on the fertility status over time is soil-dependent and also rely on the biochar type added to soil. Effects of biochar on soil fertility attributes must be analyzed as a whole to optimize gains without causing negative changes in soil fertility status, which may hamper plant growth.

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Running Title: SOIL CEC AS AFFECTED BY BIOCHAR TYPE AND RATES

Ameliorating Cation Exchange Capacity of Highly Weathered Soils with Tailored Biochars[3]

Rimena R. DOMINGUES[1,*], Carlos A. SILVA[1], Leônidas C. A. MELO[1], Paulo F. TRUGILHO[2] and Miguel A. SÁNCHEZ-MONEDERO[3]

[1] *Department of Soil Science, Federal University of Lavras, Lavras, Minas Gerais, 37200000 (Brazil)*
[2] *Forest Science Department, Federal University of Lavras, Lavras, Minas Gerais, 37200000 (Brazil)*
[3] *Department of Conservación de Suelos y Agua y Manejo de Residuos Orgánicos, Centro de Edafología y Biología Aplicada del Segura (CEBAS-CSIC), Murcia, 30100 (Spain)*

ABSTRACT

Highly weathered Brazilian soils are characterized by low fertility, high acidity and reduced cation exchange capacity (CEC). The CEC is predominantly composed of variable charges generated mainly by humified fractions of the soil organic matter (SOM). Understanding how charred matrices, e.g. biochar increase soil CEC is important to tailor biochars prior to field applications. The aim of this work was to evaluate the effects of biochars produced from chicken manure (CM), eucalyptus sawdust (ES), coffee husk (CH) and sugarcane bagasse (SB) pyrolyzed at 350, 450, and 750 ºC on the CEC of samples of a loamy Red-Yellow Latosol (RYL) and a clayey Red Latosol (RY) (Oxisols). After biochars characterization, they were mixed with the soils at 2%, 5%, 10% and 20% rates, w/w, plus a control (soil only) and left incubated for 9 months. Coffee husk biochar pyrolyzed at 350 ºC is the biochar matrix most effective in increasing soil CEC. There was a linear decrease in clayey Latosol CEC by increasing the application rate of ES and SB biochars. Total soil C increased linearly with increasing application rates of biochar, however increases in C stored in some soils do not mean more charge density in the soil colloids. Soils that were treated with CM and CH biochars showed the highest soil pH as a result of increasing application rates. Soil pH was correlated with soil CEC due to the development of more negative charges in the surface of soil and biochar. Conversely, there was no correlation between total soil C and CEC. Changes in soil CEC due to biochar use can be predicted by the biochar CEC, its effect on soil acidity, and the type of soil investigated. .

Key Words: CEC, coffee husk, contrasting soil, variable charge soil colloids, wood biochars.

INTRODUCTION

Brazilian weathered soils are characterized by the low fertility status, which is defined by high exchangeable aluminum (Al^{3+}) and potential acidity (H+Al). Also, the clay fraction of such soils is mainly composed of low chemical activity minerals resulting in extremely low cation exchange capacity (CEC), with extremely low values (Lopes and Guimarães Guilherme, 2016). In these soils, the contribution of organic matter to the soil CEC can be as high as 80%, which explains the fact that the

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[*] Corresponding author. E-mail: rimenas@gmail.com

CEC and organic carbon (OC) in these soils are strongly correlated (Madari *et al*., 2009). However, the role that OC plays in determining the CEC in Brazilian soil is not a simple task, since OC depletion is favored due to faster decomposition under warmer and moister conditions of humid tropical areas (Mielniczuk *et al*., 2003). Thus, this scenario may contribute to the intensified use as soil amendment of biochar due to its condensed aromatic compounds, which assures a higher persistence of C in soil of tropical regions (Cheng *et al*., 2008; Keith *et al*., 2011; Nguyen *et al*., 2010).

Although biochar is recalcitrant in nature, it has effective roles in increasing cation exchange capacity and heavy metal sorption due to functional groups and high specific surface area (Atkinson *et al*., 2010; Chen *et al*., 2008; Xu *et al*., 2014). Negative charge density on biochar surfaces are produced by exposure of functional groups during pyrolysis process, such as carboxylic acids, ketones and aldehydes released by depolymerization of cellulose and lignin (Ahmad *et al*., 2012; Chen *et al*., 2008; Keiluweit *et al*., 2010). Tan *et al*. (2015) found increased immobilization of Cd^{2+} with the application of biochar and attributed this positive effect to the high biochar CEC.

Variations in biochar CEC and its effects on highly weathered soils, however, depend on the feedstock and pyrolysis temperature employed (Jien and Wang, 2013; Cantrell *et al*., 2012; Ippolito *et al*., 2012; Jindo *et al*., 2014; Lehmann *et al*., 2006). High ash feedstocks are potential sources that may result in higher CEC biochar, since, during pyrolysis, chemical elements, such as Mg, K, Na, and P are capable of catalyzing the formation of surface oxygen groups, such as carboxylic acids, lactones, and phenols, which contribute to the increase of negative charges (Gaskin *et al*., 2008; Song and Guo, 2012). As pyrolysis temperature increases, O and H contents are decreased and chemical functions groups rich in negative chares are degraded and diminished in the biochar matrix, which, sharply reflects in a drastic reduction in the biochar CEC (Lee *et al*., 2010; Luo *et al*., 2011; Melo *et al*., 2013). For instance, carboxylic and phenolic groups dramatically reduces in high temperatures (> 500 ºC), which partially explains in negative correlation of biochar CEC with pyrolysis temperature (Song and Guo, 2012). In addition to these factors, observed similarities among biochars in terms of chemical functions groups may not be related to its capacity fot neutralize soil acidity; besides, biochars from different biomasses, even pyrolyzed in the same temperature, may show different CEC values. In addition, as well as humic substances, negative charges found in biochar surface are pH-dependent (Lee *et al*., 2010). Thus, it can be inferred that chance in soil CEC may be egulated by the biochar CEC, its capacity do correct soil acidity and by the rate of biochar added in soils. Interaction of biochar matrix with the negative and positive charges found in the surface of tropical colloids may also regulate the magnitude of change in CEC of the biochar-treated soil.

