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CARACTERIZAÇÃO DE BIOCARVÕES DERIVADOS DE DIFERENTES DEJETOS ANIMAIS E RESÍDUOS DAS CULTURAS E SEU USO EM CULTIVOS DE GRÃOS

Santa Maria, RS
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CHARACTERIZATION OF BIOCHARS DERIVED FROM DIFFERENT ANIMAL MANURES AND CROP RESIDUES AND THEIR USE IN GRAIN CROPS

Thesis submitted to the Doctoral Program of the Graduate Program in Soil Science, the concentration area in Chemical Processes and Elements Cycling, at the Federal University of Santa Maria, Brazil, in a partial requirement for the degree of **Doctor in Soil Science**.

Approved on 25 January 2019

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Santa Maria, RS
2019

DEDICATION

To

My beloved Parents,

and especially my grand father

who always gave me motivation

and strength to explore.

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Lê, em nome do teu Senhor Que criou;

Criou o homem de algo que se agarra.

Lê, que o teu Senhor é Generosíssimo.

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Resumo

CARACTERIZAÇÃO DE BIOCARVÕES DERIVADOS DE DIFERENTES DEJETOS ANIMAIS E RESÍDUOS DAS CULTURAS E SEU USO EM CULTIVOS DE GRÃOS

Autor: Qamar Sarfaraz
Orientador: Leandro Souza da Silva

Em um futuro próximo, o descarte de resíduos orgânicos pode ser um problema sério no Sul do Brasil, visto que a região possui grande quantidade de fazendas com criação animal e produção vegetal. O preparo de biocarvão pode ser uma estratégia para o descarte destes resíduos orgânicos de maneira adequada, obtendo benefícios para os solos agrícolas. Assim, de acordo com a disponibilidade de materiais, propusemos um estudo com o intuito de preparar biocarvões a partir de dejetos de suínos (SMB), de aves (PMB) e de bovinos (CMB) e da palha de arroz (RSB), de soja (SSB) e de milho (CSB) e: I) realizar sua caracterização com base em suas características químicas e de degradação e pela mineralização do carbono (C) quando incorporados ao solo; II) aumentar o pH do solo e reduzir a concentração de Al no solo; e III) avaliar a influência da aplicação de biocarvões no trigo em combinação com fertilizante nitrogenado ($(NH_4)_2SO_3$) e seu efeito residual na cultura da soja sob sistema plantio direto. Os biocarvões foram preparados a 450 °C em forno mufla com aumento da temperatura em 10 °C min^{-1} por 1 h. Todos os biocarvões apresentaram natureza alcalina, tendo pH>9,5. De modo geral, os teores de C e a CTC foram maiores nos biocarvões de resíduos vegetais em relação aos biocarvões de dejetos animais. Por outro lado, para os teores de nutrientes (N, P, K, Ca, Mg e micronutrientes), os biocarvões de dejetos animais apresentaram maior concentração em relação aos provenientes de resíduos vegetais. A espectroscopia FTIR dos biocarvões demonstrou a garantia da menor perda de nutrientes dos materiais durante o processo de pirólise sob baixas temperaturas. A adição de biocarvão ao solo emitiu uma pequena quantidade de CO_2, aumentando o sequestro de C no solo. A adição de biocarvão no solo nas doses de 0, 5, 10 e 20 Mg ha^{-1} aumentou o pH do solo e reduziu o Al trocável até certo ponto, o que confirma que a adição de biocarvões produzidos sob baixa temperatura pode ser uma técnica apropriada para melhorar o pH do solo e reduzir os teores de Al trocáveis em solos ácidos. A adição de 0, 10 e 20 Mg ha^{-1} de biocarvão em solo não perturbado, juntamente com o fertilizante amoniacal, aumentou a altura das plantas e a massa seca do trigo até o florescimento, enquanto que a adição de biocarvões sem N apresentou um leve aumento em relação ao controle (sem biocarvão e sem N). Os efeitos residuais do biocarvão na soja também apresentaram comportamento semelhante ao do cultivo anterior (trigo), onde a adição prévia de N aumentou a altura da planta de soja, bem como a produção de palha da cultura. Após os experimentos, amostras de solo estratificadas (0-5, 5-10, 10-15 e 15-25 cm) foram analisadas para determinação dos valores de pH e dos teores de NO_3^-, NH_4^+, P, K Ca, Mg e Al trocável. Foi possível verificar que nos 5 cm superficiais do solo os teores de NO_3^-, NH_4^+ e P foram influenciados com as doses de biocarvão e com a aplicação de N. Contudo, nas camadas mais profundas não houve diferenças significativas entre os biocarvões, bem como para a aplicação de N. O pH e o Al trocável do solo também foram diretamente afetados até 5 cm de profundidade, enquanto que com o aumento da profundidade o pH do solo diminui e o teor de Al trocável aumenta. Assim, pode-se concluir que os biocarvões preparados a partir de resíduos vegetais sob baixa temperatura são ricos em C, têm maior CTC, apresentam menor mineralização de C e promovem o aumento do pH do solo e a diminuição de Al trocável quando incorporados ao solo sob condições de incubação, enquanto que em condições de casa de vegetação todos os biocarvões foram comparativamente iguais entre si, mesmo em doses diferentes. O aumento na dose de biocarvão aumentou a retenção de nutrientes no solo, enquanto não houve diferença entre os biocarvões derivados de dejetos animais e de resíduos vegetais. Deste modo, o biocarvão pode ser considerado uma alternativa adequada para o descarte de resíduos orgânicos, promovendo o sequestro de C e o aumento da fertilidade do solo.

Palavras Chaves: *Biocarvão, pirólise lenta, pH do solo, plantio direto, efeito direto e residual*

Abstract

CHARACTERIZATION OF BIOCHARS DERIVED FROM DIFFERENT ANIMAL MANURES AND CROP RESIDUES AND THEIR USE IN GRAIN CROPS

Author: Qamar Sarfaraz
Supervisor: Leandro Souza da Silva

In near future the disposal of organic wastes may be a serious problem in Southern Brazil as the region has plentiful amounts of animal farms and crop production. Preparing biochar can be a strategy to dispose off these organic wastes in a suitable way by getting benefits in agriculture soils. So, according to the availability of the materials, we proposed a study to prepare biochars from swine (SMB), poultry (PMB) and cattle (CMB) manures and from rice (RSB), soybean (SSB) and corn (CSB) straws and I) to characterize on the basis of their chemical and degradation characteristics, and carbon (C) mineralization when incorporated in soil and II) to increase soil pH and reduce Al concentration in soil III) to evaluate the influence of biochars application on wheat in combination with nitrogen fertilizer ($(NH_4)_2SO_3$) and their residual effect on soybean crop under no tillage system. Biochars were prepared at 450 °C in muffle furnace for 1 h with 10 °C increase in temperature min^{-1}. All biochars were alkaline in nature with pH >9.5. Overall C content and CEC were higher in crop straw biochars than in animal manures biochars. On the other hand, for nutrient contents (N, P, K, Ca, Mg and micronutrients) animal manures biochars presented higher concentration as compared to the crop straw biochars. The Fourier-Transform Infrared Spectroscopy (FTIR) spectroscopy of biochars presented the assurance of the less nutrient loss from the materials during pyrolysis condition at low temperatures. The addition of biochars in soil emitted a small amount of CO_2 enhancing the C sequestration in soil. The addition of biochar in soil at rate of 0, 5, 10 and 20 Mg ha^{-1} increased soil pH and reduced the exchangeable Al up to a certain extent, that confirms that the addition of low temperature biochars can be an appropriate technique to enhance soil pH and decline exchangeable Al contents in acidic soils. The addition of 0, 10 and 20 Mg ha^{-1} of biochars in undisturbed soil along with ammonium fertilizer increased plant height, and dry mass of wheat grown up to florescence, while the addition of biochars without N showed a slight increase in comparison to control (without biochar and without N). The residual effects of biochars on soybean also presented same behavior to previous crop (wheat), where the previous N application enhanced the soybean plant height and crop straw as well. After the experiments, stratified samples (0-5, 5-10, 10-15, 15-25 cm) were analyzed for NO_3^-, NH_4^+, P, K, Ca, Mg, pH and exchangeable Al contents. We found that in soil top 5 cm the NO_3^-, NH_4^+, and P contents were influenced with biochar doses and with application of N but in deeper layers there were no significant differences among biochars, doses as well as N application. Soil pH and exchangeable Al were also affected directly up to 5 cm depth, while with the increase in depth decreases soil pH and increases exchangeable Al contents. Hence, it can be concluded that the biochars prepared from crop straws at low temperature are rich in C contents, have more CEC, presented less C mineralization, and promote soil pH increase and exchangeable Al decrease, when incorporated in soil under incubation conditions, while in greenhouse conditions all biochars were comparatively equal to each other even at different doses. The increase in biochars rate increased the nutrients retention in soil, while no difference occurred between animal manure and crop straw derived biochars. Thus, biochars can be considered a suitable alternative for organic waste disposal, while promoting C sequestration and enhancing soil fertility.

Keywords: *Biochar, slow pyrolysis, soil pH, no-tillage, direct and residual effect*

List of abbreviations

SOM	Soil Organic Matter	SOC	Soil Organic Carbon
C	Carbon	N	Nitrogen
NH_4	Ammonium	NO_3	Nitrate
P	Phosphorus	K	Potassium
Ca	Calcium	Mg	Magnesium
Fe	Iron	Zn	Zinc
Mn	Manganese	Cu	Copper
SMB	Swine Manure Biochar	PLB	Poultry Litter Biochar
CMB	Cattle Manure Biochars	RSB	Rice Straw Biochar
SSB	Soybean Straw Biochar	CSB	Corn Straw Biochar
Al	Aluminum	EC	Electrical Conductivity
CEC	Cation Exchange Capacity	GHGs	Greenhouse Gases
CO_2	Carbon Dioxide	CH_4	Methane
N_2O	Nitrous Oxide	CA	Conservation Agriculture
NT	No-Tillage	INM	Integrated Nutrient Management
MRT	Mean Residence Time	CT	Conservational Tillage
SSA	Specific Surface Area	WPH	Wheat Plant Height
WSL	Wheat Spike Length	WDM	Wheat Dry Mass
SPH	Soybean Plant Height	SPH	Soybean Plant Height
ha	Hectare	ha^{-1}	Per hectare
FTIR	Fourier-Transform Infrared Spectroscopy		

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1 GENERAL INTRODUCTION

Soil fertility is the ability of a soil to supply plant nutrients to maintain sustainable crop productivity. Soil fertility degradation and available nutrient depletion is common in agroecosystems with environmentally detrimental amounts of modern agricultural practices, which have imbalanced the responsible abiotic and biotic soil fertility factors (SUZUKI et al., 2014). Soil fertility enhancement and maintenance are challenging nowadays, as soil nutrient availability and retention have generally been declining. It is clearly urgent to reverse the trend to sustain the soil fertility of agroecosystems. Application of organic amendments such as compost and animal manure are traditional practices to rehabilitate soil nutrient retention. However, the traditional organic amendments are of short life span in soil.

During the industrial era, the concentration of many greenhouse gases (GHGs) has substantially increased in the atmosphere because of anthropogenic emissions. The enhanced greenhouse effect causes changes in the global climate. The main drivers of the anthropogenic climate change are carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). Agriculture has been identified as one of the key sectors contributing to the atmospheric increase of those gases (CIAIS et al., 2013). Carbon dioxide is released from the agricultural use of fossil fuels, from the conversion of forests to agricultural land, and from the enhanced decomposition of organic material in cultivated soils.

Common recommended management practices in tune with soil management principles include (i) conservation-effective measures that reduce risks of runoff and soil erosion such as conservation agriculture (CA) comprising no-tillage (NT) farming, mulching, cover cropping, and integrated nutrient management (INM) that provide adequate amount of plant nutrients for satisfactory crop growth and complex crop rotations, that enhance biocomplexity and provide a continuous ground cover such as cover cropping and integration of crops with livestock (LAL, 2015); (ii) growing deep-rooted plants to transfer C into the subsoil such as agroforestry; and (iii) adding recalcitrant material into the soil that is relatively resistant to microbial decomposition and has long mean residence time (MRT) (e.g. biochar).

Owing to different production conditions and indeed variety in feedstock materials used to produce biochar chemical attributes vary considerably. At an elemental level, biochar properties can be ascribed with respect to ratios of C, H, O and N. Particularly, ratios of H/C and O/C are used to determine the degree of biochar aromaticity i.e. the lower is the ratio, the greater is the aromaticity (KOOKANA et al., 2011). The nutrient concentration in biochars vary according to the feedstock type and pyrolysis temperature and conditions e.g. temperature above 200 volatilize nitrogen (N), while phosphorus (P) and potassium (K) can be lost at 700 and 800 °C respectively (DELUCA et al., 2009).

The X-ray diffraction matrix of biochar showed the amorphous structure along with crystalline areas (LEHMANN; JOSEPH, 2009) consisting of random polycyclic aromatic (graphene) layers rimmed by functional groups (ZHU et al., 2005) and mineral compounds (LEHMANN; JOSEPH, 2009). Studies have revealed that biochars produced at temperature more than 330 °C show the polyaromatic sheet formations and increase the porosity of the biochars. The increase in pyrolysis temperature decreases the particle size and hence increase the micro porosity of biochars, consequently increase surface area.

The addition of biochar can have several consequences in the soil. Typically, biochar addition increases soil pH (MAJOR et al., 2010; JONES et al., 2012), cation exchange capacity (LIANG et al., 2006), and soil water retention (NOVAK; WATS, 2013), which also increases nutrient availability for plants (MAJOR et al., 2010). Better nutrient and water availability enhance plant growth (MAJOR et al., 2010), leading at the same time to increased litter production. In addition, biochar addition itself increases organic C and some nutrient concentrations (e.g. P, K) in the soil (ANGST; SOHI, 2013).

Biochar's chemical composition and nutrient arrangement rely mainly on the feedstock and the production temperature (QIN et al., 2012; SPOKAS; REICOSKY, 2009). Moisture content of the raw biomass also aff ects the composition of the final product (GALINATO et al., 2011). For all biochars that are frequently defined as "the carbonaceous crude of biomass pyrolysis," the main constituent is C (AHMAD et al., 2014). This C is arranged into aromatic structures and occasional piles of graphite-like layers (ZIMMERMAN, 2010). Additionally, H, O, and N are the main supportive elements for C to finalize the biochar structure (MIMMO et al., 2014).

It was reported by Gaskin et al. (2008) that biochar produced from poultry manure contained more nutrients than biochars produced from others containing poor nutrient contents. Likewise, Joseph et al. (2010) documented that diff erent types of manure-derived biochars generally contained significant amounts of available plant nutrients. However, manure-derived biochars produced at high temperatures have low hydrolyzable organic N and high aromatic and heterocyclic structures (CLOUGH et al., 2013). In general, biochars produced at low temperatures (e.g. ≤ 300 °C) are richer in nutrients than those produced at high temperatures (e.g. ≥ 600 °C). Therefore, the biochars produced at relatively low pyrolysis temperatures are preferred as agricultural soil amendments (ATKINSON et al., 2010; CLOUGH et al., 2013).

Being a material with high cation exchange capacity (CEC), biochar can enhance soil CEC, improve water and nutrient retention capacity of soil because of its high surface-area, high porosity and variable-charge (AMONETTE; JOSEPH, 2009; YANG et al., 2010). Studied reported that mostly biochars are alkaline in nature and contain high pH, therefore, biochar application can enhance soil properties in terms of increasing soil pH (RONDON et al., 2007), especially in acidic soils.

Biochar addition to soil improves plant growth by providing nutrients and more importantly, recycling of nutrients and improving soil physical and biological properties (VERHEIJEN et al., 2004). Application of biochar has great positive effects on environment as it helps us to reduce the emissions and increase of greenhouse gases. Also, application of biochar to soil show immediate benefits as it improves the soil fertility which in turn gives amazing crop production. Biochar has positive impact not only on soil, but in fact, it has positive effects on water holding capacity and stability of soil (SOHI et al., 2010).

A study conducted by Steiner et al. (2008) on N retention and plant uptake on a highly weathered central Amazonian Ferralsol amended with compost and charcoal. The results showed that higher N retention and uptake by biomass can cause noticeable increase in nitrogen cycling in treatments receiving charcoal. Addition of charcoal improved the efficiency of mineral N fertilizer.

Southern Brazil is an important agriculture region, mainly known for the production of soybean, maize, rice, sorghum, wheat and black beans. About 27 million hectares (M ha) of land are under NT cropping system (BODDEY et al., 2010). A considerable number of studies reported significant increase in soil organic matter (SOM) in NT systems compared to conventional tillage (CT) system (BAYER; MIELNICZUK, 1997a; BAYER et al., 2000b; BAYER et al., 2006; CARVALHO et al., 2009). Application of biochar improves soil quality and environment by increasing storage of stable organic C (WOOLF et al., 2010), reducing CO_2 and N_2O emissions and enhancing soil inorganic N (NH_4^+ and NO_3^-) retention (ZHAO et al., 2013b).

Soil and crop managements aiming for increasing C retention and increasing N use efficiency must consider the stabilization mechanism of applied organic material. This demands a deep insight into the decomposition patterns and fate of C and N in different soil fractions to determine how long this C is retained by soil and stabilized in SOM pools. A detailed budget of carbon inputs and losses is required in evaluating the carbon sequestration potential of agroecosystems. Yet, there is a rarity of system level studies investigating the effects of organic amendment i.e. biochar type, tillage system and soil texture on the ecosystem-level C and N balance. Here we report the effect of different biochar type (animal and plant derived) applied to soil under greenhouse conditions on wheat and soybean in relation to C and N transformations under NT system.

2 STATEMENT OF PURPOSE

The SOM occupies vital position in global carbon cycle for its importance in climate regulation and ecosystem functioning. Agro-ecosystems emit significant amounts of GHGs to the atmosphere either directly or indirectly by 1) combustion of fossil fuel during the manufacture of synthetic fertilizer, agrochemicals and on-farm machinery operations, 2) changes in land use and 3) microbially mediated processes such as decomposition of SOM, nitrification and denitrification (SOUSSANA et al., 2010; JENSEN et al., 2012).

At present, CO_2 in the atmosphere represents the highest concentration during the last 650,000 to 800,000 years (LUTHI et al., 2008). On an average, agricultural soils are reported to contribute about 20% to the total emission of CO_2 and 12% of CH_4 (IPCC, 2007a). However, the soils on the other hand, could serve as a sink for atmospheric CO_2 at low to no cost ratio (LAL, 2004a; PACALA; SOCOLOW, 2004; LAL et al., 2015). Therefore, efforts aiming at reducing CO_2 concentration in atmosphere are the burning issue of the day (IPCC, 2007a), and scientists and policy makers are looking for ways to reduce or reverse the trend i.e. from atmosphere to soil. An important option to cope with climate change and reducing CO_2 emissions from soils is the sequestration of atmospheric CO_2 into soil C pools (LAL, 2011; LAL et al., 2015). Soil C pools are represented by large amounts of organic and inorganic C (QUERE, 2008; HAN et al., 2018). Soil organic carbon (SOC) exists in different pools of varying size and is estimated to be <20 to >200 Mg C ha^{-1} in the top 30 cm of soil (ARROUAYS et al., 2001; HOYLE et al., 2011). Less than 15% of SOC is represented by plant roots, fresh residues, living microorganisms, and macro fauna, while partially decomposed plant residues, humus and charcoal represent the remaining. Inorganic C exist as carbonates and bicarbonates and is mainly derived from geologic or soil parent material (DALAL; CHAN, 2001; HOYLE et al., 2011). The conversion of natural lands (forest and pasture) to crop lands reduced SOC stocks by an average of 25-75%, representing a loss of 78 ± 12 billion tons C (LAL, 1999).