Although a number of studies have shown the positive contribution of biochar on soil CEC (Dume *et al*., 2016; Jien and Wang, 2013; Yuan and Xu, 2012; Yuan *et al*., 2011a), the mechanism behind soil CEC changes in short and medium-term experiments is not clear, as well as the effect of feedstock type and pyrolysis temperature (Gai *et al*., 2014; Yuan *et al*., 2011b). Take these assumptions into account, the evaluation of CEC soils treated with biochar should be supported by other studies that integrate different biomass (rich and poor in ash and nutrients) and pyrolysis temperatures. Rates of biochar added to contrasting soils are other relevant factor do be investigated. Moreover, the influence of soil type should also be considered in order to draw a whole factors of CEC changes in soils treated with contrasting biochars added in soil at increasing rates. The aims of this study were: i) to investigate the effectiveness of biochar, and their rates, from different feedstocks and pyrolysis temperature on the CEC of two OM and textural contrasting soils; ii) to evaluate the main regulating of changes in soil CEC using as predictors biochar CEC, its effect on soil acidity degree and the soil type investigated.

MATERIALS AND METHODS

Biochars and soils characterization

Twelve biochars were produced from chicken manure (CM), eucalyptus sawdust (SE), coffee husk (CH), and sugarcane bagasse (SB) pyrolysed at 350, 450 and 750 ºC. The slow pyrolysis procedure was carried out in an electrical muffle furnace, with automatic temperature control and adapted with condensers for cooling the condensable gases that make up the pyroligneous liquid. The amount of material used in each procedure varied according to the density of each material. The samples were previously oven-dried at 105 ºC, until constant weight. The sample was heated up 350, 450 and 750 °C, at constant heating rate of 1.67 °C/ min, and kept for 30 min at the final temperatures. For convenience, biochars were referred by the feedstock abbreviation followed by the pyrolysis temperature. For instance, CH350 stands for coffee husk pyrolysed at 350 ºC. Some selected chemical and physicochemical properties of biochars are given in Table I. The volatile material and ash concentrations were determined according to standard procedure D-1762-84, established by the American Society for Testing and Materials (ASTM, 1990). The total C was determined by dry combustion using TOC and CHNS analyzers (Vario TOC cube, Elementar, Germany). Biochar pH was measured in deionized water at a 1:10 (w/v) ratio; and biochar CEC was determined by the modified ammonium acetate compulsory displacement method, adapted to biochars (Gaskin *et al*., 2008).

TABLE I
Chemical and physicochemical properties of the biochars produced from four biomass pyrolysed at 350, 450 and 750 °C.

Biomass	Temp.	Ash	VM	C	pH	CEC	LimingValue[1]
	(°C)		———	% ———		cmol$_c$/kg	ml HCl/pH unit
	350	52 ± 0.17	37 ± 0.31	31 ± 0.25	9.7 ± 0.01	41.6 ± 0.93	2.9 ± 0.00
CM	450	55 ± 0.18	31 ± 0.05	27 ± 0.51	10.2 ± 0.00	40.7 ± 0.90	2.7 ± 0.00
	750	56 ± 0.10	27 ± 0.06	25 ± 0.87	11.7 ± 0.02	21.3 ± 0.47	2.2 ± 0.01
	350	0.9 ± 0.00	37 ± 0.05	70 ± 0.27	5.9 ± 0.13	10.8 ± 0.20	0.3 ± 0.01
ES	450	0.7 ± 0.01	29 ± 0.05	79 ± 1.19	8.0 ± 0.02	2.2 ± 0.17	0.2 ± 0.01
	750	1.1 ± 0.00	6 ± 0.08	91 ± 1.96	9.3 ± 0.01	1.4 ± 0.28	0.3 ± 0.01
	350	13 ± 0.05	35 ± 0.25	61 ± 0.98	9.7 ± 0.00	69.7 ± 1.31	1.4 ± 0.01
CH	450	13 ± 0.05	26 ± 0.32	61 ± 0.27	9.8 ± 0.00	72.0 ± 1.73	1.6 ± 0.01
	750	20 ± 0.02	18 ± 0.39	66 ± 1.26	9.8 ± 0.00	18.9 ± 0.56	2.1 ± 0.01
	350	1.9 ± 0.01	35 ± 0.35	75 ± 0.64	7.0 ± 0.00	4.6 ± 0.33	0.4 ± 0.00
SB	450	2.1 ± 0.01	24 ± 0.35	82 ± 0.68	8.7 ± 0.01	1.8 ± 0.14	0.3 ± 0.01
	750	2.2 ± 0.01	8 ± 0.05	91 ± 1.02	9.7 ± 0.02	1.3 ± 0.35	0.3 ± 0.01

Error bars represent ± standard errors of the mean (n = 3). Legend: CM = chicken manure; ES = eucalyptus sawdust; CH = coffee husk; SB = sugarcane bagasse; VM = volatile matter; EC = electrical conductivity; CEC = cation exchange capacity. [1] Liming value determined by the acid-base titration method (Yuan *et al.,* 2011b).

Two soils were chosen based on their contrasting properties, including clay mineral and organic C contents. Samples of 0-20 cm soil layer were collected from a dystrophic Red Latosol (RL) and Red-Yellow Latosol (RYL) (EMBRAPA, 2006) located at Lavras, MG, Brazil (21º14'S, 45º00'W) and Itumirim, MG, Brazil (21º19'S, 44º52'W), respectively. Both soils can be classified as Oxisols according to Soil Taxonomy (USDA, 1998). Soil samples were air-dried and sieved (< 2 mm) for the incubation experiment. Soil properties were determined as described in Silva (1999) and the average are in Table II.

TABLE II
Chemical and physicochemical properties of the dystrophic Red Latosol (RL) and Red-Yellow Latosol (RYL) studied samples.

Soil attribute	RL[a]	RYL[a]
pH (1:2.5 H_2O)	4.3 ± 0.01	5.3 ± 0.01
H+Al / cmol$_c$ dm^{-3}	11.8 ± 0.03	2.9 ± 0.02
CEC / cmol$_c$ dm^{-3}	16 ± 1.63	2.4 ± 0.52
Organic carbon / %	6.6 ± 0.35	2.5 ± 0.22
Available K / mg dm^{-3}	51 ± 1.80	74 ± 1.17
Available P / mg dm^{-3}	1.8 ± 0.03	0.7 ± 0.00
Ca^{2+} / cmol$_c$ dm^{-3}	0.6 ± 0.01	1.9 ± 0.03
Al^{3+} / cmol$_c$ dm^{-3}	1.9 ± 0.06	0.3 ± 0.00
Clay / %	75 ± 0.92	23 ± 0.25

a) According to the Brazilian Soil Classification System (EMBRAPA, 2006). Error bars represent ± standard errors of the mean (n = 3).

Laboratory incubation and experimental design

Biochar samples (< 0.25 mm) were homogenously mixed with each soil type (100 g) at four application rates: 2%, 5%, 10% and 20% (w/w). An unamended control of each soil type was also included. Biochar-amended soils were placed into 250 ml plastic containers with lid and small sized holes to permit aeration. Three replicates of each treatment and time were prepared, placed randomly and incubated in the laboratory conditions in the dark at 25 ºC for 9 months. The moisture contents were maintained constant at 70% of maximum water-holding capacity by replacing water by weight to the container. The biochar-amended and unamended soils were analyzed at the end of 9 months to determine their physical and chemical properties.

A completely randomized experimental design was used including three pyrolysis temperature (350, 450, 750 ºC) combined with four application rates (2, 5, 10 and 20%, w/w) for each biochar (CM, ES, CH, SB) and soil type (RL and RYL).

Soil analyses after incubation

After 9 months of incubation the biochar amended soil samples were oven-dried at 65 ºC and analyzed for pH, total C, and CEC. The pH was measured in deionized water at the ratio of 1:2.5 (wt/v), after shaking the slurry for 5 minutes and 30 minutes of equilibration. The total soil C was determined in 0.2 g of ground and sieved (<75 µm) samples by dry combustion using a TOC analyzer (vario TOC cube, Elementar, Germany). Soil CEC was determined by a modified ammonium acetate compulsory displacement method (Gaskin *et al*., 2008). During the whole process of the CEC determination, it was employed a vacuum filtration system, in which samples were filtered in a 0.45 µm pore size membrane. Initially, 2 g of biochar sample was leached with 20 mL of deionized water five times to remove excess of salts. In sequence, samples were washed with a 1 mol L^{-1} of sodium acetate (pH 8.2) three times, followed by five portions of 20 mL of ethanol to remove free (not-sorbed) Na^+ ions. Samples were then washed with 20 mL of 1 mol L^{-1} ammonium acetate four times to displace the Na^+ on the exchangeable sites of the biochar. The leachates were collected and stored in a 100 mL volumetric flask and Na contents in leachates were determined by flame photometry. The CEC corresponds to the amount of Na adsorbed per unit mass of biochar, expressed as cmolc kg^{-1}.

Pearson correlation analysis was applied to measure association between net CEC with net C; or net CEC with net pH. Net values are defined as changes in soil induced by biochar and calculated by subtracting, at each application rate, the average of the attribute of the biochar-amended soil from the average of the control soil.

Statistical analysis

The data were subjected to analysis of variance (ANOVA) for significant differences between factors as pyrolysis temperatures, incubation time, and their interaction. When significant F-tests were obtained (0.05 probability level), pyrolysis temperature factor separation was achieved using Tukey's honestly significant difference test and the linear regression was used to examine incubation time. The ANOVA was then performed for the two soils and for two biochar separately. The net CEC was correlated, by analysing Pearson, with the net C and net pH. Data were statistically analysed employing SISVAR (Ferreira, 2011).

RESULTS AND DISCUSSION

Soil cation exchange capacity

Changes in the soil CEC were observed in most cases in response to biochar application rates. In general, the increasing biochar application rate in both soils increased linearly the soil CEC with the addition of CM (Fig. 1A and Fig. 1E) and CH (Fig. 1C and Fig. 1G) biochars. Conversely, the addition of ES (Fig. 1B and Fig. 1F) and SB (Fig. 1D and Fig. 1H) biochars reduced linearly the soil CEC or no differences in negative charge density in soils treated with biochar were observed as compared to the control.