Similarly, N_2O concentration in the atmosphere has been raised by 20% since last century and is still increasing at a rate of 0.2–0.3% yr^{-1} (BATES et al., 2008). Agricultural soils are reported to contribute about 60% of the anthropogenic N_2O emissions into atmosphere (IPCC, 2007a).

The quantification of C transformations and N supplying capacity of organic amendments applied to a soil has immense importance to examine synchronization and N release capacity.

Application of organic amendments like manure is an important management strategy for restoration of these degraded soils and providing better soil conditions to below-ground soil microbial composition and above-ground plant community development (ABBASI; KHIZAR, 2012). Continuous application of organic amendments in the form of animal manures, crop residues, and other organic materials can effectively restore and improve the productivity potential of the soil. Previous reports clearly suggested improvement in SOM status, overall physical, chemical and microbiological environment of the soil amended with organic substrates/materials (KHALIQ et al., 2006; ZINGORE et al., 2008; ABBASI; TAHIR, 2012).

In recent years, biochar has emerged as potential organic amendment to sustain soil productivity and an effective approach to mitigate climate change. Biochar is the product of thermal degradation of organic materials in the absence of air (pyrolysis), and is distinguished from charcoal by its use as a soil amendment (LEHMANN; JOSEPH, 2009; SOHI et al., 2010). The observed effects of biochar on soil fertility have been explained mainly by a pH increase in acid soils (ZWIETEN et al., 2010a) or improved nutrient retention through cation adsorption (LIANG et al., 2006; BEUSCH et al., 2019; CHENG at al., 2018). However, biochar has also been shown to change soil biological community composition and abundance (KIM et al., 2007; LIANG et al., 2010). Biochar has been described as a possible means to improve soil fertility as well as other ecosystem services and sequester C to mitigate climate change (LEHMANN et al., 2006; LEHMANN, 2007a; SOHI et al., 2010).

The effectiveness of using biochar as an approach to mitigate climate change rests on its relative recalcitrance against microbial decay and thus on its slower return of terrestrial organic C as CO_2 to the atmosphere (LEHMANN, 2007b). Both the composition of the decomposer community as well as metabolic processes of a variety of soil organism groups may be important in determining to what extent biochar is stable in soils, as is known for wood decay (FUKAMI et al., 2010). Changes in microbial community composition or activity induced by biochar may not only affect nutrient cycles and plant growth, but also the SOM cycling (WARDLE et al., 2008). In addition, biochar may change emissions of other GHGs from soil such as N_2O or CH_4 (TAGHIZADEH-TOOSI et al., 2011). Such changes may either reduce or accelerate climate forcing. The driving processes are still poorly identified (ZWIETEN et al., 2009). A more rapid mineralization of indigenous soil C or greater emission of other GHGs as a result of biochar additions may counteract the benefits of reduced emissions elsewhere in the life cycle of a biochar system. A systematic examination of the ways in which different microbial and faunal populations may play a role in these biogeochemical processes is still lacking. Another implication of greater nutrient retention in soil is improved fertilizer use efficiency (FUE). Especially in the case of N, greater FUE leads to either reduced costs for farmers, or greater yields for a given fertilizer application rate. N availability often limits crop growth, and N fertilizers represent a large investment for farmers. In the Brazilian Amazon, Steiner et al. (2008) observed greater N use efficiency by crops growing in an acidic soil amended with 11 t ha^{-1} wood biochar over 2 years. With the application of 11 t ha^{-1} of biochar in bands, the yield of wheat could be improved more at low rather than high fertilizer application rates. Also, at this low biochar application rate, the wheat yield obtained with a high fertilizer application rate could be reproduced with half the amount of fertilizer (BLACKWELL et al., 2010).

The N present in organic fertilizers is mainly in organic form, which has to be mineralized before becoming plant-available form. Hence, it is essential to study mineralization-immobilization turnover of organic amendments applied alone or their integrated use with mineral N fertilizer to estimate the amount and release rate of the applied N (RIBEIRO et al., 2010). Under controlled environmental conditions, previous studies indicated that added N from mineral N fertilizers disappeared shortly after fertilizer application because of simultaneous nitrification denitrification (ABBASI; ADAMS, 2000; ABBASI et al., 2001). On the other hand, mineralization from organic N sources i.e. cattle manure, sheep manure and poultry manure showed that during incubation a maximum of 50 mg N kg^{-1} was released from cattle and poultry manure into mineral N pool (ABBASI et al., 2007). However, the mineralized N also disappeared from the system after 90 days incubation. Under field condition these N losses may be high because of the chances of leaching, that had been controlled under laboratory incubation studies. The mineralization studies conducted in most parts of the world facing the same issues. To overcome this problem, it is possible to use integrated approach by combining mineral N with labile and stable organic fractions (materials) to check rapid N disappearance due to slow mineralization by labile organic material and chances of immobilization from stable organic material. Combining mineral N fertilizers with organic resources may result in temporary immobilization and subsequent release of fertilizer-applied N due to stimulation of microbial activity from the residue additions, thereby improving the persistence and retention capacity of applied N for longer period in mineral N pool (VANLAUWE et al., 2001; GENTILE et al., 2011). Delgado et al. (2010) reported that N losses from the inorganic fertilizer inputs were significantly higher (31%) than N losses from crop residue (13%). The authors further reported greater N retention in soil with crop residue inputs (73%) than with mineral N fertilizer (26%), suggesting that the slower cycling pool of crop residue protects against N losses.

The SOC additions and losses are strongly influenced by climate (LAL, 2007), soil texture (SOUSSANA et al., 2010), source of organic residues (ROCHESTER, 2011), and soil management practices (CHRISTOPHER; LAL, 2007). Among soil management practices, CT is known to produce sustained increase in decomposition due to the modification of soil environment and disruption of soil aggregates (BALESDENT et al., 2000). On the other hand, adoption of NT practice helps in maintaining crop residues on soil surface, reduces soil disturbances and C mineralization, enhancing stabilization of crop residues as humified organic matter (WEST; POST, 2002; LAL, 2007). In an experiment Allmaras et al. (2004) reported 26% more humification of residues under NT when compared to 11% of the same residues with moldboard plow and chisel till. Similarly, in another experiment in Ohio, USA, 11.9% of the corn residues were found to be stabilized as humified SOC for NT and 8.3% for plow till (PUGET et al., 2005).

There are number of evidences, that biochar influences a range of soil properties and hence increasing the crop productivity. The nature and extent of the biochar impact on soil vary widely depending upon the feedstock type, pyrolysis temperature and pyrolysis conditions as well. Unlike other soil amendments, fertilizer, green manure, composting and vermi-composting, biochars impacts are not yet well understood and either in terms of their use mechanism and durability in soil are hidden facts yet.

3 HYPOTHESIS

Release substantial N into mineral N pool from biochars thereby can be utilized as N nutrient source.

- Biochars will sequester C in soil as pyrogenic carbon instead of escaping of C into the environment in form of carbon dioxide (CO_2) will slow down the C mineralization in soil.
- The soil acidity will be decreased by different types of biochar by increasing the soil pH and by decreasing the exchangeable Al.
- Slow down the rate of mineralization of added mineral N fertilizers hence increase the retention and persistence capacity of mineral N for a longer period in mineral pool.

4 OBJECTIVES

General Objective

Keeping in view the general objective of the present study was to quantify the relative potential rates of mineralization and subsequent nitrification of different biochars and nitrogen applied alone or in different combinations under greenhouse conditions.

Specific Objectives

Our objectives include,

- To determine the difference between animal and plant derived biochar in relation to their elemental concentrations.
- To increase the pH and decline soil acidity of soil using different biochar types under incubation conditions.
- To investigate residual effect of biochar on subsequent crop (soybean crop) with N application as mineral fertilizer.
- To investigate the effect of biochars on nutrient retention in soil after crop harvest.

5 ARTICLE I - CHARACTERIZATION AND CARBON MINERALIZATION OF BIOCHARS PRODUCED FROM DIFFERENT ANIMAL MANURES AND PLANT RESIDUES[1]

Abstract

Disposal of animal wastes and crops straws produced in Southern Brazil may be a serious problem in future. Preparing biochars and use them in agricultural soils can be a beneficial way to get rid of these wastes. However, a sustainable use of biochar in agricultural soils depends on their specific composition and characteristics. A study was proposed with objectives to characterize and evaluate carbon (C) mineralization of biochars produced from different animal wastes and crop straws. Six types of biochars were prepared from animal manures (poultry litter, swine and cattle manures) and crop straws (rice, soybean, and corn straws) at 450 °C in a muffle furnace for 1 h. The biochars were analyzed for chemical characteristics (elemental variables, thermal decomposition, cation exchange capacity, pH, electrical conductivity, specific surface area, and surface functional groups) and an incubation experiment was conducted to evaluate C mineralization from soil biochar mixture. Biochars produced from straw feedstock contain more C as compared to the biochars produced from animal manures. Nitrogen was low while P, K, Ca, and Mg were found reasonably higher in all biochars except swine manure biochar (3% N). Cattle manure produced more ash whereas crop straw biochars presented more hemi-cellulose, except rice straw biochar. Cellulose and lignin contents were substantially lower in all biochars, presenting the partial decomposition at high temperatures. Maximum CEC was observed in swine manure biochar while overall CEC was higher in plant derived biochars. All biochars were alkaline in nature with highest pH (10.4) for rice straw biochar. It is obvious from FTIR spectroscopy of all biochars the spectra less than 600 cm^{-1} illustrate the presence of the inorganic elements, confirming the lesser loss of nutrients from the biochar produced at lower temperature. The plant derived biochars presented lower CO_2 emissions when incorporated to soil at 1 and 2% of C. Hence, biochars from crop straws are rich in C, alkaline in nature, high CEC, present low CO_2 emissions, can sequester C and could enhance soil fertility.

Keywords: Biochar; slow pyrolysis; FTIR spectroscopy; animal manures; crop straw.

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Highlights

- Animal manures and plant residues biochars prepared at low temperature are rich in nutrients
- High pH of biochars can act as liming agent, could be beneficial for acidic soils
- Elevated cation exchange capacity of biochars may be beneficial for soil to increase the nutrient holding capacity of soil
- Rich in carbon and enhances the C sequestration, instead of rapid mineralization

5.1 Introduction

In Southern region of Brazil can be found immense amounts of diverse animal manures and plant residues, as the region has a huge number of animal farms and crop production. Swine and poultry farms are the principal sources of the manure produced in the region. Rice is cultivated on about 1,000 M ha area [1], while soybean and corn are also major crops grown in the region (more than 6,000 M ha area) [2]. In the region, no-tillage planting system is used to grow crops for a long time and crop straws are left on the surface at the time of harvesting. There may be noted an uneven decomposition of these organic materials and different environmental impacts can be noticed, such as releasing carbon dioxide (CO_2) into the atmosphere and N can be immobilized by microorganisms or can be escaped into the atmosphere in form of N_2O, N_2 and NH_3.

Biochar is an alternative and beneficial strategy to dispose-off the animal manures and plant residues rather than keeping them on the place or applying to soil directly [3]. Biochar is a solid C rich material obtained from organic waste burning in the absence or low supply of oxygen [4]. A huge amount of different biomasses can be found to produce biochars such as animal manures, plant residues, sewage sludge, and agricultural wastes. Its production from different residues and wastes for the use in agricultural soils may be a valuable mean to decrease the negative impacts of emissions (greenhouse gases) from the huge wastes, from manures and plant residues and also improving soil conditions by the addition C-rich biochars [5,6].

There are number of aspects which can influence the biochar production and characteristics such as the type of carbonization process, carbonization temperature [7], time of carbonization, and type of feedstock. The biochars prepared at low temperatures have more yield, minor compactness of the aliphatic compounds and are amorphous in nature. Amonette and Joseph reported minute CH_4, H_2 and C loss from biochars produced at low temperature [8]. Lang *et al*. [9] found N losses from the biochars prepared above 400 ºC. On the other hand, it is recommended that biochars produced at 450 ºC are suitable for agriculture in relation to their production and nutrient concentrations [10]. As a consequence, biochars produced from different feedstock and from different techniques present assorted characteristics such as total carbon (TC), pH, liming effect [11], electrical conductivity (EC), cation exchange capacity (CEC), density (D), and specific surface area (BET-SSA) [12].

The information above related to the mode of preparation of biochars vary for its physical and chemical analysis in relation to its use. A variety of processes used in different studies makes even more difficult in comparing the output regarding the influence of feedstock properties on the biochar characteristics. Keeping in view the availability of the feedstock in Southern region of Brazil, we decided to prepare biochars from poultry litter, and swine and cattle manure, and rice, soybean, and corn straws. So, depending on the collection of feedstock type, we hypothesized that the biochars produced from animal manures and crop straws will be different in their chemical characteristics from each other. In this way, they can be differentiated and characterized for further use in agriculture.

The objectives of the study were to evaluate the chemical characteristics of the biochars produced from different animal and crop residues and to evaluate their C mineralization when biochars are incorporated to soil.

5.2 Material and methods

5.2.1 Material collection

Animal manures i.e. poultry litter, swine manure (solid) and cattle manure (solid) were collected from the experimental areas of the Animal Science department at Federal University of Santa Maria (29°43'14.4"S 53°43'31.2"W). The crop straws (rice and soybean) were collected from the experimental areas of the Soil Science department, at Federal University of Santa Maria, while corn straw was collected from a field area located in a near municipality – Paraíso do Sul (29°35'10.3"S 53°07'26.3"W). Impurities, like stones from manures and grasses from straws, from all raw materials were taken off manually. Raw materials were dried in the air-forced oven during approximately 48h up to a constant mass at 60 ºC. Manures were milled and passed through a mesh with 4.0 mm openings, while all crop straws were milled and passed through a mesh with 8.0 mm openings.

5.2.2 Biochar preparation

All six biochars, denoted as swine manure biochar (SMB), poultry litter biochar (PLB), cattle manure biochar (CMB), rice straw biochar (RSB), soybean straw biochar (SSB), and corn straw biochar (CSB), were prepared at low temperature. This procedure was taken keeping in mind the findings of Novak *et al*. [13], that biochars produced at low temperature contain more functional groups and are more suitable for agriculture use, while biochars prepared at higher temperatures consume more energy as well as lose more nutrients. Prior to prepare biochars, all materials were well mixed to make a homogenized mixture. A known mass of raw material was kept in pre-weighed ceramic crucibles and put in a muffle furnace (Forno Jung, Number 7549, Brazil) with an increase in temperature of 10 ºC min^{-1} until a final residence time of 1 h at 450 ºC. After 1 h of residence time in a muffle furnace, the furnace was turned off and was left down to cool at room temperature, and crucibles containing biochars were taken out and weighed. Biochar production was measured using formula as follows:

$$\text{Biochar production (\%)} = \frac{\text{Mass}_{(\text{Biochar})}(\text{g})}{\text{Mass}_{(\text{Feedstock})}(\text{g})} \times 100 \qquad \text{Eq. 1}$$

5.2.3 Biochar analysis

To analyze, the biochars were milled and passed through a mesh containing 1.0 mm pore size. Total carbon (TC) and nitrogen (N) were measured in elemental analyzer (Thermo Scientific, Flash EA 1112, Milan, Italy). Triplicate samples of biochars were extracted by 0.1 M HNO_3 solution following method used at Embrapa (2009) [14] to determine total phosphorus (P), potassium (K), calcium (Ca), and magnesium (Mg). The P was measured by using spectrophotometer following the Murphy & Riley [15] method, while K, Ca, Mg and micronutrients (Cu, Zn, Mn, Fe) were measured by the method proposed by Tedesco *et al*. [16].

Thermal decomposition analyses were performed to evaluate the decomposition of materials (biochars) by high heat (450 ºC). Prior to evaluating decomposition, biochars were analyzed for moisture contents by putting a known mass of biochars in a muffle furnace at 105 ºC for 24 h. Ash was measured by putting a known mass of biochars in small ceramic crucibles in a muffle furnace at 550 ºC for 8.0 h and ash content was calculated as follows.

$$\text{Ash (\%)} = \frac{\text{Mass of ash after 550 °C (g)}}{\text{Mass of dry biochar (g)}} \times 100 \qquad \text{Eq. 2}$$

Fiber fractions of the biochars were also evaluated with duplicate samples, determining cellulose, hemicellulose, lignin and soluble fractions by the method of Van Soest *et al*. [17] with some modifications. The procedure was modified by increasing the burning time period of biochars in a muffle furnace at 550 ºC for 10 h.

Cation exchange capacity (CEC) was measured through the method used by Enders *et al*. [18] while electrical conductivity (EC) and pH were measured using distilled water with ratio 1:10 (w/v), using three replicates for all biochars. Brunauer Emmett Teller specific surface area (BET-SSA) of biochars was measured at Ceramic Material Laboratory (LACER) of Federal University of Rio Grande do Sul, using Volumetric (Manometric) Gas Sorption method by Surface Area Analyzer (Quantachrome Instruments, N32-28E, USA) [19]. For Fourier-transform infrared (FTIR) spectroscopy, the biochar samples were mixed with spectroscopic-grade KBr and analyzed by Spectrometer Perkin-Elmer, Model Spectro One.

5.2.4 Incubation experiment setup

The Typic Hapludult (U.S Soil Taxonomy) soil was collected from the experimental areas (29°43'14.2"S 53°42'15.0"W) of the Soil Science department at Federal University of Santa Maria. Top soil (0 to 25 cm) was collected, air-dried, ground and sieved in a 2.0 mm mesh. The texture of the soil was sandy loam (61.71% sand, 25.72% silt, and 12.56% clay). Soil was analyzed from composite sample for pH $_{(1:2.5\ w/v)}$ (4.8), TC (1.2%), Ca (15.5 $cmol_c\ dm^{-3}$), Mg (9.3 $cmol_c\ dm^{-3}$) and Al (16.89 $cmol_c\ dm^{-3}$). To evaluate the C mineralization, we set an experiment using a set of cups with capacity of 100 ml containing 80 g of soil mixed with 1 and 2% of C, in accordance with carbon contents in each biochar, because of different densities of the biochar originated from animal manure and crop straw. One extra treatment (soil only) was also included, instead of using individual control for each biochar type. The set of experimental cups was kept in a biological oxygen demand (BOD) incubator at 25 ºC for 49 days. Field capacity moisture was maintained throughout the experimental period by adding a few drops of water at each sampling day, when needed.

Statistical analysis

Results from each parameter were analyzed using software Statistix 8.1 and performed analysis of variance (ANOVA) to evaluate the difference among different biochars produced from the different feedstock. Least significance difference (LSD) was performed for parameters of biochars at 5% level of significance to differentiate the means. Data on the C mineralization was analyzed by software R version 3.5.1 with assistance of RStudio.

5.3 Results and Discussion

5.3.1 Chemical properties of biochars

Biochar yield was comparatively low as in previous studies [20] because the oxygen was not controlled during the production of the biochars. Biochar production varied for all the materials showing maximum production in cattle manure and poultry litter (58% and 57%, respectively), while minimum production was noted by corn straw (26%). Chemical properties of biochars produced from different feedstocks at 450 ºC pyrolyzing temperature for 1 h are presented in Table 1.