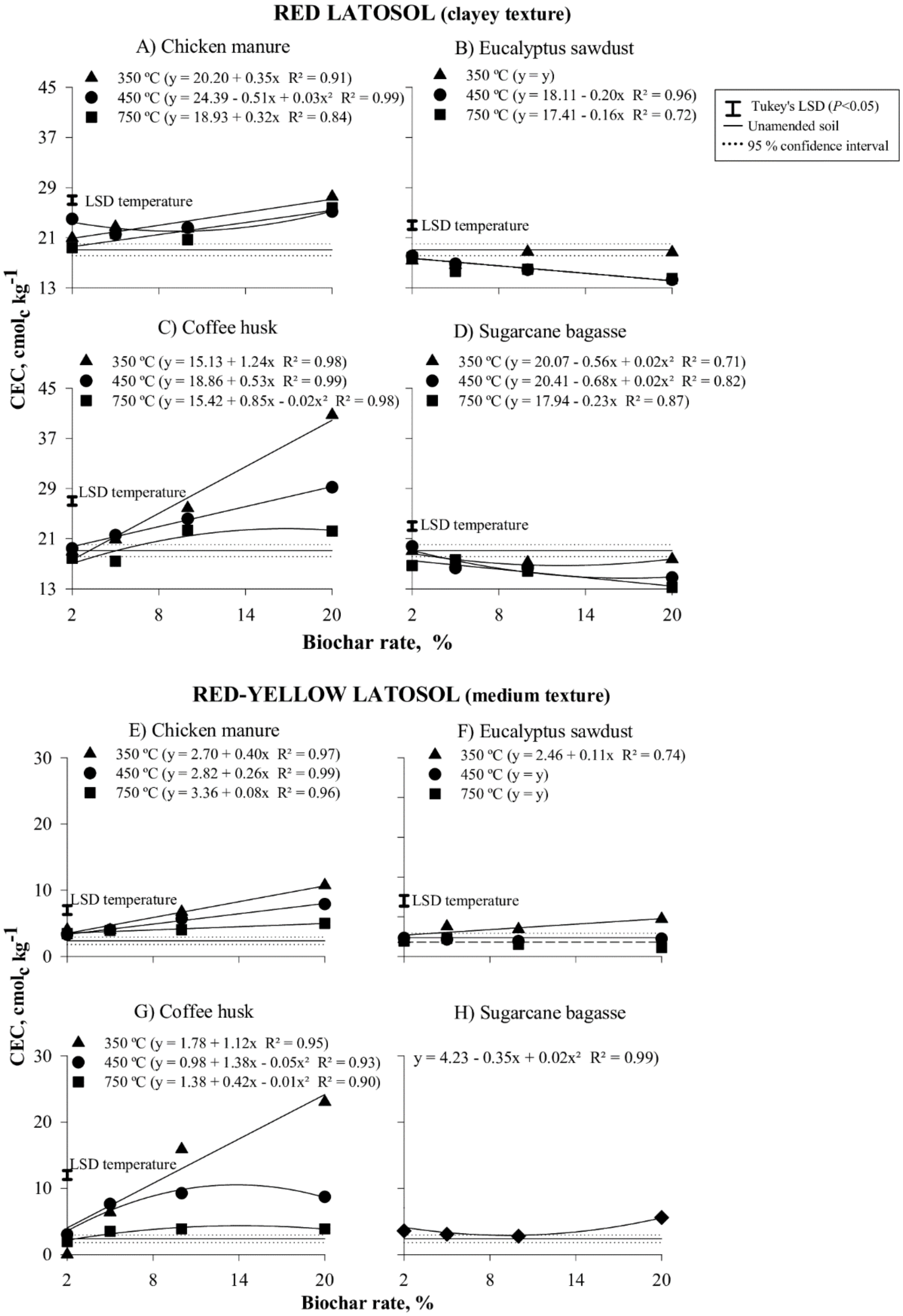

Fig. 1 The CEC of the Red Latosol (clayey texture) and Red-Yellow Latosol (medium texture) as a function of biochar rates of chicken manure (A, E), eucalyptus sawdust (B, F), coffee husk (C, G) and sugarcane bagasse (D, H) produced under different pyrolysis temperature, after 9 months of incubation of soil-biochar mixtures. Tukey's LSD ($P < 0.05$).

The highest increase in CEC was reported for the soil amended with CH350, effect whose magnitude differed from the other verified for other biochar temperatures at higher rates (Figs. 1C and 1G). In the RL soil, the rate of 20% of CH350 increased almost twice the soil CEC (from 19.1 to 40.4

cmol$_c$ kg^{-1}) after 9 months of incubation as compared to the control (Fig. 1C), while in the RYL soil the same treatment soil-CEC was up 10 folder higher (from 2.3 to 23.1 cmol$_c$ kg^{-1}) the soil CEC (Fig. 1G). Despite the high rate (20%), it was possible to achieve a high CEC with a single biochar application, surpassing even CEC values found in anthropic soils of the Amazon region in Brazil (Falcão *et al*., 2009; Liang *et al*., 2006). The positive effect of CH350 addition in soils was linked to the high CEC of these materials (≈ 70 cmol$_c$ kg^{-1}, Table I), which is consistently higher than the soil CEC itself. Negative charge density on biochar surfaces produced at low temperatures is attributed to the exposure of functional groups, such as carboxylic acids, ketones, and aldehydes as the depolymerization of cellulose and lignin occurs during pyrolysis (Chen *et al*., 2008; Ahmad *et al*., 2012). In addition, the high CEC observed for CH biochar can be explained due to the high K concentration in this waste, which, during pyrolysis, can intercalate and cause the separation of carbon lamellae by the oxidation of cross-linking carbon atoms, resulting in formation of surface groups at the edge of the carbon lamellae (Adinata *et al*., 2007). In another study, the addition of 15 t/ha of coffee husk biochar (prepared at 500 ºC) in acid soils also increased the soil CEC from 24.9 to 34.9 cmol$_c$ kg^{-1} after three months of incubation, which is result the intrinsic CEC of biochar (79 cmol$_c$ kg^{-1}) be higher than the whole soil (Dume *et al*., 2016).

For the same feedstock, as the pyrolysis temperature increased the effect of application rates on soil CEC reduced substantially in both soils (Figs. 1C and 1G). At high pyrolysis temperatures the CEC of biochars is drastically reduced due to the loss of oxygenated functional groups (Bruun *et al*., 2011; Chen *et al*., 2008; Novak *et al*., 2009; Zimmerman, 2010), which is in line with the small effect of CH750 on the soil CEC evaluated in this study. Losses of organic chemical groups in CH750, in the 1600 cm^{-1} region (Domingues *et al*., 2017), could explain the sharp decrease in CEC of this biochar in comparison to CH350 and CH450. Although CH450 has CEC values (Table I) and functional groups (Fig. 1C) similar to those observed in the CH350 its effect on soil CEC was much lower than that of CH350 (Figs. 1C and 1G). Differenced changes in soil CEC due to CH350 and CH450 use, in relation to CH750 application, can be associated with thermal stability of lignocellulosic compounds during pyrolysis. During the charring procedure, up to 350 °C, the mass of cellulose is 75-80%, while at from 330 to 430 °C, the cellulose is rapidly thermally degraded as result of intense depolymerization, remaining only 15% of cellulose found in the initial biomass (Shen *et al*., 2010; Van de Velden *et al*., 2010). Thus, CH350 will probably have a greater cellulose concentration than CH450. Consequently, this higher content of cellulose may increase microbial activity, leading to oxidation and then formation of functional groups in the biochar structure (Cheng *et al*., 2008, 2006; Glaser *et al*., 2002).

Chicken manure biochars also increase linearly CEC with increasing application rate, since CEC reached values up to 27.5 coml$_c$ dm^{-3} in the RL and 10.8 cmol$_c$ kg^{-1} in the RYL after incubation with CM350. Soil CEC was reduced as the biochar pyrolysis temperature is increased (Fig.1A and Fig. 1E). In the CM biochars, the intensity of all organic functional bands remained largely unchanged after the biomasses were subjected to the charring process, regardless of the pyrolysis temperature used

(Domingues *et al*., 2017). Protection of organic groups, even at high pyrolysis temperature, may be associated with the high ash content found in coffee husk and chicken manure (Table I). Ash acts as a heat resistant component to thermal degradation, which may protect organic compounds against degradation and may hinder the formation of aromatic structures as charring intensity advances (Enders *et al.,* 2015).

There was a linear decrease in the CEC of the RL soil at as biochar rate is increased, especially for ES and SB biochars (Figs. 1B and 1H). Soil CEC reduced gradually from 19.1 $\mathrm{cmol_c\ kg^{-1}}$ (unamended soil) to a minimum of 14.3 and 13.2 $\mathrm{cmol_c\ kg^{-1}}$ when the soil was amended with 20% of ES750 and SB750, respectively. In the RYL (medium texture), soil CEC slight increases after the application of ES350 and SB, regardless of the pyrolysis temperatures, with soil CEC values of 2.36 and 3.23 $\mathrm{cmol_c\ dm^{-3}}$ higher than the CEC of biochar not treated soil, respectively (Figs. 1B and 1H). Such results can be explained by the low CEC values (Table I) as well as by the dilution effect at these high application rates, since the CEC of these biochars (ES and SB) is much lower than those of the soils. Similar results were observed by Schulz and Glaser (2012) that demonstrated that soil CEC was not increased by wood biochar addition. Although the length of time in our study can be high as compared to other short-term incubation studies with biochar (Basso *et al*., 2013; Bruun *et al*., 2008; Houben *et al*., 2013; Keith *et al*., 2011; Wang *et al*., 2014; Yuan *et al*., 2011a), it is not enough to cause changes linked to biochar surface oxidation as verified in other studies (“the ageing effect”). Such oxidation of organic biochar matrix would take long periods under field conditions to take place as it is observed in the Terra Preta soil (Liang *et al*., 2006). This is one of the reasons why is so important to tailor the biochar prior to its application in order to benefit from the short-term effect of charred matrix use in tropical soils.

Soil carbon

The application of increasing rates of biochar increased linearly the mean soil total C in both soils; furthermore, all over the trials, except for CM treatments, the total C increased with increasing pyrolysis temperature (Fig. 2). Increase in C content as the pyrolysis temperature is elevated occurs due to the higher degree of polymerization, leading to a more condensed and aromatic C structure in the biochar (Lehmann and Joseph, 2009). The higher is the formation of aromatic structures, the higher is the resistance of the biochar to microbial degradation (Keiluweit *et al*., 2010; Keith *et al*., 2011). This explains the high levels of biochar reaming C in treated soils even after 9 months of incubation.