Maximum TC was found in SSB (69.17%) and CSB (67.78%), whereas TC in biochars produced from animal manure ranged from 16.42 to 38.27% in CMB and SMB, respectively. The less TC contents of the manure biochars can be attributed to the low pyrolysis temperature that did not allow to concentrate C in feedstock. The high TC contents at biochars from soybean and corn straw might be related to the depletion of the H and O during pyrolysis process. Elevated TC in straw biochars can be related to the C fixation in biomass at high temperature, that encourages the C sequestration. The results of TC in RSB are similar to the findings of Jindo *et al*. [21], who reported less TC contents (49.0%) in the biochar produced at low temperature (400 ºC) from rice straw.

The N concentration is relatively low in all biochars, probably attributed to the high temperature during pyrolysis conditions, the burning of organic material, and the nitrogen loss as volatiles (NH_3, N_2O, NO_2) from the original material. Lang *et al.* [9] reported that the biochars produced above 400 ºC contain relatively low N contents due to loss of N from the parent material at high heat. Highest N was determined in SMB (3.00%), followed by SSB (2.13%) and PLB (1.82%). On the other hand, CSB (0.79%), RSB (0.87%) and CMB (0.95%) showed the lowest N concentration. N concentration in PLB was similar to the N concentration (2.0%) of biochar produced by Chan *et al*. [22] at 450 ºC from poultry litter. Usually, legumes have more N concentration in plant tissues and the biochar properties are in direct proportion to its original N concentration in parent material. Moreover, Song and Guo [7] prepared biochars from poultry litter at 300 to 600 ºC with 50 ºC interval for each biochar. Their results showed that biochars prepared at lower temperature (i.e. 300 ºC) had more nutrients concentration as compared to the biochars produced at 600 ºC.

The P concentrations in SMB and PLB are relatively high, 4.88 and 3.33%, respectively, which are far higher than the 1.9% results obtained by Gunes *et al*. [23] from poultry manure biochar produced at 300 °C for 2 h. On the other hand, the crop straws biochars presented the lower P contents, showing that the biochars produced from animal manures are, in general, richer than the biochars produced from crop residues. Alike to the trace elements, there is a possibility to preserve P in biomass during the slow pyrolysis process. Higher P contents, of 43.0 g kg^{-1}, were observed when poultry litter biochars were produced by fast pyrolysis at 450 ºC [24]. High P concentration in SMB and PLB may be accredited to the C loss and forming stable P. Biochars produced at low temperatures have more soluble P, that becomes insoluble at high temperature [25].

The K concentration varied in all biochars ranging from 0.69% in SSB to 5.97% in RSB. The low concentration of K in SSB may be accompanied to the reason that the soybean straw was collected a week later after harvesting, while rice straw was collected at same time of harvesting. As K is a nonstructural component of plat tissue, it could easily be released after harvesting, even more after some rainfall. Data about K concentration in biochars found in literature are contradictory. While Yu *et al*. [26] reported K loss from wheat straw at different increasing temperatures, Chan and Xu [27] found increase in K contents with increasing temperature. These last authors also reported that poultry litter biochar may have K contents from 1.41 to 7.49%.

The Ca and Mg contents are much higher in PLB and SMB than in the other biochars. Maximum Ca was found in PLB (23.89%), which can be related to the experiment from where poultry litter was collected, because the experimental site poultry trays were a bit higher from ground, so it has a possibility that the litter we collected from that area would be a mixture with poultry feed as well as egg shell. In the biochars from straws, Ca in CSB was the minimum (0.61%) following RSB (1.53%) as compared to the SSB. In contradiction, Wang *et al*. [28] and Cao and Harris [29] found more Ca and Mg contents biochars prepared at 500 ºC from poultry litter and animal manures respectively.

Comparatively, micronutrients contents were found higher in the biochars produced from animal manures than the contents found in biochars produced from crop straws. Comparing overall biochars, Mn concentrations were higher in all biochars ranging from 97 mg kg^{-1} to 1041.7 mg kg^{-1} in SSB and RSB respectively. This behavior can also be related to the soil reduction process in flooded rice fields, increasing Mn solubility and its uptake by rice plants, resulting in a higher Mn content in rice straw compared to other crop residues. The elevated concentrations of micronutrients in biochars are due to the mass loss which resulted in concentrate micronutrients in char products. Hossain *et al*. [30] found in his research that with the increase in temperature trace elements concentration increases, in relation to the temperature used and with mass loss. He *et al*. [31] evaluated that the temperature higher than 350 °C favors the stability of trace elements due to the mass loss.

All biochars had a different ash percent, highest in CMB (77.32%), while minimum ash percentage (10.32%) was found in CSB (Table 2). In comparison to the crop residues, the animal manures had more ash contents. Moreover, RSB had more ash as compared to the SSB and CSB, which may be ascribed to the partial change caused by the organic and inorganic substances during pyrolysis conditions [18]. Hemicellulose is the difference between acid detergent fiber and neutral detergent fiber in the Van Soest's method. Maximum (85.95%) hemicellulose was found in SSB whereas minimum (44.08%) was noted in PLB. A small amount of cellulose was found in all biochars showing maximum 0.116% in CSB and minimum 0.004% in CMB. Overall hemicellulose and cellulose contents were lower in biochars prepared from animal manures than the biochars from crop straws, except for RSB which had 77.03% and 0.011% of hemicellulose and cellulose contents, respectively.

The degradation of organic material obtained from animal wastes and plant residues shows a huge difference in lignin contents. Crop residues showed higher lignin, of 0.68, 0.96 and 0.97% for RSB, SSB and CSB, respectively, while in animal manures minimum (0.24%) was found in PLB. Virheijen *et al*. [32] reported that the chemical composition of produced biochars is directly proportional to the chemical compositions of the parent material. As the cellulose and lignin have thermal degradation in range of 240 to 350 ºC and 280 to 500 ºC, respectively [33], it can be concluded that the material with higher lignin will have higher C contents while a material with low lignin contents will provide lower C content [32]. From our values regarding C contents in biochars from animal manures, we can emphasize SMB has more C as compared to the PLB and CMB, so it will have more lignin contents in the feedstock as well as in biochar. In same way, all biochars from crop residues showed higher values for lignin and C contents than biochars from animal manures, which shows the positive relationship between them. Comparing biochars from animal manures and plant residues, more soluble fractions were found in animal manures for SMB, PLB, and CMB (39.53, 55.67 and 17.84%, respectively). In the case of plant residues, RSB had higher (22.32%) soluble fraction as compared to SSB and CSB. The higher soluble fractions might be attributed to the elevated CEC of the RSB and for having more exchangeable cations (H^+, K^+)[34].

The cation exchange capacity (CEC) is the capacity of biochar to adsorb cations. In biochars produced from animal manures and crop residues, CEC was found considerably high, minimum of 117.5 and 127.5 $cmol_c\ kg^{-1}$ in PLB and CMB, respectively, and SMB showing the maximum (170 $cmol_c\ kg^{-1}$) (Table 3). This characteristic reinforces the capacity of biochars to hold cations when applied to soil, as well as an important alternative to improve degraded or low fertile soils. CEC of biochar can be associated to the deprotonation of H^+ from the surface of the mineral particles or organic molecules with variables charges, in consequences to the increase of pH to alkaline of biochar [35]. Furthermore, abiotic oxidation reaction and carboxylation on the surface of the biochars particles may contribute in surface charge generation, literally increasing the CEC of biochars [36].

The C:N ratio is an important property of an organic material because of the fact that it has a direct impact on the decomposition of the residues and N cycling in soil. In the present study, C:N is higher in biochars from crop residues (32.50, 50.74 and 66.69 for SSB, RSB and CSB, respectively) as compared to the C:N of biochars produced from animal manures (12.11 to 17.28 in PLB and CMB, respectively) (Table 3).

Biochars were highly alkaline, with pH ranging from 9.46 to 10.41 in SSB and RSB, respectively. Biochars prepared at low temperatures generally are neutral to slightly alkaline [6, 32] but in our case, all biochars prepared from animal manures and crop straws had higher pH as compared to the reported previously, same results were observed by Revell *et al*. [24]. The pyrolysis process distills the volatile and acidic compounds producing the bio-oil or bio-gas, keeping alkaline components in biomass. The pH of PLB was also similar to the findings of Chan *et al*. [22].

Electrical conductivity (EC) is the concentrations of all soluble salts present in solution. In the present findings, EC of the biochars produced from animal manures and crop residues was also higher, ranging from 0.75 to 9.56 mS cm^{-1} at pyrolysis temperature 450 ºC. Soybean straw biochar presented lowest EC while in PLB there was more EC as compared to others. The pH and EC of biochars increase with the increase in temperature of pyrolysis [7].

Previous studies reported that surface area and pore size are related to the pyrolysis temperature and biomass nature [38]. Specific surface area (Table 3) of the biochars prepared from animal manures are higher as compared to the biochars produced from crop straws. The SSB and PLB presented the SSA almost three to four times of the SSB and CSB, which can be attributed to presence of functional groups inside the pores, which may contribute on decreasing the SSA [39]. Usually, the biochars produced from wood material exhibit larger specific surface area as compared to the non-woody material (grasses, straws).

Biochars produced from different animal manures and crop straws were analyzed to evaluate the functional groups structure of biochars using the FTIR technique. In the FTIR spectra for SMB ((Figure 1), peaks 1400 and 1600 cm^{-1} are related to the stretching O-H and C-O (Phenols) [40]. Peak 788 cm^{-1} illustrates the C=C aromatic rings while peaks smaller than 600 cm^{-1} are related to the vibrational chains of inorganic metals e.g. M-X (M-metals and X-halogens for example peaks 565-495-464 cm^{-1} are related to the metal presence, maybe KCl and $CaCl_2$). 989 cm^{-1}: PO_4^{3-} strains [41]. Peaks in spectra for PLB (Figure 1), 1,793 cm^{-1} related to the chains C=O (carboxyl, aldehyde, ketones and esters), 1601 cm^{-1} shows C=C, C=N and C=N bonds (aromatic components, acetone and quinone), 1393 cm^{-1} is related to the O–H bonding (phenols, ligneous syringyl), 1008 cm^{-1}: P–O (symmetric and asymmetric stretching of PO_2 and $P(OH)_2$ in phosphate, 873 cm^{-1}: C–H chains (aromatic C-H out of deformation plane, 797 cm^{-1}: Pyridine (pyridine ring vibration and C–H deformation) [42], 753-710 cm^{-1}: C=C bonds with aromatic rings and spectra less than 601 $cm^{–1}$ shows the presence of inorganic metals [41]. Figure 1 (CMB), 1615: C=O or C=C chains (aromatic rings chains), 1400 cm^{-1}: H–C–H (aliphatic compounds), 1104 cm^{-1}: –C–O– chains, 1,011 cm^{-1}: $PO_4^{3–}$, 196-776 cm^{-1}: Si–O–Si strains [43]. 1244 and 1208 cm^{-1}: C=C aromatic rings and phenols respectively, 747-695 cm^{-1}: C=C aromatic rings [41]. In spectra for RSB in Figure 1, 1672 cm^{-1}: strains C=C of aromatic rings, 1432 cm^{-1}: O–H groups (carboxyl) and C–H, 1251 cm^{-1}: C–O strain with characteristics of oxygenated functional groups (present in Cellulose), 893-782 cm^{-1}: C– H with aromatic groups [44,45], 572: inorganic metals like K and Ca. Spectra from figure 1 (SSB), 1692-1594: hydroxyl chains (–COOH), 1088-898-837: presence of $–CO_3^{2–}$¸1034: CH_2 chains [46], 772/1407: symmetric vibration chains (–COO–)[47], 711: –C=C (aromatics rings). 636 and less: inorganic metal presence [41]. The CSB spectra from Figure 1, 1592: C=O chains of aromatic rings, 1386: OH– strains (Phenols), 840: C–H chains of aromatic rings [48], 1702: Carbonyl or carboxyl aromatic rings [49], 885-760: C=C chains (aromatic rings). FTIR spectra for biochars clear that the moisture left the structure during pyrolysis process, it is maybe notable the dehydration of C-OH groups and sharp division of some hydrocarbons object maybe formed.

5.3.2 Carbon dioxide (CO_2) emission

Regardless of having added a great amount of TC (1 and 2%) in soil, lesser the amount of C was released from the treated soil, as shown in Figure 2. The efflux of CO_2 remained changing during all collection periods, in the first temporal collection (3 days) of CO_2 were the higher than the all other intervals, gradually decreased during the late period of incubation. The cumulative CO_2 emission up to 49 days from biochars incorporated to soil at 1% C (Figure 2A) was the highest for CMB treatment (245.6 mg kg^{-1}), following that 242.2 mg kg^{-1} from the RSB treatment. Same pattern was observed for PLB and RSB treatments (Figure 2B), which had maximum CO_2 emission of 317.35 mg kg^{-1} and 314.12 mg kg^{-1}, respectively. The minimum total CO_2 emission for both 1 and 2% of biochar in soil was observed for CSB, which reached 180.0 mg kg^{-1} and 221.4 mg kg^{-1}, respectively. Even with the highest C contents in biochars, SSB and CSB emitted smaller amounts of CO_2 than most other biochars, encouraging the C sequestration. In overall comparison, the CO_2 emission results it can be found that the biochars produced from crop straws released less amount of CO_2 as compared to the biochars from animal manures, which can be related to the more fixed C in the biochars produced from crop straws as compared to that of animal manures. Per day, CO_2 release was found higher in PLB and RSB when applied at 2% (6.5 and 6.4 mg kg^{-1}, respectively) as compare to other biochars and control (2.2 mg kg^{-1}). Shen *et al*. [50] reported that in long period incubation the addition of biochars decrease the average daily CO_2 efflux as compared to the short period incubation experiments. In contrast to their description, our results demonstrate the lower amounts of CO_2 emissions when prepared at low temperature. Spokas and Reicosky also demonstrated that the biochars prepared at 400-510 ºC could impede the C mineralization. But, the mechanism by which biochar addition to soil can affect the CO_2 emission of soils is poorly stated [51]. Although, effects of biochars addition to soil on C cycling can impact the CO_2 emissions in soil-water-gas system, but the alteration in C microbial biomass that resulted from biochar additions may affect the C mineralization. Moreover, the air-water balance established in experiment and the liming properties of biochars (pH>9.5 for all biochars) could absorb partly the CO_2 released from soil biochar system [52].

Based on the biochars properties and nutrient concentrations, we found that the biochars produced from crop straws are rich in C contents, can sequester more C in soil and have more CEC and pH, in comparison with animal manures biochars. Consequently, applying biochars to an acidic soil such as those found in Southern region of Brazil, can enhance soil fertility by increasing nutrients retention capacity and by increasing soil pH, keeping more nutrient available to crops.

5.4 Conclusion

Biochars produced from animal manure and crop straws using muffle furnace had demostrated different characteristics including production of biochars percentage. Carbon and other nutrients concentrations (P, K, Ca, Mg) were found in higher concentration, except in case of N which was very low in all biochars. In thermal decomposition analysis of biochars, cellulose and lignin were decomposed readily, by being converted into soluble fractions, whereas hemi-cellulose contents were partially decomposed during the pyrolysis process. Cation exchange capacity of biochars was higher which may increase the nutrient holding capacity of soil when applied to soil as fertilizer. The pH and EC of the biochar was also high, which assure that biochars prepared at 450 ºC can play an important role in increasing the pH of soil when applied to an acidic soil. On the FTIR spectroscopy spectruns it is evident that during slow pyrolysis at low temperature there was no formation of aromatic rings and a minimal nutrient loss in all biochars. During mineralization of biochars, SSB and CSB emitted a negligible amount of CO_2, which ensures that these biochars can be produced to sequester C, instead of leaving the raw material on soil surface.

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Table 1. Chemical characteristics of biochars produced from swine manure (SMB), poultry litter (PLB), cattle manure (CMB), rice straw (RSB), soybean straw (SSB) and corn straw (CSB).

Nutrient	Animal Manures			Crop Straws			LSD
	SMB	PLB	CMB	RSB	SSB	CSB	
TC (%)	38.27 c	22.11 d	16.42 e	43.95 b	69.17 a	67.78 a	2.42
N (%)	3.00 a	1.82 b	0.95 c	0.87 c	2.13 b	0.79 c	0.33
P (%)	4.88 a	3.33 b	0.94 c	0.60 c	0.83 c	0.45 c	0.54
K (%)	3.67 c	5.60 b	2.66 d	5.97 a	0.69 f	2.23 e	0.27
Ca (%)	7.02 b	23.89 a	1.36 e	1.53 e	2.65 c	0.61 e	0.77
Mg (%)	5.84 a	2.79 b	0.07 c	0.05 c	0.13 c	0.04 c	0.20
Cu (mg kg^{-1})	20.70 b	7.70 d	31.20 a	17.60 c	20.50 b	18.40 c	1.90
Mn (mg kg^{-1})	462.60 b	262.70 c	476.60 b	1041.70 a	97.90 e	159.80 d	18.70
Zn (mg kg^{-1})	508.60 a	35.90 e	75.30 b	67.60 c	48.00 d	66.60 c	7.20
Fe (mg kg^{-1})	282.80 b	28.80 e	855.40 a	118.90 c	41.50 d	33.10 e	7.90

Different lower-case letters in horizontal lines show the significant difference among different biochars at 5% level of significance.

Table 2. Thermal decomposition parameters (characteristics) of biochars produced from swine manure (SMB), poultry litter (PLB), cattle manure (CMB), rice straw (RSB), soybean straw (SSB) and corn straw (CSB).

Characteristic	Animal Manures			Crop Straws			LSD
	SMB	PLB	CMB	RSB	SSB	CSB	
Ash (%)*	50.33 c	72.61 b	77.32 a	37.97 d	14.39 e	10.32 f	0.17
H-Cell (%)	59.88 d	44.08 e	81.93 b	77.03 c	85.98 a	83.30 ab	2.71
Cell (%)	0.037	0.009	0.004	0.011	0.160	0.116	ns
Lig (%)	0.60 c	0.24 d	0.25 d	0.68 b	0.96 a	0.97 a	0.07
SF (%)	39.53 b	55.67 a	17.84 d	22.32 c	13.07 e	15.81 d	2.71
Cell:lig	0.06 c	0.4 d	0.04 d	0.02 e	0.18a	0.12 b	0.01
Ash (%) (Residual)	0.18 c	0.13 d	0.64 a	0.24 b	0.06 e	0.08 e	0.03

Different lower-case letters in horizontal lines show the significant difference among different biochars at 5% level of significance. (*Ash was measured direct by putting biochars in muffle furnace at 550 ºC for 10 h, ash residual, H-Cell (hemi-cellulose), Cell (Cellulose), Lig (lignin), SF (Soluble Fractions) were determined through Acid Detergent Fiber (H_2SO_4) and Neutral Detergent Fiber.

Table 3. Cation exchange capacity, C:N and pH, EC and specific surface area (SSA) of biochars produced from swine manure (SMB), poultry litter (PLB), cattle manure (CMB), rice straw (RSB), soybean straw (SSB), and corn straw (CSB).

Characteristic	Animal Manures			Crop Straws			LSD
	SMB	PLB	CMB	RSB	SSB	CSB	
CEC (cmolc kg-1)	170.0 a	117.5 c	127.5 c	162.0 b	165.0 b	152.0 b	17.23
C:N	12.74 e	12.11 e	17.28 d	50.74 b	32.50 c	66.69 a	3.63
pH	10.24 b	9.99 b	9.59 d	10.41 a	9.46 d	10.08 c	0.15
EC ($mScm^{-1}$)	4.08 b	9.56 a	3.60 c	9.42 a	0.75 d	3.85 c	0.27
SSA (m^2/g)	12.357	12.959	7.041	4.619	3.610	4.235	-

Different lower-case letters in horizontal lines show the significant difference among different biochars at 5% level of significance. pH and EC (electrical conductivity) were measure in (1:10) biochar water ratio because of more volume of the biochars obtained from crop straws.