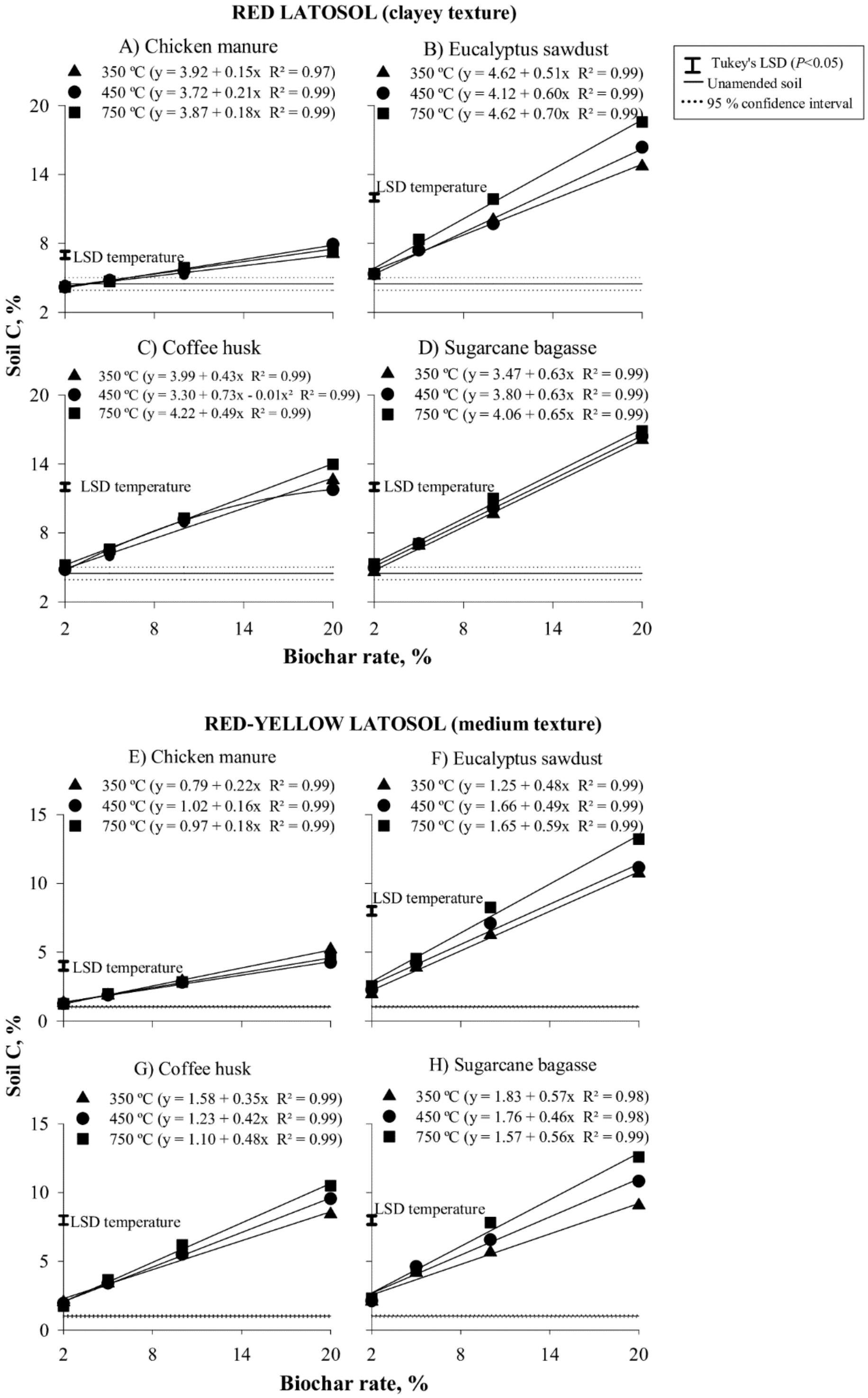

Fig. 2 Total C content in the Red Latosol (clayey texture) and Red-Yellow Latosol over biochar rates of chicken manure (A, E), eucalyptus sawdust (B, F), coffee husk (C, G) and sugarcane bagasse (D, H) produced under different pyrolysis temperature, after 9 months of soil-biochar mixture incubation. Tukey's LSD ($P < 0.05$).

The highest increase in soil C content occurred when ES biochar was applied (especially for ES750) as compared to all biochars studied (Figs. 2B and 2F). In the RL (Fig. 2B) and RYL (Fig. 2F), the total

C contents were, respectively, 13.2 and 18.6 % for ES750 at 20% application rate, which is 3.1 and 11.2 times higher in comparison to C content in biochar not-treated soils.

In the RL, soil amended with CH and SB the total C reached a maximum of 14.0 and 16.9%, respectively. While for the RYL soil, the highest values of C were 10.9% (CH) and 12.6 % (SB). With the application of CM biochar, there were the lowest increases of C content in soils (Figs. 2A and 2E). Wood-derived biochars and biomasses pyrolyzed at 750oC are, thus, suitable sources of stabilized and recalcitrant to store organic matter in tropical soils. Increase in soil contents of soils treated with this more condensed and with a high aromatic character is not a guarantee so soil with more reservoirs of nutrients, high CEC and enhanced fertility status.

Soil pH

Soil pH increased significantly in both soils (RL and RYL) with the addition of all biochars after 9 months of incubation (Fig. 3). Soils treated with CM and CH biochars showed markedly the highest soil pH (compared to other biochar treatments), which is positively correlated with biochar rates added to soils. (Figs. 3A, 3C, 3E and 3F). The pH of the RL amended with CM- regardless of the pyrolysis temperature - increased from 3.4 to a maximum of 7.4 and 9.2 (CH750). The maximum pH of RYL soil were 9.2 (CM750) and 10.0 (CH750), which were much higher than those values reported for the control soil (4.6). This pH increase is consistent with the alkali commonly found in chicken manure biochars as is pointed by its high liming value (Table I). Base cations, such as Ca, Mg, and K were found in high concentrations in precipitated forms of oxides, hydroxides, and carbonates, which are concentrated in the ash fraction of the biochar (Houben *et al*., 2013). Such presence of cations and alkaline specis reduces the contents of acidic surface functional groups (Singh *et al*., 2010). Solubilization of these alkaline substances make biochars function as a liming agent when applied to soil (Novak *et al*., 2009; Yuan *et al*., 2011b). Increases in soil pH reported in our study are in agreement with the findings of other researchers (Sigua *et al*., 2016; Wang *et al*., 2014; Yuan *et al*., 2011a).

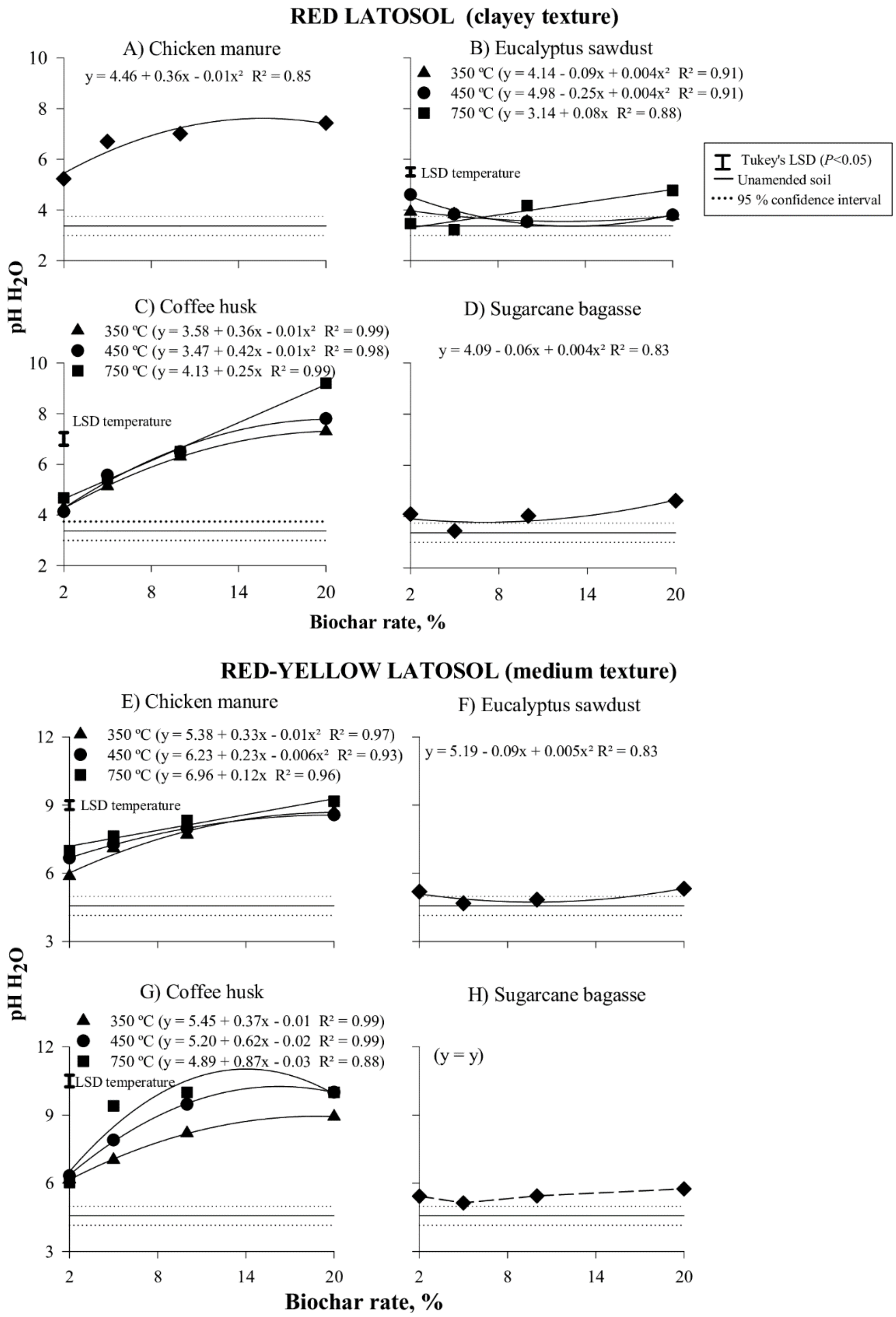

Fig. 3 The pH of the dystrophic Red Latosol (clayey texture) and Red-Yellow Latosol (medium texture) over biochar rates of chicken manure (A, E), eucalyptus sawdust (B, F), coffee husk (C, G) and sugarcane bagasse (D, H) prepared under different pyrolysis temperature, after 9 months of incubation of soil-biochar mixtures. Tukey's LSD ($P < 0.05$).

The lowest increases of pH, in both soils, were observed by the addition of ES and SB biochars (Fig. 3B, 3D, 3F and 3H), which reached a maximum of 4.8 (ES750) and 4.6 (SB, regardless of temperature), being only 1.4 and 1.3 unit higher than the control RL soil (Figs. 3B and 3D). In the RYL, there was no difference ($p<0.05$) among the pyrolysis temperatures, which were increased from 4.6 to 5.3 and 5.8, respectively, for ES and SB at the highest application rate (Figs. 3F and 3H).

Biochar effects on soil CEC

It is highly probable that the changes on soil CEC caused by biochars additions are a result of the high CEC values of the some biochars, which are associated by combination of feedstock characteristic and charring condition (especially pyrolysis temperature). Anthropogenic soils (Indian Black Earth) of the Amazon region have almost the double the CEC compared to the adjacent soil without anthropogenic historic of intervention, which is attributed to high C charge density of the pyrogenic organic matter added in these soils (Liang *et al*., 2006). According to Cunha *et al*. (2009), CEC of anthropogenic soils was strong correlated to humin fraction (more stable fraction of SOM) and total C. These authors also verified that humin enrichment in anthropogenic soils in comparison to adjacent soils is possibly inherited from the carbonized material.

Pearson's correlation was carried out considering the whole data set (for individual soils) between CEC and total C of biochar-amendment soils, in order to understand the relationship of C from biochars on the changes of soil CEC (Table III).

TABLE III
Pearson's correlation coefficient calculated for the whole dataset of measurements

Parameters	Pearson's correlation coefficient (r)	
	CEC-Red Latosol	CEC-Red Yellow Latosol
Soil total C	-0.162^{NS}	0.149^{NS}
Soil pH	0.705*	0.529*

^{NS} non-significant; *Significant at $P \leq 0.05$

The increase in soil C by biochar addition did not explain the increase of soil CEC, which is demonstrated by the lack of correlation for both soils (Table III). This can be verified, for example, in the treatments with C-rich biochars (ES and SB), which caused an increase of C but did not change soil CEC; on contrary, in some situations a reduction on the CEC of the soil was verified, mainly due to the dilution effect of biochar high-rate addition in soil.