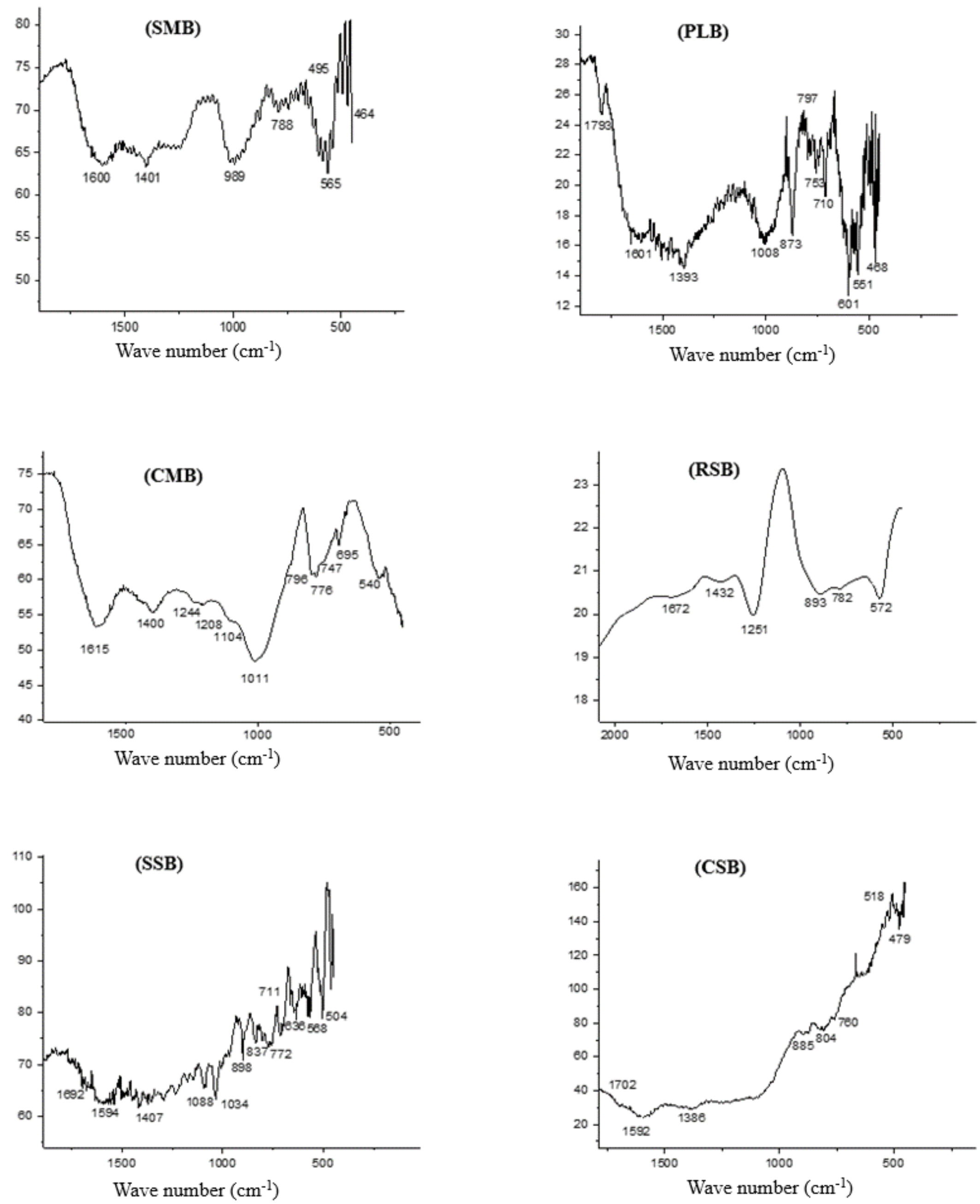

Figure 1. Fourier-Transform Infrared Spectroscopy (FTIR) of biochar produced from biochars produced from swine manure (SMB), poultry litter (PLB), cattle manure (CMB), rice straw (RSB), soybean straw (SSB), and corn straw (CSB).

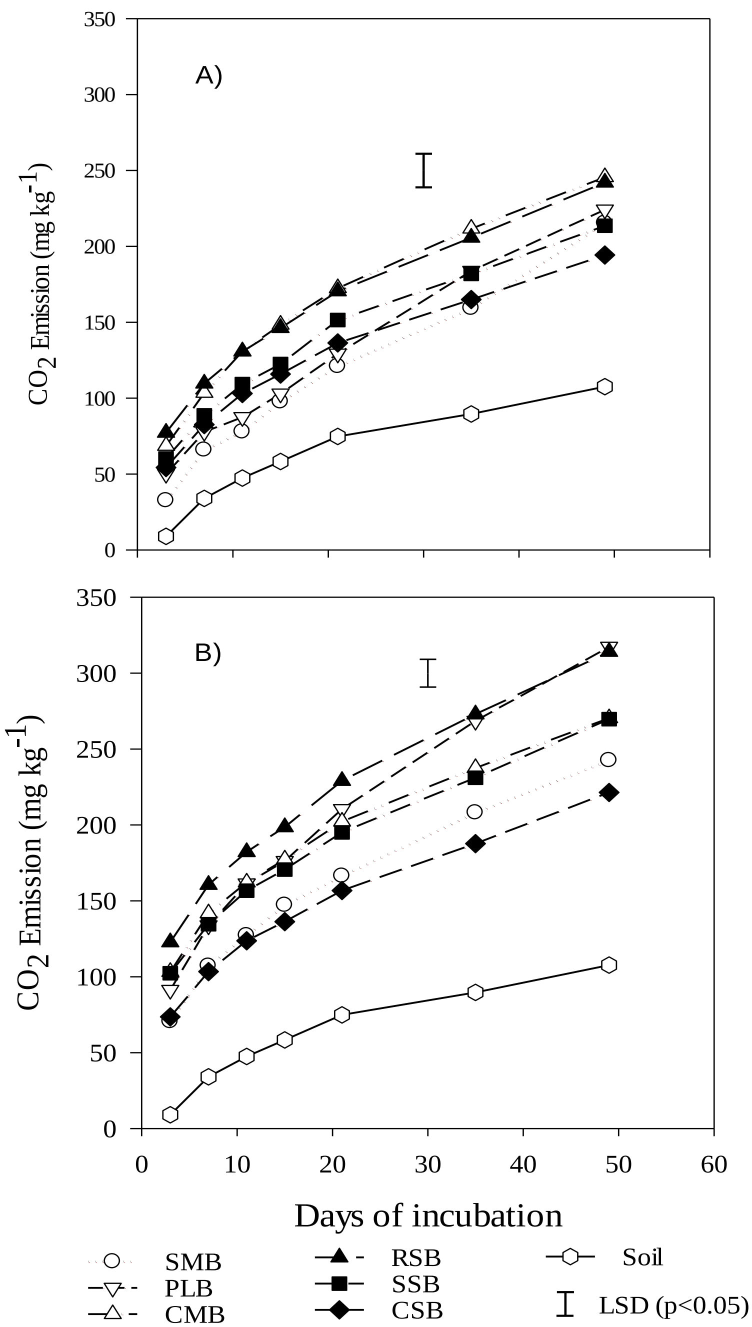

Figure 2. Carbon dioxide (CO_2) emission from amended soil with biochars produced from swine manure (SMB), poultry litter (PLB), cattle manure (CMB), rice straw (RSB), soybean straw (SSB), and corn straw (CSB) at (A) 1 % and (B) 2% dose of carbon. The vertical bars in figures show the LSD values ($p<0.05$).

6 ARTICLE II - EFFECT OF DIFFERENT BIOCHARS ALONG WITH AMMONIUM FERTILIZER ON WHEAT AND THEIR RESIDUAL EFFECT ON SOYBEAN[2]

Abstract

Reduction in soil organic matter affects directly soil quality and, consequently, soil fertility, which may be one of the environmental problems in tropical agricultural soils. Biochar, due to its recalcitrant nature, can stay for more time in soil as compare to the traditional organic amendments. A study was proposed with objectives, use biochars prepared from animal manures (poultry litter and swine and cattle manures) and crop straws (rice, soybean, and corn straws) to increase the pH of acidic soil, adsorb Al and to evaluate their effects on wheat crop under no-tillage system and to evaluate their residual effect on soybean crop. An incubation experiment was conducted for 63 days to evaluate alteration in soil pH and exchangeable Al content. A greenhouse experiment was conducted with undisturbed soil collected up to 0.25 m depth in polyvinyl pipes (PVC) with and without N application under complete randomized design with two extra treatments (control 1 – no biochar and no N; and control 2 – no biochar but with N). Wheat crop was sown up to florescence and subsequently soybean was sown to evaluate the residual effect of biochars on crop growth and dry mass. Incorporation of biochars increase soil pH and decrease Al significantly. The addition of N in combination with the biochars increased the wheat plant height, dry mass and enhanced greatly the soybean plant height and dry mass yield as well. Hence, it can be concluded that the biochar can act as conditioner in soil to retain more nutrient and for more time instead of used as fertilizer.

Keywords: *Biochar; soil pH; no-tillage; residual effect*

[2]Article is prepared according to the format of "*EUROPEAN JOURNAL OF AGRONOMY*"

Highlights

- Biochar prepared from animal manures and crop residues can increase soil pH and reduce soil acidity.
- Animal manure and crop residues biochars increase wheat dry mass under no-tillage system.
- The addition of N fertilizer along with biochars increases the plant height and dry mass in comparison to biochars alone.
- Nitrogen application with biochar can enhance crop yield of subsequent.

6.1 Introduction

Soil organic matter (SOM) plays an important role to retain nutrients and water in soil, and its low content in tropical agricultural soils may be a major basis of poor fertility. Reduction of SOM and its effects on soil quality and soil fertility are considered to be one of the most serious environmental problem to agricultural production in tropical soils (Agegnehu et al., 2015; Lal et al., 2009). Dissimilar to the conventional organic materials used for soil amendments, biochar is recalcitrant material with capability to keep soils amended for longer time, that can be used to enhance soil fertility as well as getting more yields by its ameliorating effects and sorptive capacity for more nutrients (Chan et al., 2008). Recently, a number of researches can be found directing their studies about climate change, carbon sequestration, soil amendments, and crop production using biochars prepared from a huge variety of feedstock (Solaiman et al., 2012).

Usually, biochars prepared at 400 ºC or higher temperatures are alkaline in nature with high pH, that incline to increase soil pH and elevate cation exchange capacity (CEC), decrease exchangeable aluminum (Al) depending upon the exchangeable base cations (Masud et al., 2014). A number of studies reported that biochars can immobilize ammonium nitrogen (NH_4^+-N) because of their high adsorptive capacity and hence inhibit nitrification and hence reduce the H^+ release in soil (Nelissen et al., 2012). Moreover, the soil physical and chemical conditions and the agricultural management practices play an imperative role in effectiveness of the soil amendment using biochar (Kammann et al., 2011).

There are a number of studies reporting the C sequestration, alteration in soil conditions, nitrogen (N) dynamics in soil, and crop production. All of the previous studies reported were under incubation conditions, greenhouse conditions or field condition and were conducted with incorporation of biochars in the topsoil. In Southern Brazil, acidic soil conditions are reported and no-tillage system is common in the region for agriculture since many years. However, there are no studies reporting the application of biochars in no-tillage system evaluating their impacts on soil properties as well as crop growth and production.

Based on the biochar properties and soil conditions we hypothesized that biochar will increase soil pH up to a certain extent, making limestone application not necessary to increase the soil pH. Secondly, we hypothesized that different biochars will influence wheat growth depending on the CEC of the biochar and N application. Third hypothesis was that biochars will enhance soybean growth under residual effects of biochars applied before.

Keeping in view the biochar properties and soil management practices we proposed a study with the following objectives: I) to evaluate the influence of different biochars on soil pH and Al concentration under short-term incubation conditions; II) to evaluate the influence of different doses of biochars with and without N application on wheat cultivation under no-tillage soil conditions; and III) to evaluate the residual effect of biochar on soybean as the subsequent crop.

6.2 Material and Methods

For biochars preparation, all feedstocks were collected from the experimental areas of the Federal University of Santa Maria – RS (29°43'14.4"S and 53°43'31.2"W), except for corn straw, that was collected from a nearby city i.e. Paraíso do Sul – RS (29°35'10.3"S and 53°07'26.3"W).

6.2.1 Biochar preparation and analysis

Prior to prepare biochar, materials were cleaned manually by taking out the small stones from animal manures and grasses and other weeds from straws. The six different biochars, swine manure biochar (SMB), poultry litter biochar (PLB), cattle manure biochar (CMB), rice straw biochar (RSB), soybean straw biochar (SSB), and corn straw biochar (CSB), were prepared at 450 ºC for 1.0 h in a muffle furnace preceded by 10 ºC min^{-1} subsequent increases in temperature. All the biochars were analyzed for pH (1:10 w/v), electrical conductivity (EC 1:10 w/v), total carbon (C) and total nitrogen (N) were analyzed by dry combustion method in an elemental analyzer (Thermo Scientific, Flash EA 1112, Milan, Italy). For phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg) and micronutrients biochar samples were extracted by 0.1M HNO_3 (Embrapa, 2007) and were measured by using spectrophotometer (Murphy and Riley, 1962), flame photometer and other cations and micronutrients by atomic absorption spectrophotometer (AAS), respectively.

6.2.2 Soil collection and analysis

A 0.25 m depth undisturbed soil layer of Typic Hapludult (US Soil Taxonomy) was collected in polyvinyl pipes (PVC) (0.29 m height × 0.20 m diameter) from experimental areas of the Department of Soil Science (29°43'14.2"S and 53°42'15.0"W) of the Federal University of Santa Maria. A quantity of soil was collected separately for analysis and incubation experiment, and air-dried, ground, and passed through 2.0 mm sieve. Prior to installing experiments, the soil was analyzed for pH (4.8 $_{(1:2.5\ w/v)}$), total C (1.2%), N (0.8%), P (4.8 mg kg^{-1}), K (28 mg kg^{-1}), Ca (15.5 cmol$_c$ dm^{-3}), Mg (9.3 cmol$_c$ dm^{-3}) and Al (16.89 cmol$_c$ dm^{-3}) for fertilizer recommendations (Tedesco et al., 1995).

6.2.3 Incubation experiment

An incubation experiment was conducted by taking 500 g of soil in plastic pots with 1 kg capacity at soil science laboratory (room temperature) during September and November 2017 at Federal University of Santa Maria with biochars incorporated into the soil at doses equivalent to 0, 5, 10 and 20 Mg ha^{-1} of biochar for 63 days. The experiment was conducted in complete randomized design (CRD) with three replicates and an extra treatment (control) was also installed for whole experiment instead of using a separate control for each biochar. Field capacity moisture was maintained throughout the experiment. Samples were taken at day 7, 14, 28, 42 and 63 for soil pH and Al contents measurement.

6.2.4 Greenhouse experiment

Undisturbed soil samples were taken to the greenhouse to conduct the wheat experiment with different doses of biochar along with ammonium fertilizer. A three replicated experiment was installed under complete randomized design (CRD) with three factors (6×2×2) composed by the six biochar types (SMB, PLB, CMB, RSB, SSB, and CSB), two biochar doses 10 Mg ha^{-1} (33.5 g column^{-1}) and 20 Mg ha^{-1} (67 g column^{-1}), and two N doses 0 and 110 kg ha^{-1} (1.6 g ammonium sulfate column^{-1}). The experiment also included two extra treatments, one without any application (control 1 – without biochar and N) and other without biochars but with N application (Control 2

– without biochar, but with N), considering not important a separate control for each biochar type for a single soil type.

Eight seeds of ‘Sinuelo’ wheat variety were sown in PVC columns containing the surface biochars application. Before sowing, up to 3 cm of the soil was mixed with biochars to keep the seeds with a soil + biochar mixture instead of keeping them only in biochars. After the seeds germination, only four healthy seedlings were left for growth up to anthesis. As the soil was poor in nutrients concentrations, recommended doses of P equivalent to 170 kg P_2O_5 ha^{-1} (1.3 g triple super phosphate $column^{-1}$) and K equivalent to 120 kg K_2O ha^{-1} (0.65 g potassium chloride $column^{-1}$) were also applied to all treatment units. On wheat harvest, 103 days after sowing, the aerial part was kept in the oven for dry mass calculation and further analysis.

After wheat harvest, soybean (variety 5958 RSF IPRO) was sown to estimate the residual effect of biochars on subsequent crop. Only three out of six seedlings were maintained up to inflorescence (66 days). Recommended doses of P and K, equivalent to 90 kg P_2O_5 ha^{-1} (0.69 g g triple super phosphate $column^{-1}$) and 120 kg K_2O ha^{-1} (0.65 g potassium chloride $column^{-1}$) were also applied in all experimental unites while no N was applied. After harvesting, soybean stacks were kept in the oven for dry mass and further analysis. After drying completely, the biomass was milled and digested using HNO_3-$HClO_4$ (Embrapa, 1997) to analyze P, K, Ca, Mg, and micronutrients (Zn, Mn, Cu, and Fe). Cations were determined by atomic absorption spectrophotometer (AAS) and P by colorimetry (Murphy and Riley, 1962). Total N was determined by dry combustion method in an elemental analyzer (Thermo Scientific, Flash EA 1112, Milan, Italy).

Statistics

The data from incubation experiment were divided into 3 groups in relation to the dose of application i.e. 0, 5, 10 and 20 Mg ha^{-1} and analyzed for analysis of variance (ANOVA) to determine the difference among means of factors (biochar type × time) using statistical software SigmaPlot 12.3 and the least significant difference test (LSD) was performed to find out the difference among different biochar types and different time intervals. The greenhouse experiment data were analyzed in statistical software R 3.5.1 with the assistance of RStudio to evaluate the main effect and interaction effect among different factors (biochar type × nitrogen × biochar doses). The figures to differentiate the means between different factors were made using SigmaPlot 12.3.

6.3 Results

6.3.1 pH and Al alteration in soil amended with biochar

Alteration of soil pH during incubation with different rates of SMB, PLB, CMB, RSB, SSB, and CSB are presented in Figure 1. Soil pH was greatly influenced by the biochar applications at 5, 10 and 20 Mg ha^{-1} overtime. As the initial pH of the soil was 4.8, we noted a sharp increase in soil pH by biochar incorporation. Fluctuation in soil pH was observed throughout the incubation period. Despite the biochar doses, all biochars increase the soil pH, maximum pH (6.7) was noted at day 42 from the application of CSB at 20 Mg ha^{-1}. Up to day 42 of incubation, soil pH was noted maximum, afterward started a slight decrease in all doses as well as biochar types.

In control treatment, a slight pH increase was observed in the beginning, which kept fluctuation in the same range throughout the incubation period. Throughout fluctuation in soil pH is due to the continues mineralization process during the incubation process. At day 28 of incubation, the maximum soil pH value reached with addition of 10 and 20 Mg ha^{-1} biochars was 6.2 and 6.5, respectively, and at day 42, 6.3 and 6.7, respectively. A significant ($p< 0.05$) interaction was found between biochar and doses of biochar incorporated to soil. In comparison with control, soil pH was raised about 0.47 and 1.23 points by the incorporation of RSB and CMB at 10 and 20 Mg ha^{-1}, respectively.

Decrease of exchangeable Al by the use of different biochars in an incubation experiment for 63 days is presented in Figure 2. Biochar types with different doses significantly affected the exchangeable Al over time by decreasing the Al concentration. From very 1st day up to day 28 of incubation a huge gradient is observed by decrease soil exchangeable Al, afterward a short increase was also observed for all biochars as well for the three application rates. There are slight changes in different days of incubation from biochars at 5, 10 and 20 Mg ha^{-1}. After 63 days of incubation, PLB (2.16 $cmol_c$ dm^{-3}) and CMB (1.85 $cmol_c$ dm^{-3}) treatments were observed with lowest soil exchangeable Al under 10 and 20 Mg ha^{-1} doses of biochar, respectively.

6.3.2 Wheat and soybean production

From the results of table 1, it can be seen that treatments with application of biochars had no significant effect on wheat plant height (WPH) among them. In comparison to control treatment, biochars application increased the WPH only when no N was applied. On the other, application of N increased the WPH as compared to the treatments without N application only when using 10 Mg ha^{-1} of PLB and CSB and 20 Mg ha^{-1} of CMB, SSB and CSB. Maximum heights (98.4 and 97.9 cm) when using N were noted by application of PLB at 10 Mg ha^{-1} and CSB at 20 Mg ha^{-1}. The addition of N in control 2 (no biochar, with N) also increased WPH significantly.

Same pattern was followed by the wheat spike length (WSL) (Table 1). Not a single biochar had an effect on WSL even with different application rates 10 and 20 Mg ha^{-1}. Following similar pattern from the WPH, there was a significant increase in the WSL with addition of N for some of the biochar treatments, whereas the control 2 (with N) also had a significant increase in WSL as compared to the control 1 (no N).

For wheat dry mass (WDM), there was no difference observed among biochar treatments, but a significant increase on yield was detected when biochar treatments are compared to the control, but only when no N was added. With addition of N fertilizer, a huge increment was observed in WDM for all biochars, except for PLB and RSB. Nonetheless, a significant increase was observed among treatments without and with N but the biochar doses did not show a reasonable difference among them. Control treatment showed more than 100% increase in WDM with application of N. Maximum WDM (15.2 Mg ha^{-1}) was observed with addition of 20 Mg ha^{-1} of CMB and addition of N, while minimum (4.5 Mg ha^{-1}) was observed from control (no biochar, no N). Biochars alone did not affect the WDM, this may be attributed to the low N contents in biochar and elevated C:N of the biochars which may prevent the N supply to crop plants and crop yield.

In comparison of biochars residual effect on soybean plant height (SPH), there was no significant difference among different biochars, and between the 10 and 20 Mg ha^{-1} doses of biochars. The treatments with N application to wheat crop showed a slight increase (14%) in plant height. Similar to the other treatments, control 2 also showed an increase in SPH when N was added in previous crop.

Biochars applied on wheat influenced the soybean dry mass (SDM) among different treatments in comparison to control 1 treatment. Maximum (17.3 and 17.9 Mg ha^{-1}) SDM was observed with application of PLB at 10 and 20 Mg ha^{-1} (no N), respectively, showing no significant rise with increase doses of biochar. The treatments with N application showed only difference between de control treatment with all treatments that received biochar. Whereas, comparing the N added treatments to those with zero N, there was a significant increment on all the treatments, except for PLB under 10 and 20 Mg ha^{-1} biochar addition and for CMB at 20 Mg ha^{-1}.

6.3.3 Nutrient concentration in wheat and soybean tissues

Biochar types had no significant difference on N content in wheat straw (Table 3) when applied at 10 Mg ha^{-1} and treatments with 20 Mg ha^{-1} had a significant difference among them while with increase in the doses N content in wheat straw also become almost double. In comparison to control (4.3 g kg^{-1}), maximum N content were noted as 8.3 g kg^{-1} and 9.9 g kg^{-1} by application of PLB and CSB at 10 and 20 Mg ha^{-1}, respectively. The application of N to soil in combination to biochars increased the N content in wheat straw for SMB, PLB, and CSB treatments at 10 Mg ha^{-1}. In the other hand, treatment combinations with 20 Mg ha^{-1} biochar applications decreased their N content in wheat straw when N was applied, but showed a significant difference only for CSB treatment.

Overall in comparison to control (P = 1.3 g kg^{-1}) biochars demonstrated the difference in P contents among their different types with application rate at 10 as well as 20 Mg ha^{-1}. Increase in dose of the biochars increased P content in plant tissues except CMB, where P was significantly decreased with increase in dose (20 Mg ha^{-1}). The addition of N fertilizer combined with biochars did not increase P in plat tissues except SMB and RSB (33% increase) with application rate at 20 Mg ha^{-1}. In other biochars, the P content in plant tissues decreased in some extent but remained very next to the contents observed without N application.

The application of different biochars types had no significant effect on the K content in wheat straw while were significantly difference between doses of biochars. About 25 and more than 100% increase in K was observed with increase of dose and with control (9.1 g kg^{-1}) respectively except SSB at 20 Mg ha^{-1}. Addition of N decreased the K content in wheat tissues with biochars application rate at 10 Mg ha^{-1} while at 20 Mg ha^{-1} there was no significant change observed.

In comparing Ca and Mg and micronutrients (Zn, Cu, Mn and Fe), similar behavior was observed, with no significant change from biochar types and doses of biochars. Ca and Mg contents increase with increase in dose of biochars, but without any significant difference. Micronutrients, Mn and Fe were not altered by biochar types while N application increased their concentrations as well.

No significant outcome was observed (Table. 4) in N content in soybean straw in relation to residual effect of biochars after wheat crop, even with control 1 treatment (without N), whereas a slight increase in N content was observed with increase in biochars dose 10 Mg ha^{-1} to 20 Mg ha^{-1}. Treatments with N application in previous crop exhibited 25 to 33% increase in comparison to those without N application, while remained without a significant increase within biochars and within doses of biochars. In comparison to N, P was affected by the biochars types (2.1 and 2.0 g kg^{-1}) with SMB and PLB at 10 Mg ha^{-1} while remained unchanged at 20 Mg ha^{-1}. The application of N decreased the P content up to 16% in soybean straw from treatments with 10 Mg ha^{-1} while PLB and SSB at 20 Mg ha^{-1} proved no difference between treatments with N and without N. Potassium content in soybean tissue had no effect due to biochar type, even with application rate. Treatments with addition of N previous wheat crop, stated no effect with and without N application while only a significant increase was observed with application rate of biochars, 20 Mg ha^{-1} increased the K content up to 22%.

Exactly, secondary and micronutrients follow the way of no influence by biochar type and application rate as well as with N and without N. Maximum Ca (22.2 g kg^{-1}) and Mg (2.2 g kg^{-1}) were observed with treatments in combination with N application from CMB at 10 Mg ha^{-1} and SMB 20 Mg ha^{-1} respectively. Micronutrients (Mn, Fe) remained non-significant with different biochars, dose of application and even with and without N but a slight increase was observed in treatments with combination to N fertilizer.

6.4 Discussion

It has been well known that addition of organic material to soil significantly impact soil pH and data on soil pH demonstrate that the biochar addition can enhance the pH of an acidic soil due to its high alkalinity. At the initial days, N mineralization and alkalinity were the factor together to increase the soil pH, whereas later, NH_4^+ nitrification contributes to the fluctuation and decrease in soil pH. In initial days the mineralization of organic N consumed protons and left the soil pH to increase, while a decrease in soil pH may be attributed to the nitrification of NH_4^+ later on releasing the protons (Mehmood et al., 2015; Xu and Coventry, 2003). High $CaCO_3$ content and proton consumption ability of corn straw biochar increase soil pH and decrease the soil exchangeable acidity (Chintala et al., 2014). The increase in soil pH help in the exchangeable Al to participate as insoluble hydroxyl Al species (Ritchie 1994). Soil pH can be increased by addition of biochars in soils, when added biochars can release the base cations onto acid soils that can participate in exchange reactions and replace Al and H from soil surface and decrease soil acidity (Yuan and Xu, 2011).

Aluminum concentration in soil is of more importance in soil acidity, because of its higher charge and occupying more exchange site and releasing a higher number of H^+ in soil solution, consequently, decreasing the soil pH and increasing soil acidity. Although, in sandy textured soil there is no presence of Al up to toxic level but in consequence to the soil pH, it is more important to tackle it in relation to the increase the soil pH. The reduction in exchangeable Al, which transform it into Al-OH and precipitated in the presence of biochars. Reduction of the active Al^{3+} specie in soil is paramount for reducing soil acidity, hence enhancing the soil fertility (Masud et al., 2014). In their study, the authors reported that with biochar addition in maize crop, two factors acted for Al neutralization, one is the alkaline effect of biochars, while the hydroxyl release from roots due to nitrate uptake act in a complementary manner.

From our results on agronomic parameters as well as wheat dry mass yield, biochars had a significant effect in comparison to control. However, no significant difference was observed between doses of biochars, but a slight increment in plant height and dry mass yield can be related to the doubled dose of biochars contained double amount of N also that helped caused a slight increase in wheat plant height and yield. On the other hand, the addition of NH_4^+ fertilizer ensured that N concentration in biochars was not sufficient for wheat growth and addition of N fertilizer increased the wheat dry mass under no-tillage system. In our experiment, lesser impact of the biochar alone can be related to the lower N contents in all biochar except PLB, SMB and SSS which had N (1.8, 3 and 2.1%) and affected more efficiently as compared to CMB, RSM and CSB. It is greatly possible that the N present in biochars was washed out with irrigation to the treatment columns. While in case of addition of N in presence of the biochars favored the N uptake by plants and retained N in soil biochars mixture for longer time. The results were in confirmation with findings of (Chan et al., 2007), who reported that greenwaste biochars did not affect the radish biomass yield even at 100 t ha^{-1} while addition of N fertilizer increase yield significantly. He attributed the radish yield to the soil physical condition especially reduction in tensile strength and higher field capacity water, both of these favored the soil to root growth and increasing the ability to absorb N.

Same pattern was observed in as residual effect of biochars on soybean plant height and dry mass yield, where the addition of N in combination to biochars had favored the plant growth as well as dry mass yield. The high dry mass yield can be related to the positive changes occurred in soil quality by the use biochars which enhanced the nutrient use efficiency. Biochars alone did not affect the WDM, this may be attributed to the low N contents in biochar and elevated C:N of the biochars which may prevent the N supply to crop plants and crop yield. Our results are in confirmation with the findings of Solaiman et al., (2010), who found that oil mallee biochar increased the wheat yield when mineral fertilizer was applied together. Furthermore, a four years experiment on cassava with application of biochar and its residual effect on chili showed that positive significant effect chili yield when N was applied together (Wisnubroto et al., 2017).

Generally, a number of studied reported the growth and yield with addition of biochars alone or mixed with different fertilizers. For example, Abbasi and Anwar (2015) reported that poultry litter biochar increased maize dry mass yield in combination with N fertilizer up to 26% in comparison to control, while in same experiment they did not find any positive increase in wheat dry mass yield. Long term benefits may include the SOM for longer time and elevated nutrient holding capacity, slow nutrient release due to high CEC of the biochars (Steiner et al., 2008). The rice husk biochar increases the growth and yield of crops by increasing NO_3^- retention in soil (Wang et al., 2012). Similar effect has been reported by (Prommer et al., 2014), who described that the addition of biochar enhances the ammonia oxidizer populations and accelerates the net nitrification rates that may retain NO_3^-. However, in our case, we had used ammonium sulfate as N source, and hence due to increase in CEC of soil by addition of biochars can retain NH_4^+ and nitrification may occur when needed. Our results are in accordance with Steiner et al. (2008) findings, who reported that biochar elevated soil CEC and absorb nutrients for more time.

Nutrient concentration in wheat and soybean shoots demonstrate that the biochar addition to soil enhanced the nutrient concentration in plant tissues, direct effect on wheat crop as well as residual effect on soybean. Here the results on nutrient concentration in plant tissues are in similar findings of Chan et al. (2007) and Abbasi and Anwar (2015), who stated that the increased nutrients uptake with the use of biochars can be related to the nutrient use efficiency increased by biochar addition. Organic waste biochar can enhance the maize yield up to 6.24 Mg ha^{-1} (Widowati and Asnah, 2014). They observed that dual application of biochar and smaller dose of KCl enhanced maize yield up to 26%.

In general, the incorporation of animal manure and crop straw derived biochars have a significant influence on soil pH and exchangeable Al. In our study, the crop straw derived biochars presented a constant increase in soil pH and Al decline as compared to the animal waste derived biochars, on the other hand, animal waste derived biochars presented more fluctuation in soil pH and Al alteration. Overall in greenhouse experiment, among different biochars the addition of N affected greatly the agronomic parameters of both wheat (direct effect) and soybean (residual effects). The nutrient concentration in plant tissues was also affected with addition of N fertilizer in combination with biochars instead of biochars application alone that can be related to the presence of less N in biochar applied to soil and plants absorbed other nutrients (P, K).

6.5 Conclusion

Biochars prepared from animal manures and crop residues being alkaline in nature and elevated CEC influence the soil pH and adsorb Al very effectively, however depending on the parent material, each of the biochar had distinct effect depending upon the type of feedstock and dose applied. In greenhouse experiment, each of the biochars had same influence and doses of the biochars also had no influence, but addition of N fertilizer enhanced the wheat plant height, spike length and dry mass as well. Addition of N to the biochars influenced the nutrient concentration in wheat straw balancing the nutritional status in wheat straw. In relation to the residual effect of biochars, again the biochars had no significant influence on the soybean plant height and dry mass, whereas had an impact when N was applied in previous crop (wheat). On the other hand, nutrient concentration in soybean aerial part followed similar trend as in wheat biomass, as the N addition had great impact as compared to treatments where biochar was applied alone. Hence, we can conclude that biochars can have a significant effect on plant growth as well as on crop yield when used along with N fertilizer, so biochar from animal and plant wastes can act as soil conditioner instead of as a fertilizer.

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Crop	Parameter	Control	SMB	PLB	CMB	RSB	SSB	CSB	SMB	PLB	CMB	RSB	SSB	CSB
			10 Mg ha^{-1}						**20 Mg ha^{-1}**					
	Without Nitrogen													
Wheat	WPH (cm)	65.0bBα	72.2aAα	76.3aBα	80.3aAα	82.0aAα	78.5aAα	71.7aBα	80.8aAα	78.0aAα	72.3aBα	79.6aAα	74.7aBα	77.7aBα
	WSL (cm)	7.0aBα	6.8aBα	7.1aBα	7.3aAα	7.6aAα	6.7aBα	6.3aBα	7.6aBα	8.4aAα	7.0aBα	8.3aAα	7.0aAα	7.3aBα
	WDM (Mg ha^{-1})	4.5aBß	5.7aBα	5.9aBα	5.02aBα	7.6aBα	7.2aBα	6.5aBα	5.9aBα	8.0aAα	7.4aBα	9.1aAα	7.0aBα	7.6aBα
	With Nitrogen													
	WPH (cm)	91.2aAα	81.7aAα	98.4aAα	88.7aAα	86.0aAα	95.0aAα	83.7aAα	86.1aAα	84.7aAα	81.7aAα	87.8aAα	97.9aAα	89.0aAα
	WSL (cm)	9.0aAα	8.7aAα	9.2aAα	7.9aAα	8.7aAα	9.1aAα	8.6aAα	9.3aAα	8.9aAα	8.4aAα	8.5aAα	8.1aAα	8.7aAα
	WDM (Mg ha^{-1})	10.0aAα	11.7aAα	10.7aAα	12.5aAα	15.1aAα	11.6aAα	11.0aAα	12.9aAα	11.7aAα	15.2aAα	11.7aAα	12.2aAα	12.8aAα
	Without Nitrogen													
Soybean	SPH (cm)	72.0aAα	77.7aAα	81.3aAα	80.7aAα	85.3aAα	81.7aAα	82.3aAα	87.7aAα	84.3aAα	83.0aAα	79.3aAα	84.3aAα	86.3aAα
	SDM (Mg ha^{-1})	7.9cBß	15.5aBα	17.3aAα	12.1bBα	12.0bBα	11.8bBα	9.9cBα	17.4aBα	17.9aAα	15.7aAα	14.2bBα	13.8bBα	11.8cBα
	With Nitrogen													
	SPH (cm)	78.0aAα	90.3aAα	89.0aAα	92.0aAα	91.3aAα	86.3aAα	86.7aAα	92.7aAα	92.0aAα	94.0aAα	85.3aAα	87.3aAα	78.0aAα
	SDM (Mg ha^{-1})	11.1bAß	18.1aAα	17.1aAα	16.9aAα	16.6aAα	16.4aAα	16.3aAα	18.3aAα	17.4aAα	15.2aAα	16.6aAα	17.7aAα	15.2aAα

Lower-case letters within rows show the difference among different biochars, upper case letters within columns indicate the effect of nitrogen application, α and ß within rows indicate the effect of different doses of biochars. Least significant difference (LSD) test was performed to differentiate the differences among different treatments.

Table 2. Analysis of variance (ANOVA) to investigate the main and interactive effects of I (Control 1 + Control 2), Nitrogen (N), Biochar (B), Dose (D) on selected variables in wheat straw.

	I	N	B	D	I × N	N × B	N × D	B × D	N × B ×D
TC	***	***	***	-	**	*	ns	-	**
TN	**	**	**	ns	**	***	***	*	***
P	***	ns	***	*	ns	**	ns	*	ns
K	***	***	***	***	ns	**	ns	**	*
Ca	Ns	*	ns	ns	ns	ns	ns	ns	ns
Mg	Ns	***	***	ns	ns	ns	ns	ns	ns
Mn	***	**	-	ns	**	ns	ns	ns	ns
Fe	Ns	***	**	ns	ns	ns	ns	ns	ns

I= (control 1 and control 2, which were added in experiment as extra treatments), total carbon (TC), total nitrogen (TN), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), manganese (Mn), iron (Fe). ***P<0.001, **P<0.01, *P<0.5, -P<0.1, ns = non-significant.

Table 3. Effect of swine manure biochar (SMB), poultry litter biochar (PLB), cattle manure biochar (CMB), rice straw biochar (RSB), soybean straw biochar (SSB), and corn straw biochar (CSB) on nutrient concentrations in wheat straw.