Soil pH was correlated with soil CEC increase in all biochar-amended soils (Table III). The highest correlation coefficient found in the RL soil was most likely due to the higher content of organic matter in the soil and due to the influence of increased pH on the development of negative charges in soil and biochar colloids. CEC is strongly pH-dependent in tropical soils and some alkali biochars are capable of raising the soil pH and, consequently, the soil CEC (Hossain *et al*., 2011; Melo *et al*., 2013; Novak *et al*., 2009).

The observed increase in the CEC of soils by the addition of CH and CM biochars was a result of the high CEC of these materials and also by a liming effect. Available evidences so far suggest that the intrinsic CEC of biochars is consistently higher when they have high nutrient content than in low-ash biomass derived biochars (Mukome *et al*., 2013; Gaskin *et al*., 2008). During the process of converting biomass into biochar at lower pyrolysis, chemical elements such as Mg, K, Na, and P are able of catalyzing the formation of oxygenated surface groups in the edge of the biochar matrix (Díaz-Terán *et al*., 2003), with the formation of carboxylic, lactones and phenols, which contribute to the increase of the negative charge density. However, negative charges of surface groups may be drastically reduced with increasing pyrolysis temperature (Song and Guo, 2012). This explains why the CH feedstock, even with high K concentration, pyrolysed at low temperatures (350 °C and 450 °C) resulted in the formation biochar with high potential CEC.

To better establish the interaction of these correlations and in order to predict the soil CEC after a biochar addition we proposed an equation based on significant parameters of Table III:

$$CECfinal_{soil} = (CEC_{biochar} \times Mass_{biochar}) + \left(CEC_{soil} \times Mass_{soil}\right) + netpH$$

where $CEC_{biochar}$ is the CEC of the biochar (cmol$_c$ kg^{-1}); $Mass_{biochar}$ is the mass of biochar estimated from application rate (g g^{-1}, rate at 2% is equal to 0.02); CEC_{soil} is the CEC of the unamended soil; $Mass_{soil}$ is the mass of soil to complete total weight of 1 (g g^{-1}, if $Mass_{biochar}$ is 0.02 then the $Mass_{soil}$ is 0.98); *netpH* is the net change in pH of soil induced by biochar addition at the same rate.

For a better illustration of the functionality of equation (Eqn. 1), a graphical comparison between estimated CEC values and measured CEC is shown in Fig. 4.

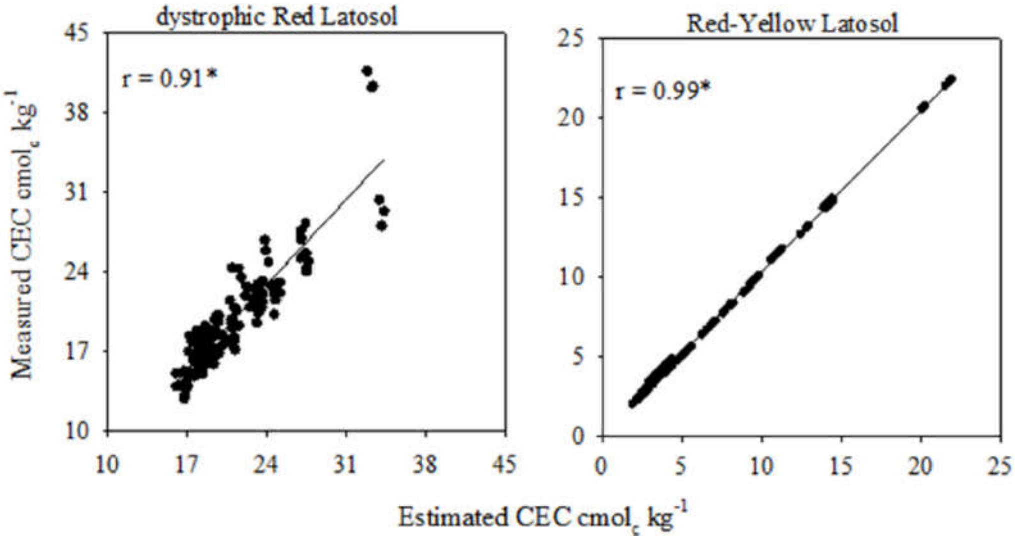

Fig. 4 CEC estimated by Eqn. 1 [$CECfinal_{soil}$ = ($CEC_{biochar}$ x $Mass_{biochar}$) + (CEC_{soil} x $Mass_{soil}$) + netpH] and CEC measured by the sodium acetate method.

As far as we are aware, this was the first attempt to develop a decision support tool for predicting the magnitude of the biochar changes on soil cation exchange capacity. This equation to anticipate if the addition will result in positive, negative or neutral effect on soil CEC, using as predictor the biochar CEC, its effect on soil acidity and the type of soil investigated.

CONCLUSIONS

In summary, the positive effects in soil CEC was predominantly affected by biochars with high CEC and liming value, which are linked to high-ash biochars produced at low-temperatures (350 ºC). Therefore, it is not plausible to suppose that soils amended with low-CEC biochars like eucalyptus and sugarcane, regardless of the charring conditions employed, will impact the soil CEC in comparison to both Oxisol biochar not-treated samples.

Coffee husk biochar pyrolysed at 350 ºC is the biochar matrix most effective in increasing soil CEC, mainly those soil samples with low OM and clay contents. Chicken manure produced at 350 ºC is effective in correcting soil acidity, but its effect on soil CEC is lower than CEC values verified in soils treated with coffee husk. Thus, the type and extent of pyrolysis temperature degradation on the biochar organic matrix functional groups, besides the rate and the effect of the biochar on soil pH, and soil texture, are the main factors regulating the magnitude of changes on soil CEC.

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