Nutrient	Control	SMB	PLB	CMB	RSB	SSB	CSB	SMB	PLB	CMB	RSB	SSB	CSB
	10 Mg ha^{-1}							20 Mg ha^{-1}					
Without Nitrogen													
N (g kg^{-1})	4.3bBß	4.5bBß	8.3aBα	8.2aAα	8.2aAα	8.2aAα	4.2bBß	9.4aAß	9.6aAα	6.7cAα	7.7bAα	8.4aAα	9.9aAα
P (g kg^{-1})	1.3cAα	2.8aAα	1.9aAα	2.79aAα	1.9aAα	2.1aAα	2.2aAα	3.3aBα	2.5aAα	1.76bAα	2.9aBα	2.2aAα	2.4aAα
K (g kg^{-1})	9.1bAß	16.3aAα	18.8aAα	13.4aAß	17.9aAα	11.2bAß	15.4aAß	20.5aAα	21.8aAα	18.1aAα	21.4aAα	13.9aAα	19.5aAα
Ca (g kg^{-1})	9.1aAα	8.9aAα	8.8aAα	9.9aAα	10.7aAα	10.9aAα	9.4bAα	9.1aAα	10.9aAα	9.7aAα	10.8aAα	11.9aAα	14.6aAα
Mg (g kg^{-1})	4.0aAα	3.9aBα	3.9aAα	3.7aAα	3.4aBα	3.9aBα	3.5aAα	4.2aAα	4.4bAα	3.7bAα	3.2bAα	4.2bAα	3.5bAα
Mn (mg kg^{-1})	220.9aAα	170.2aAα	171.4aAα	232.1bAα	223.9aAα	141.6aAα	155.0aAα	199.2aAα	208.8aAα	399.9aAα	126.9aAα	111.4aAα	116.7aAα
Fe (mg kg^{-1})	85.3aBα	66.4aBα	100.4aBα	77.1aBα	63.7aBα	75.3aBα	76.9aBα	69.7aBα	91.9aBα	70.4aBα	66.8aBα	62.6aBα	62.6aBα
With Nitrogen													
N (g kg^{-1})	8.3aAα	14.7aAα	11.1bAα	8.4bAα	8.8bAα	7.4cAα	6.8cAα	8.4aAß	7.6aAß	8.0aAα	6.9aAα	7.3aAα	6.6aBα
P (g kg^{-1})	1.8aAα	3.1aAα	2.3aAα	1.8aBα	1.7aAα	1.9aAα	1.6aAα	4.5aAα	2.9aAα	1.9aAα	1.9aAα	2.0Aaα	1.7aAα
K (g kg^{-1})	8.8bAß	13.2bBß	17.6bAα	10.9bAß	18.5aAα	7.5aBß	12.8bAß	20.1aAα	24.0aAα	14.7aBß	19.2aAα	7.7aBß	19.4aAα
Ca (g kg^{-1})	12.1aAα	10.1aAα	10.9aAα	12.0aAα	10.9aAα	13.2aAα	9.8aAα	11.7aAα	12.3aAα	11.2aAα	12.0aAα	13.4aAα	10.1aBα
Mg (g kg^{-1})	4.1aAα	5.4aAα	4.3bAα	4.3bAα	4.0bAα	4.6bAα	3.9bAα	4.6aAα	4.2bAα	4.1bAα	3.7cAα	4.7aAα	3.9cAα
Mn (mg kg^{-1})	498.1aAα	197.4aAα	247.9aAα	275.5aBα	250.2aAα	261.4aAα	269.9aAα	168.7aAα	272.4aAα	205.9aAα	216.9aAα	189.8aAα	201.3aAα
Fe (mg kg^{-1})	109.8aAα	100.2aAα	114.5aAα	107.3aAα	94.7aAα	117.9aAα	107.1aAα	88.3aAα	111.0aAα	103.7aAα	119.4aAα	100.6aAα	100.0aAα

Lower-case letters within rows show the difference among different biochars, upper case letters within columns indicate the effect of nitrogen application, α and ß within rows indicate the effect of different doses of biochars. Least significant difference (LSD) test was performed to differentiate the differences among different treatments.

Table 4. Residual effect of swine manure biochar (SMB), poultry litter biochar (PLB), cattle manure biochar (CMB), rice straw biochar (RSB), soybean straw biochar (SSB), and corn straw biochar (CSB) on nutrient concentrations in soybean shoots.

Nutrient	Control	SMB	PLB	CMB	RSB	SSB	CSB	SMB	PLB	CMB	RSB	SSB	CSB
	10 Mg ha^{-1}							20 Mg ha^{-1}					
Without Nitrogen													
N (g kg^{-1})	19.0aBα	19.0aBα	26.0aAα	18.0aBα	20.0aBα	18.0aBα	19.0aBα	21.0aAα	27.0aAα	20.0aBα	19.0aBα	21.0aBα	18.0aBα
P (g kg^{-1})	1.1cAß	2.1aAα	2.0aAα	1.8bAα	1.6bAα	1.6bAα	2.0aAα	2.1aAα	2.0aAα	1.7aAα	1.8aAα	1.7aAα	1.9aAα
K (g kg^{-1})	7.8bBß	12.6aAα	13.9aAα	10.9aBα	14.2aBα	13.1aAα	13.2aBα	14.0aAα	17.4aAα	12.2aBα	16.3aAα	12.7aAα	14.4aBα
Ca (g kg^{-1})	14.9aAα	12.8aAα	15.9aAα	13.5aBα	12.1aBα	16.6aBα	14.7aAα	11.0aBα	19.1aAα	14.1aAα	11.0aAα	14.7aBα	14.4aBα
Mg (g kg^{-1})	1.8aAα	1.8aAα	1.8aAα	1.6aAα	1.2aAα	1.8aAα	1.6aAα	1.7aAα	1.8aAα	1.6aAα	1.0aAα	1.9aAα	1.4aAα
Mn (mg kg^{-1})	126aBα	127aAα	222aAα	137aBα	128aAα	118aAα	130aBα	121bAα	262aAα	154bAα	135bAα	87bAα	97bBα
Fe (mg kg^{-1})	44.5aAα	45.5aAα	52.3aAα	50.5aAα	37.5aAα	63.9aAα	53.6aAα	89.4aAα	67.0aAα	66.9aAα	54.5aAα	39.0aAα	54.4aAα
With Nitrogen													
N (g kg^{-1})	28.0aAα	30.0aAα	23.0aAα	26.0aAα	28.0aAα	29.0aAα	30.0aAα	26.0aAα	28.0aAα	27.0aAα	27.0aAα	29.0aAα	31.0aAα
P (g kg^{-1})	1.1bcAß	1.8aBα	1.4aBß	1.2bBα	1.3aBα	1.3aBα	1.2bBα	1.8aBα	1.9aAα	1.5aBα	1.4aBα	1.5aAα	1.2bBα
K (g kg^{-1})	12.6aAα	14.8aAß	16.4aAß	15.5aAα	17.4aAα	13.4aAα	14.3aAα	18.0aAα	19.5aAα	15.4aAα	18.1aAα	13.2aAα	18.7aAα
Ca (g kg^{-1})	27.7aAα	15.6aAα	19.0aAα	22.2aAα	19.6aAα	26.1aAα	16.7aAα	17.8aAα	21.9aAα	17.4aAα	16.3aAα	22.6aAα	22.2aAα
Mg (g kg^{-1})	1.8aAα	1.8aAα	1.7aAα	1.9aAα	1.4aAα	2.0aAα	1.6aAα	2.2aAα	1.8aAα	1.7aAα	1.1aAα	2.0aAα	1.6aAα
Mn (mg kg^{-1})	280aAα	169aAα	170aAα	225aAα	188aAα	175aAα	207aAα	146aAα	255aAα	165aAα	166aAα	135aAα	201aAα
Fe (mg kg^{-1})	57.2aAα	42.6aAα	49.6aAα	61.4aAα	53.4aAα	52.5aAα	56.1aAα	52.3aAα	59.4aAα	66.4aAα	48.8aAα	43.8aAα	51.3aAα

Lower-case letters within rows show the difference among different biochars, upper case letters within columns indicate the effect of nitrogen application, α and ß within rows indicate the effect of different doses of biochars. Least significant difference (LSD) test was performed to differentiate the differences among different treatments.

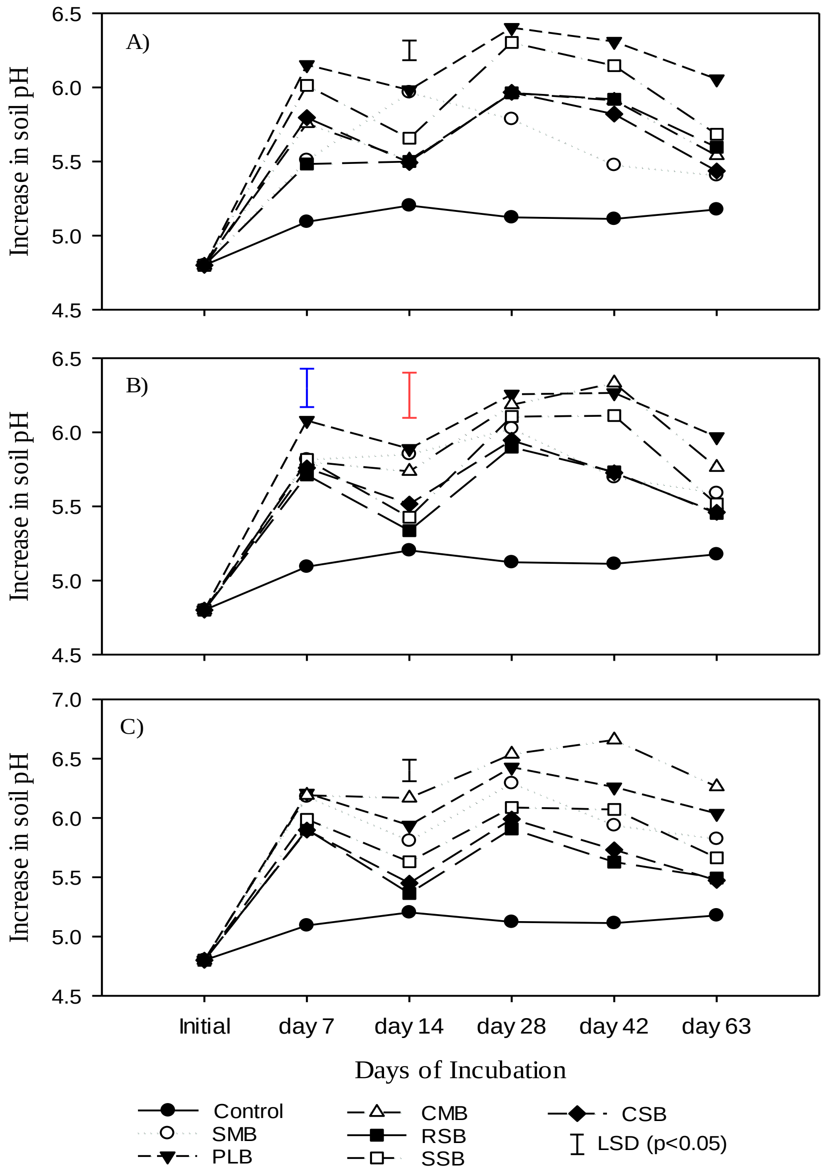

Figure 1. pH change at different time intervals by use of biochars at different levels (A) 5 Mg ha^{-1}, (B) 10 Mg ha^{-1} and (C) 20 Mg ha^{-1} of swine manure biochar (SMB), poultry litter biochar (PLB), cattle manure biochar (CMB), rice straw biochar (RSB), soybean straw biochar (SSB), and corn straw biochar (CSB).Vertical bars indicate the LSD values ($p<0.05$), in Graph A) LSD = 0.0660, graph B) red color bar LSD = 0.1525 (for Biochar type), blue color bar LSD = 0.1290 (for time period), graph C) LSD = 0.0905

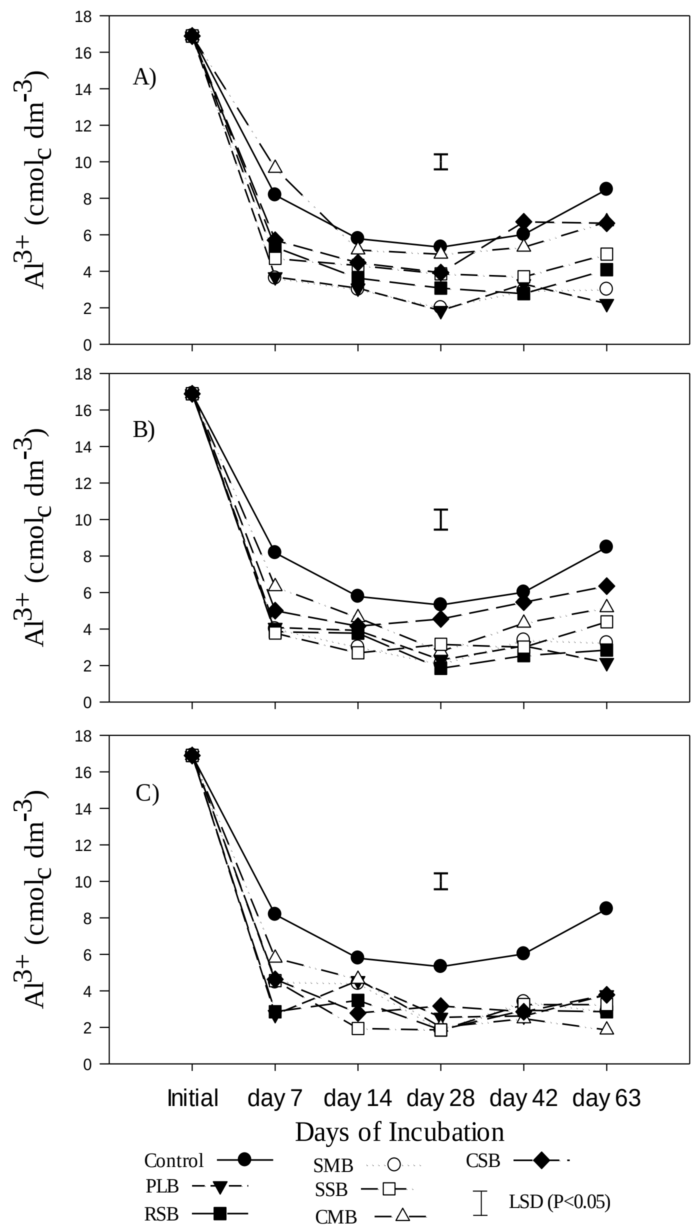

Figure 2. Exchangeable Al content at different levels (A) 5 Mg ha^{-1}, (B) 10 Mg ha^{-1} and (C) 20 Mg ha^{-1} of swine manure biochar (SMB), poultry litter biochar (PLB), cattle manure biochar (CMB), rice straw biochar (RSB), soybean straw biochar (SSB), and corn straw biochar (CSB). Vertical bars indicate the LSD values ($p<0.05$), in Graph A) LSD = 0.4140, graph B) LSD = 0.5510, graph C) LSD = 0.4365

7 ARTICLE III – POST-HARVEST NUTRIENT RETENTION IN A TYPIC HAPLUDULT AMENDED WITH DIFFERENT ANIMAL AND PLANT DERIVED BIOCHAR TYPES UNDER NO-TILLAGE SYSTEM[3]

Abstract

The surface application of biochars may have certain limitations related to their effect in nutrients retention capacity in subsoils. We designed a greenhouse experiment to evaluate the impact of the application over the soil of different biochars derived from animal and plant residues on surface and subsurface layers of an acidic soil. We applied biochars to wheat crop under no tillage system and evaluated their residual effects on subsequent soybean crop. After that, the undisturbed soil was stratified in 0-5, 5-10, 10-15 and 15-25 cm layers to evaluate the effect of biochars on N, P, K, pH and exchangeable Al. From the results, we found that in top 5 cm NO_3^-, NH_4^+, and P were influenced with biochar doses and with application of N, but in deeper layers there were no significant differences among biochars, doses as well as N application. The K was affected throughout the soil depths even with and without application of NH_4^+ fertilizer. Soil pH and exchangeable Al were also affected with biochar application up to 5 cm depth, whereas in deeper layers increase the pH as well as exchangeable Al. Thus, from the findings it can be concluded that biochars can hold N, P, and K, and increase soil pH and decrease exchangeable Al up to certain extent, independent of the type and dose of application over the soil under no-tillage system.

Keywords: Biochar, stratification, pH, residual nutrient, no-tillage

[3]Article is prepared according to the format of "*REVISTA BRASILEIRA DE CIÊNCIA DO SOLO*"

7.1 Introduction

Production and application of biochars to soil make some fundamental changes in soil nutrient cycling, increasing soil fertility and increment in crop productivity. Acidic, infertile, and low organic matter content soils respond positively to biochar application while the outcomes of these soils are variable (Prommer et al., 2014). There are a number of factors that regulate the nitrification process i.e. soil pH, temperature, soil moisture, N supplying substrate, soil microbes and soil types (Che et al., 2015), as the nitrification process is major factor in N cycle in soil as well as nutrient use efficiency (Zhao and Xing, 2009). To understand the nitrification process and its impact on environment for different soils is decisive to improve the soil fertility as well as environmental protection, it is needed to understand the soil processes. Low pH, high Al, low CEC are the major factors for limiting crop growth. Liming of acid soils is common practice use to increase soil pH and consequently increasing the crop yield. However long-term and rigorous use of liming in soil may be the basis for soil compaction, disequilibrium of Ca, K and Mg in soil, and hence reduced crop yields (Wang, 1995). A number of studies have been reporting to understand the nitrification and acidification in forests and temperate soil (Boer et al., 1992). The effect of biochar on NH_4^+ application in tropical and subtropical area under no tillage system is poorly understood and have little information. Based on the views on acidic soils and management practices to correct soil acidity as well as enhancing soil fertility and hence increasing production, we decided to use biochars derived from animal manures and plant residues to increase soil pH, decline in soil acidity and increase the crop production.

In this study, we aimed to evaluate the N, P and K nutrient retention in soil after two consecutive crops, i.e. wheat and soybean, previously amended with different types and doses of biochars and with and without application of NH_4^+ fertilizer. Based on biochars characteristics, we hypothesized that amendments using biochars produced from different animal manures and plant residues will improve soil nutrients retention capacity and increase soil pH in different layers, biochars will slow down nitrification process and hold N in NH_4^+ form.

7.2 Material and methods

7.2.1 Soil and biochar

Soil was collected from the experimental area of the Soil Department of the Federal University of Santa Maria (29°43'14.2"S and 53°42'15.0"W) for soil analysis and soil column in polyvinyl pipes (PVC) (0.29 m height × 0.20 m diameter) up to 0.25 m were collected for experiments under no-tillage system. Prior to installing experiments, the soil was analyzed for pH (4.8 $_{(1:2.5\ w/v)}$), total C (1.2%), N (0.8%), P (4.8 mg kg^{-1}), K (28 mg kg^{-1}), Ca (15.5 cmol$_c$ dm^{-3}), Mg (9.3 cmol$_c$ dm^{-3}) and Al (16.89 cmol$_c$ dm^{-3}).

For biochars preparation, all feedstocks were collected from the experimental areas of the Federal University of Santa Maria – RS (29°43'14.4"S 53°43'31.2"W) while corn straw was collected from a nearby city Paraíso do Sul – RS (29°35'10.3"S 53°07'26.3"W). Biochars, swine manure biochar (SMB), poultry litter biochar (PLB), Cattle manure biochar (CMB), rice straw biochar (RSB), soybean straw biochar (SSB) and corn straw biochar (CSB) were prepared at 450 ºC for 1 h in a muffle furnace with an increase in temperature 10 °C min^{-1}. All the biochars were analyzed for pH, electrical conductivity (EC) total carbon (C), total nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg) and micronutrients.

7.2.2 Experimental setup

A greenhouse experiment was conducted to evaluate the influence of different biochar types on wheat under no-tillage system with biochar application rate at 0, 10 and 20 Mg ha^{-1} with three replicates and their subsequent effect on soybean. After the soybean harvest soil columns were stratified as 0-5, 5-10, 10-15 and 15-25 cm layers to evaluate the influence of different biochars on the whole 0-25 cm profile. The stratified soil sample were then air-dried, ground and passed through 2 mm sieve, then were analyzed for NH_4^+, NO_3^-, P, K, Ca, Mg and Al in different soil layers.

7.3 Results and discussions

7.3.1 Primary nutrient concentration

It has been recognized that biochars can adsorb both NO_3^- and NH_4^+ nitrogen because of their large surface areas and presence of a range of different functional groups, consequently increasing the soil fertility and crop production. On biochars surface both acidic and basic sites can be found which can affect the adsorption of cations as well anions (Joseph et al., 2010). From the results (Table 1) in layer 0-5 cm, it can be seen that retention of NO_3^- is influenced by the different biochar types in both levels of application. Maximum NO_3^- (25.0 mg kg^{-1}) was adsorbed in treatment with CSB. The increase in dose of biochars increases NO_3^- retention in soil. Minimum NO_3^- was found in PLB (3.0 mg kg^{-1}) and control (5.5 mg kg^{-1}) treatment respectively. The addition of N fertilizer had no significant effect on NO_3 retention in top 5 cm soil while an increase in NO_3^- was observed when N was applied as NH_4 form. The N application to soil decreased the NO_3^- in columns with CMB, SSB and CSB both in 10 as well as 20 Mg ha^{-1}.

Data on soil layer 5-10 cm (Table 2) shows that increase in depth of soil decreased the NO_3 retention in soil both in different biochar types as well as doses of biochars. There was no effect noted among different biochar types, even with different doses of biochars i.e. 10 and 20 Mg ha^{-1}. The N application to crops also didn’t affect the NO_3^- in soil after harvest. Maximum NO_3^- (8.0 mg kg^{-1}) was observed in soil column amended with SMB at 20 Mg ha^{-1} while Minimum (1.1 mg kg^{-1}) was observed in soil column treated with SSB at 20 Mg ha^{-1}. No NO_3^- was found in deeper layers i.e. 10-15 and 15-10 cm (Tables 3 and 4), even an application of N fertilizer to an acidic soil had no effect on soil NO_3^- contents under no tillage conditions. Presence of $NO_3^–$ in soil layer 0-5 cm confirms the nitrification process occurs in top soil which was mixed with biochar (2.5 cm) based on the great volumes of the plant residues derived biochars. The application of alkaline biochar with high adsorptive capability adsorb $NO_3^–$ and NH_4^+ and hence reduce N loss from soil (Chen et al., 2013).

The NH_4^+ contents in soil were not affected by different biochar types after crop harvest (Table 1), even an increase in dose of biochars had no significant effect in NH_4^+ retention in soil in top soil layer (0-5 cm). A slight increase in NH_4^+ was observed with increase in dose of each biochar. Ammonium content in soil was also influenced directly with application of NH_4^+ fertilizer in soil in wheat crop under no tillage system. The N application increased the NH_4^+ retention in soil while the dose of biochar had not a significant effect on NH_4 retention in top 5 cm soil layer. Maximum NH_4^+ (67.6 mg kg^{-1}) was observed with application of CSB at 20 Mg ha^{-1} whereas minimum was observed in control treatment (control with N application). The most important biochar physical property to retain NH_4^+ and NH_3 is the surface area and pore structure. NH_3 also act as Lewis acid that could react with carboxyl groups of biochar and produce NH_4^+ or amide group (Spokas et al., 2012). However, NH_3 being an alkaline gas, the acidic surface groups on biochar with low pH can protonate NH_3 gas to NH_4^+ ions thereby promoting their adsorption onto the cation exchange sites of biochar (Bandosz, 2006), hence reducing the NH_4^+ loss through NH_3.

In soil layer 5-10 cm decreased NH_4^+ content as compared to top 5 cm soil, the decrease in NH_4^+ concentration shows the weak influence of surface application of biochars derived from animal manures and plant residues. An increase can be seen with increase in dose of biochars but there was no statistically ($p<0.05$) significant difference found between the two doses of biochars. The application of N to soil also didn't affect the NH_4^+ in soil up to 10 cm depth. A decrease and slight increase can be observed in both doses of biochars for example, in soil column SMB had NH_4^+ contents 15.7 mg kg^{-1} at 10 Mg ha^{-1} that decreased with 20 Mg ha^{-1} to 6.6 mg kg^{-1} while in case of CSB increased from 9.3 mg kg^{-1} to 12.2 mg kg^{-1} with increase in dose of biochar. In both control treatments (with N and without N) NH_4^+ was almost same 15.5 mg kg^{-1} without N and 14.6 mg kg^{-1} with N application. As compared to NO_3^-, the NH_4^+ was found continuously up to 20? cm layers collections (table 3 and 4), but with the increase in soil depth the concentration also remained gradually decreasing. The increase in dose of biochars had also a little influence in NH_4^+ contents whereas there was not a significant between doses of biochars, even in case of SSB and CSB the NH_4^+ content decreased 78 and 38% respectively with increase in dose of biochar (table 3). With increase in soil depth the NO_3^- contents decreased and in final 2 layers (10-15 and 15-25 cm) no NO_3 was noted that can be directly attributed to the no tillage soil conditions that we couldn't mix the soil and biochar at grater depths.

The available P remained changing with increase in depth, in top 0-5 cm layer P was influenced with biochar types as well as the increase in dose of biochars under no tillage system. Highest P (177.9 mg kg^{-1}) was found in soil column treated with CMB at 10 Mg ha^{-1} while minimum (33.7 mg kg^{-1}) was observed in control (no biochar, no N). The addition of N fertilizer enhanced the P retention in soil in all treatments with 20 Mg ha^{-1} except the soil treated with SMB where the addition of N fertilizer did not change the P content in soil, while the P contents remained non-significant with biochars dose at 10 Mg ha^{-1} with N application together. In control treatments addition of N also increased the P retention in soil.

With increase in depth, decrease in available P (Table 2) was observed but among different biochar types, no difference was observed when applied at 10 Mg ha^{-1} without N fertilizer, while a higher concentration was noted in column treated with SMB at 20 Mg ha^{-1} when compared with the other biochars and also when compared to 10 Mg ha^{-1} SMB treatment. The addition of N fertilizer also had not a significant impact on available P contents between 5 to 10 cm depth. In control treatments, no difference was found with and without application of mineral N fertilizer. As compared to top soil layers 0-5 and 5-10 cm, the available P in the subsoil layers (10-15 and 15-25 cm) was remained uninfluenced with different biochar types, doses of biochars as well as in combination with mineral N fertilizer (table 3 and 4), while a minute difference among treatments and doses can be noted. In the acidic soils, the P sorption is higher than the neutral or alkaline soil because of its low pH and Fe, Al and Mn oxides are dominant at low pH and fix P and reduce its availability (Geelhoed et al., 1997). Addition of biochars in low pH soil can increase the soil pH and increase available P in soil solution by the increase in negative charged surfaces and pH may be increased by proton consumption reaction and hence forming hydro-oxides of Al and Fe.

The biochar types, doses of biochars as well as combination of N affected strongly the available K in soil after the crop harvest. The available K ranged from 15 to 248 mg kg^{-1} affected by control (no biochar, no N) and RSB respectively without an application of N fertilizer (table 1). The application of N decreased the K retention significantly in both 10 and 20 Mg ha^{-1}. With increase in soil depth the available K concentration decreased while the influence of different biochars on K remained significant among different biochar types, doses and combination of N. In sublayer 5-10 cm the highest K (267.7 mg kg^{-1}) was observed in soil column treated with RSM at 20 Mg ha^{-1} while minimum (14.3 mg kg^{-1}) was observed in control treatment (no biochar, no N) (table 2). From the data of 10-15 and 15-20 cm (table 3 and 4) similar behavior has been observed that with increase in biochar dose the K content increases while the addition of mineral N fertilizer decreases the K contents in soil.

7.3.2 Soil pH and Al alteration

Biochar pH ranges from 5.5 to 10.5, that depends on content and composition of the mineral fractions that may be different depending upon the feedstock and pyrolysis conditions (Spokas et al., 2012). That's why biochar can alter the NH_4^+ and NO_3^- dynamic in soil system through their adsorptive properties and pH. Soil pH was greatly influenced by the addition of biochars alone, and along with NH_4^+ fertilizer (figure 1). The addition of biochars at 10 Mg ha^{-1} increased the soil pH sufficiently, highest soil pH was observed from the soil column treated with CSB, SSB, PLB and RSB as well in layer 0-5 cm. With increase in soil depth pH also decreased gradually even CSB, SSB and PLB decreased in layer 5-10 cm and remained decreased up to 15-20? cm (Figure 1A). Increased dose of biochars also increased the soil pH drastically. Soil treated with RSB at 20 Mg ha^{-1} showed maximum soil pH, whereas SSB didn't increase the soil pH with an increase in its dose (figure 1.B). On the other hand, RSB decreased the soil pH in sublayer (15-20 cm) again up to an acidic level. Application of ammonium fertilizer also had an influence on soil pH in layer 0-5 cm, because in addition to NH_4 fertilizer pH was increased up to a certain level (PLB, SMB), after that level then decreased quickly in 5-10 cm layer at 10 Mg ha^{-1} while PLB remained in slow decrease as compared to SMB at 20 Mg ha^{-1}. In deeper soil layers there are not significant differences can be noted but the pH remained decreasing with increase in soil depth. The pH increase in surface layer can be related to the presence of biochar's negatively charged phenolic, carboxyl and hydroxyl groups on surface of biochar which tend to bind H^+ from soil solution by reducing soil H^+ and hence increase in pH (Chintala et al., 2014). The pH increment increases the CEC by reducing the base cations leaching in competition H^+ ions (Gul et al., 2015). In our studies the biochar affected the only surface layer while underneath layers were not affected directly with addition of biochar even at 20 Mg ha^{-1}. The addition of NH_4^+ as fertilizer in soil decreases the soil pH whereas an increase occurs with application of biochar to an acid soils (Li et al., 2018).

A huge gradient can be seen by addition of different biochars in soil over undisturbed soil (no tillage system). Minimum exchangeable Al was observed in soil layer 0-5 cm (figure 2), that kept it increasing with increase in soil depth. Lowest exchangeable Al was observed in SSB at both 10 and 20 Mg ha^{-1}. The addition of ammonium fertilizer didn't influence the exchangeable Al content in an acidic soil under no tillage system while the influence of amendment was limited to a very shallow depth (5 cm), after that remained increasing and reached near to its original Al content in both 10 and 20 Mg ha^{-1}. The addition of biochars increases the alkaline metals (Ca^{2+}, Mg^{2+} and K^{+}) oxides in acidic soil and hence soluble Al^{3+} reduces by an increase in pH (Steiner et al., 2007).

7.4 Conclusion

Surface application of different biochar can have a limited impact on soil nutrients especially to an acidic soil. The biochars had a significant effect up to 5 cm soil depth by retaining NO_3^- while can hold higher quantities of NH_4^+ up to more depths under no tillage system. Phosphorus can be adsorbed by biochars when applied at surface while in deeper layers biochars don't influence the P retention in soil. Potassium is greatly influenced with surface application of biochars but decrease the K retention in soil with application of NH_4^+ fertilizer together. Soil pH and exchangeable Al also can have a prodigious positive impact up to a certain depth with superficial application of biochars that may not have an impact in depth.

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Table 1. Nutrients concentration in 0-5 cm after crop harvest with application of swine manure biochar (SMB), poultry litter biochar (PLB), Cattle manure biochar (CMB), rice straw biochar (RSB), soybean straw biochar (SSB) and corn straw biochar (CSB) under no-tillage system.

Nutrient	Control	SMB	PLB	CMB	RSB	SSB	CSB	SMB	PLB	CMB	RSB	SSB	CSB
				10 Mg ha^{-1}						20 Mg ha^{-1}			
							Without Nitrogen						
NO_3 (mg kg^{-1})	5.5 cAß	15.1bAα	3.0 cBα	20.4aAß	15.8 bAα	21.5 aAα	25.0 aAß	14.4 cBα	3.6 cBα	33.0 bBα	4.8 cBß	29.5 bBα	45.0 aBα
NH_4 (mg kg^{-1})	1.2aAß	15.8aAα	13.2aBα	50.0aAα	17.1aBα	45.5aAα	39.8aAα	37.1aAα	18.2aAα	20.3aAß	14.4aBα	27.8aAα	27.1aBα
P (mg kg^{-1})	33.7bBß	130.7aAß	64.4bAß	177.9aAα	30.1cBα	33.2cBα	19.3cBα	247.9aAα	128.4bBα	24.4cBß	27.9cBα	38.9cBα	77.2bBα
K (mg kg^{-1})	15.3cAß	69.3bAα	58.3bAß	59.0bAß	105.7aAß	42.0cAα	80.3bAα	75.3cAα	137.7bAα	88.7cAα	248.7aAα	38.3cAα	98.7cAα
							With Nitrogen						
NO_3 (mg kg^{-1})	5.9 cAß	19.1 aAß	11.5 aAα	8.4 cBα	17.3 aAß	2.4 dBα	4.3 dBα	26.5 aAα	13.7 bAα	10.4 bAα	22.4 aAα	5.4 cAα	14.5 bAα
NH_4 (mg kg^{-1})	19.6aAα	33.5aAα	39.6aAα	33.8aAα	62.2aAα	35.9aAα	37.6aAß	23.6aAα	37.7aAα	34.2aAα	50.9aAα	36.0aAα	67.6aAα
P (mg kg^{-1})	117.8aAα	114.9aAß	97.7aAß	135.2aAα	163.4aAα	173.4aAα	133.1aAß	206.6aAα	160.5aAα	186.4aAα	188.8aAα	197.3aAα	220.3aAα
K (mg kg^{-1})	18.7aAß	42.7bBß	55.7aAß	31.0bBß	52.0aBß	22.0bBα	33.7bBα	69.3cAα	97.3aBα	58.3cBα	117.3aBα	29.0dAα	50.7cBα

Lower-case letters within rows show the difference among different biochars, upper case letters within columns indicate the effect of nitrogen application, α and ß within rows indicate the effect of different doses of biochars.

Table 2. Nutrients concentration in 5-10 cm after crop harvest with application of swine manure biochar (SMB), poultry litter biochar (PLB), Cattle manure biochar (CMB), rice straw biochar (RSB), soybean straw biochar (SSB) and corn straw biochar (CSB) under no-tillage system.

Nutrient	Control	SMB	PLB	CMB	RSB	SSB	CSB	SMB	PLB	CMB	RSB	SSB	CSB
	10 Mg ha^{-1}							20 Mg ha^{-1}					
	Without Nitrogen												
NO_3 (mg kg^{-1})	7.8aAα	6.9aAα	1.1aAα	1.2aAα	6.7aAα	1.00aAα	2.5aAα	8.0aAα	1.0aAα	6.0aAα	5.4aAα	6.0aAα	5.8aAα
NH_4 (mg kg-1)	15.5aAα	14.0aAα	15.0aAα	13.6aAα	15.0aAα	17.3aBα	9.2aAα	14.7aAα	15.6aAα	10.8aAα	13.2aAα	10.7aAα	15.4aAα
P (mg kg-1)	8.5bAß	53.1aBß	17.1aAα	12.9aAα	16.3aAα	19.5aAα	36.6aAα	178aAα	22.1bAα	11.6bAα	14.5bAα	34.8bAα	18.1bAα
K (mg kg-1)	14.3cAß	54.0bAß	79.7bAß	33.5cAα	114.7aAß	29.7cAß	60.7bBß	136.3aAα	133.3bAα	56.3cAα	267.7aAα	31.0cAα	122.3bAα
	With Nitrogen												
NO_3 (mg kg-1)	3.6aAα	1.6aAα	3.2aAα	7.1aAα	4.6aAα	1.2aAα	1.1aAα	6.7aAα	1.2aAα	1.8aAα	2.6aAα	1.1aAα	1.3aAα
NH_4 (mg kg-1)	14.6aA	15.7aAα	11.8aAα	9.6aAα	10.0aAα	9.4aAα	9.3aAα	6.6aBα	10.8aAα	12.9aAα	12.7aAα	8.7aAα	12.2aAα
P (mg kg-1)	9.2cAß	108aAß	21.2bAα	7.3bAα	9.4bAα	36.1bAα	15.9bAα	163aAα	26.1bAα	13.0bAα	18.1bAα	19.0bAα	17.5bAα
K (mg kg-1)	15cAß	32.3bAß	41.3bBß	11.3bAα	65.3aBß	13.3bAα	22.3bAß	73.0cBα	123.3bAα	32.0cAα	205.3aBα	11.3dAα	55.3cBα

Lower-case letters within rows show the difference among different biochars, upper case letters within columns indicate the effect of nitrogen application, α and ß within rows indicate the effect of different doses of biochars.

Table 3. Nutrients concentration in 10-15 cm after crop harvest with application of swine manure biochar (SMB), poultry litter biochar (PLB), Cattle manure biochar (CMB), rice straw biochar (RSB), soybean straw biochar (SSB) and corn straw biochar (CSB) under no-tillage system.

Nutrient	Control	SMB	PLB	CMB	RSB	SSB	CSB	SMB	PLB	CMB	RSB	SSB	CSB
		10 Mg ha^{-1}						20 Mg ha^{-1}					
Without Nitrogen													
NO_3 (mg kg-1)	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_4 (mg kg-1)	9.2aAα	7.0bAα	2.4bAα	6.0bAα	2.4bAα	23.4aAα	12.7bAα	12.3aAα	6.1aAα	5.6aAα	8.2aAα	4.5aAα	7.8aAα
P (mg kg-1)	7.8 ns	10.8 ns	29.4 ns	21.3 ns	18.3 ns	11.4 ns	67.9 ns	35.7 ns	12.5 ns	8.6 ns	16.4 ns	48.5 ns	25.6 ns
K (mg kg-1)	0.7abA	21.7bAß	39.3bAß	15.0bAα	60.6aAß	19.0bAα	26.3bAß	68.3bAα	69.0bAα	28.3cAα	121.0aBα	26.7cAα	53.3bAα
With Nitrogen													
NO_3 (mg kg-1)	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_4 (mg kg-1)	13.2aAα	4.8aAα	11.7aAα	11.6aAα	4.2aAα	8.0aAα	13.1aAα	12.8aAα	13.4aAα	8.0aAα	20.24aAα	6.5aAα	13.2aAα
P (mg kg-1)	11.6 ns	19.8 ns	28.7 ns	6.9 ns	13.3 ns	14.2 ns	15.2 ns	21.9 ns	27.4 ns	30.5 ns	21.9 ns	66.9 ns	17.7 ns
K (mg kg-1)	11bAß	17.3bAß	18.3bBß	12.3bAα	38.7aBß	12.0bAα	15.6bAα	42.7cBα	76.3bAα	17.7dAα	153.0aAα	9.3dBα	29.0dBα

Lower-case letters within rows show the difference among different biochars, upper case letters within columns indicate the effect of nitrogen application, α and ß within rows indicate the effect of different doses of biochars, ns indicates the no difference among different biochar types, doses of biochars and with and without N application.

Table 4. Nutrients concentration in 15-25 cm after crop harvest with application of swine manure biochar (SMB), poultry litter biochar (PLB), Cattle manure biochar (CMB), rice straw biochar (RSB), soybean straw biochar (SSB) and corn straw biochar (CSB) under no-tillage system.

Nutrient	Control	SMB	PLB	CMB	RSB	SSB	CSB	SMB	PLB	CMB	RSB	SSB	CSB
	10 Mg ha^{-1}							20 Mg ha^{-1}					
	Without Nitrogen												
NO_3 (mg kg-1)	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_4 (mg kg-1)	7.2aAα	11.7aAα	9.2aAα	10.2aAα	8.4aBα	7.9aBα	13.4aBα	18.4aBα	13.1aAα	9.9aAα	8.9aα	10.6aBα	14.76aAα
P (mg kg-1)	4.7aBß	18.9aAα	6.4aAα	4.3aAα	4.7aAα	2.9aAα	3.6aAα	22.1aAα	8.0aAα	3.5aAα	3.4aAα	3.7aAα	4.3aAα
K (mg kg-1)	7.3bAß	24.3bAα	20.7bAß	15.0bAα	39.7aAα	14.3bAα	27.3bAα	32.6bAα	49.0aAα	17.0cAα	39.0bAα	19.7cAα	23.3cAα
	With Nitrogen												
NO_3 (mg kg-1)	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_4 (mg kg-1)	10.6aAα	13.1cAα	8.0cAα	17.5cAß	38.5bAα	50.5aAα	52.3aAα	15.2cAα	10.8cAα	57.6aAα	30.9bα	34.3bAα	49.3aAα
P (mg kg-1)	18.9aAα	16.6aAα	15.5aAα	14.0aAα	11.0aAα	7.8aAα	4.7aAα	21.8aAα	9.7aAα	10.2aAα	11.9aAα	22.4aAα	8.8aAα
K (mg kg-1)	7.7aAß	14.7aAα	19.0aAα	19.3aAα	23.7aAß	13.3aAα	16.6aAα	27.0aAα	26.0aBα	22.0aAα	38.0aAα	12.7bAα	22.3aAα

Lower-case letters within rows show the difference among different biochars, upper case letters within columns indicate the effect of nitrogen application, α and ß within rows indicate the effect of different doses of biochars, ns indicates the no difference among different biochar types, doses of biochars and with and without N application.

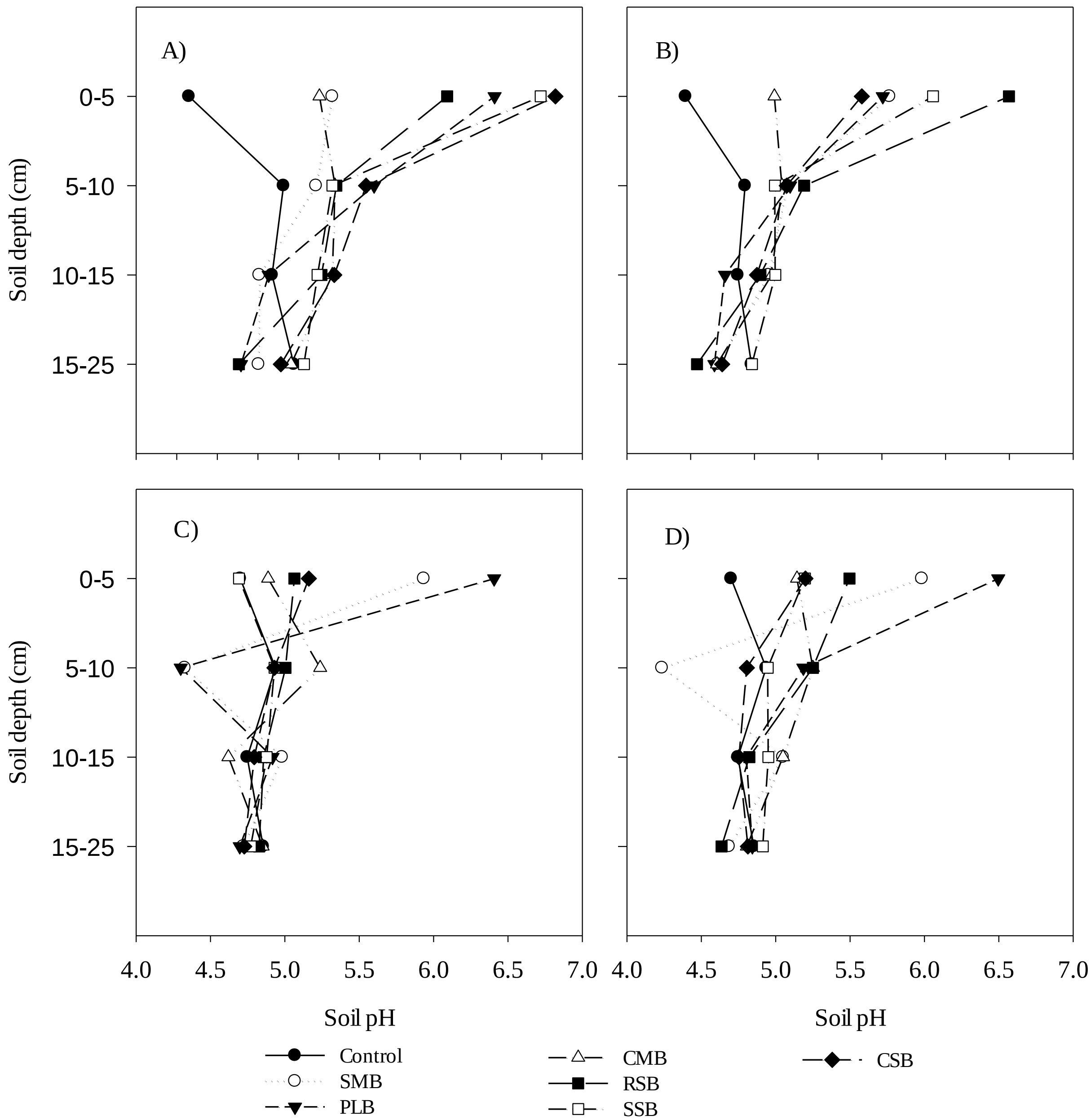

Figure 1. pH changes in different soil layers with surface application of swine manure biochar (SMB), poultry litter biochar (PLB), Cattle manure biochar (CMB), rice straw biochar (RSB), soybean straw biochar (SSB) and corn straw biochar (CSB), A) 10 Mg ha^{-1}, B) 20 Mg ha^{-1}, C) 10 Mg ha^{-1} with N and D) 20 Mg ha^{-1} with N.

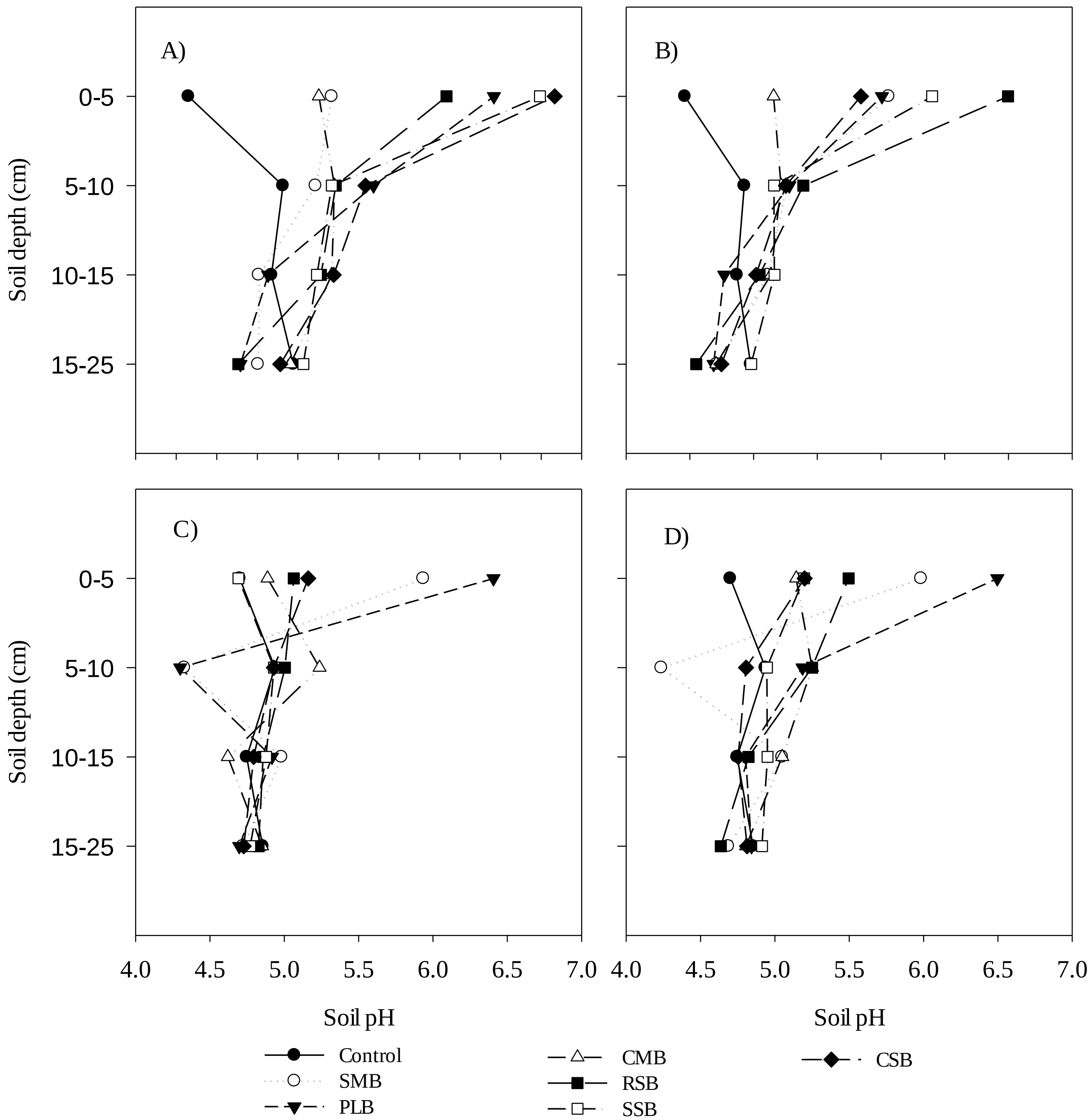

Figure 2. Soil exchangeable Al in different soil layers with surface application of swine manure biochar (SMB), poultry litter biochar (PLB), Cattle manure biochar (CMB), rice straw biochar (RSB), soybean straw biochar (SSB) and corn straw biochar (CSB), A) 10 Mg ha^{-1}, B) 20 Mg ha^{-1}, C) 10 Mg ha^{-1} with N and D) 20 Mg ha^{-1} with N.

8 GENERAL DISCUSSION

8.1 BIOCHAR PROPERTIES

A number of amendments are used to increase the soil organic matter all over the world i.e. mulching, green manuring and composting. In recent years the preparation of biochar has added a glance in research to conserve soil organic matter by addition of biochars produced from different organic wastes. Biochars can be prepared by different methods gasification, slow pyrolysis, fast pyrolysis and torrefaction. Biochar characteristics depend on the type of material used (feedstock), and the process by which the biochar is prepared. The availability of organic material in Southern region of Brazil is much more depending on the huge amount of animal farming and agricultural areas. The region is known for rice, maize and soybean production and the crop straws are always left on soil at the harvesting time. Depending upon the availability of the material we decided to collect animal manure and different crop residues, so we collected swine, poultry and cattle manure while on the other hand we collected the rice, soybean and corn straw to make the biochars. The lower yield of the biochars can be related to the no fully controlled condition during pyrolysis. All biochars prepared at 450 ºC showed distinct production rate among different materials. The biochars from animal prepared from manures presented high yield as compared to the biochars from crop straws. Crop straws biochars were rich in total C content as compare to the biochars from animal manures. The high TC contents in crop straws may be attributed to the favoring behavior of straws for C aromaticity as compare to the manures.

In addition to the operating conditions of pyrolysis, the composition and chemical structure of biomass feedstocks is closely related to the composition and chemical structure of the biochar produced. Cellulose and lignin, for example, had thermal degradation in a range between 240 - 350 ºC and 280 – 500 ºC (DEMIRBAS, 2004). Therefore, the relative proportions of these components will affect the carbon content of biomass where higher lignin content biomass will provide higher carbon content in biochar compared with that produced from biomass with lower lignin content (VERHEIJEN et al., 2010). In our study lignin and Hemi-cellulose contents in Soybean straw found higher (GHAFFAR; FAN, 2013) as compared to the rice straws (GHAFFAR; FAN, 2013) this may be a factor of high TC in SSB as compared to the RSB. However, the results taken from this study show that C content in CMB is lower than in SMB and PLB. This is possible because the content of protein and fat in swine and poultry manure is higher than that of in CMB. Nitrogen concentration in biochars is generally lower as compare to the feedstock providing the favorable environment during pyrolysis process to escape out in the form of N_2O, NH_3 and N_2. In our analysis the swine manure and poultry litter biochars showed high N content as compared to the crop straws except SSB that indicates the high N fixing capability of legumes. On the other hands, manures containing the high N as compare to the crop straws, consequently lost less N. High N content in SMB and PLB can be related to the controlled conditions of their feeds because their raw materials were collected from the experimental united. Pyrolysis of PL enriched the inherent non-volatile elements including P in biochar products. The enrichment became more prominent at higher pyrolysis temperatures in response to the decreasing biochar yield (SONG; GUO, 2012). Many studied reported smaller amounts of P and K in after pyrolysis but in our case the P was reported higher in SMB and PLB as compared to other biochars while K was sufficient on an average 3.5% in all biochars with maximum values in RSB that can be related to the collection strategy of our material which was collected on the same time when harvesting was done while lowest K content can be confirmed due to the late collection from the field so that rainfall occurred between harvesting and collection time. Biochars prepared from poultry litter can condense the P contents in biochars (LI et al., 2018). They prepared biochars at 300, 450 and 600 ºC and reported that poultry litter (PL) contains significant amount of both inorganic phosphorus (IP) species (e.g., dicalcium phosphate ($CaHPO_4$), amorphous tricalcium phosphate ($Ca_3(PO_4)_2$, and octa calcium phosphate ($Ca_8H_2(PO_4)6{\cdot}5H_2O$)) and organic phosphorus (OP) species (e.g., phytates, phospholipids, and nucleic acids) and most of the OP in PL was converted to inorganic forms during pyrolysis, as indicated by the drastic decreases in the proportion of OP yet abrupt increases in the proportion of IP in the derived biochars relative to raw PL. The increase in pyrolysis temperature increases P content in biochars, in our studies we have analyzed TP, in which might be found higher IP. Usually, Ca and Mg are found in biochars in lesser concentration while in our study biochars prepared from animal manures especially PLB and SMB were rich in Ca and Mg, the only reason that can be found that the feedstock were collected from highly controlled experiments where the feed and manures mixed together as wasted materials. Previous studies reported that micronutrients behave like C, P and K during pyrolysis processes. The higher concentration of micronutrients seems to be in similar behavior but we cannot say it 100% surety because we didn’t analyze feedstock. In the thermal decomposition of the biochars, C contents is directly proportional cellulose and lignin contents of the feedstock. From the C in biochars it is evident that the plant residues biochars have more cellulose and lignin contents as compared to the animal manures. In general, it is known that biochars are alkaline in nature and contain high pH as compared to their original source materials and pH increases with increase in temperature. In our characterization study all biochars proved even at low temperatures biochars can be with high pH. The reasons for high CEC of the biochars produced are, increase in surface area after pyrolysis and an increase in charge density on the surface. Generally, the higher the pyrolysis temperature the higher the biochar surface area. This high surface area is in the form of micro/nanopores as correctly suggested to increase the CEC. And also, biochars produced at low pyrolysis temperatures have a high number of oxygenated functional groups (carboxyl, hydroxyl, phenol etc) and sorption primarily occurs by chemisorption. The FTIR spectra for biochars clear that the moisture left the structure during pyrolysis process, it maybe notable the dehydration of C-OH groups and sharp division of some hydrocarbons object maybe formed.

8.2 BIOCHARS INFLUENCE ON CARBON MINERALIZATION

In incubation experiment, we measure CO_2 emission to evaluate the C mineralization in soil with application of biochar in relation to C contents e.g. 1 and 2% to a Typic Hapludult. Less CO_2 emission was observed from the biochars from crop straws, that can be attributed to the formation of aromatic rings and fixation of C in biochars releasing less amount of CO_2 in atmosphere, consequently affecting positively on atmosphere. The addition of biochars to soil may affect the C cycle and have an impact on soil water gas system, change may occur in soil microbial biomass C and consequently affecting the carbon mineralization.

8.3 EFFECT OF BIOCHARS ON SOIL pH AND AL CONTENTS

Soil pH is influenced by addition of biochars to an acidic soil that may be related to the biochars high alkalinity, because each of our biochar prepared had a pH more than 9.5, which shows the capability of biochars to increase the soil pH when amended with biochars. During the incubation period, the pH remained fluctuating which may be attributed to the nitrification and denitrification processes simultaneously (XU; COVENTRY, 2003). On the other hand, biochars decreased exchangeable Al content at a certain extent rather than that our soil was not Al toxic, but removal of exchangeable Al shows the capacity of biochars to correct the degraded soils by removing Al contents and by increasing the soil pH and consequently increasing soil fertility.

8.4 BIOCHAR EFFECTS ON CROP YIELD UNDER NO-TILLAGE SYSTEM

A number of studies show the biochars effects on soil properties and crop growth but for each experiment there were same method used i.e. incorporation of biochars in soil. In this study, we mixed biochar only at 2–3 cm soil depth assuming the no-tillage effect on soil. In agronomic parameters the biochars did not have a specific difference among their values of plant height, spike length and dry mass. But, the addition of N fertilizer increased the dry mass yield up to two folds showing the same effect between two controls also which we had installed together, while addition of biochar had a certain difference from the control (no biochar, no nitrogen) but among biochars there was no difference. The difference from control can be understood that a minute amount of N in biochars enhanced the wheat plant height, and dry mass. Addition of N also affected the nutrient concentrations in plant aerial part of wheat, almost double the N concentration in plant tissues. Between doses of biochars didn't affect the N concentration in plant tissues. The high P and K were noticed in plant tissues in comparison to control treatments (no biochar, no N and no biochar, with N) that shows that biochar may act as regulating agent in soil by holding nutrients in soil.

In residual effects of biochars on soybean a slight increase in plant height was noted while in treatments without previously added N increased the dry mass yield among treatments. As well as dose of biochars, on the hand the treatment received N previously (in wheat crop) had no effect on soybean dry mass but in control dry mass yield was significantly low.

In nutritional concentrations in consideration to the residual effects of biochars, N was significantly different with and without N treatment units, while P and K contents decreases in treatments where N was applied previously. Secondary and micronutrient concentrations were not altered among biochar types, doses, even with and without N.

9 GENERAL CONCLUSION

Animal and plant waste derived biochars presented distinct properties in relation to their elemental variables, thermal degradation and FTIR spectroscopic analysis. Animal derived biochars presented more elemental concentrations, presenting advanced degradation levels while the biochars from crop straw had more pH, EC and CEC. The thermal degradation analysis of biochars present high cellulose and lignin contents which presents the more need to be allowed in furnace to be degraded. The CO_2 emission from the soil amended with biochars showed the animal waste derived biochars released more CO_2 as compared to crop straws derived biochars when mixed with soil at 1 and 2% in relation to C present in biochars. On the other hand, in incubation experiment soil amended with biochars at 5, 10 and 20 Mg ha^{-1} increased the soil pH up to an average of 1.0 point, and decreased the soil exchangeable Al from 16.98 $cmol_c$ dm^{-3} to 2.0 $cmol_c$ dm^{-3}. The results from soil pH and exchangeable Al show a great acceptability of preparing biochars from animal manure and crop straws and applying them to soil instead of applying them directly to soil. The addition of biochars to soil with N fertilizer can enhance the agronomic parameters as well as yield parameters of the crops under no-tillage planting system. Addition of biochars to soil favors micronutrients uptake by crop plants from soil. So, it would be better to consider biochars as soil conditioner instead of organic fertilizer for soil amendment in relation to soil fertility and plant nutrition.

10 FUTURE RESEARCH PERSPECTIVES

I think we have mounted a new scheme to the research in relation with biochars and no tillage system. From collection of material up to each step of experiments there has been a specific precautionary measure, we would suggest for any future research with biochars and no tillage system.

- It would be better to take one material and prepare biochars with different temperatures and at different resident time, so could be evaluated better its properties for acidic as well as basic soils.
- There would be a large-scale experiment to differentiate the differences among different biochars as well as their doses on soil pH, exchangeable Al.
- To determine the direct and indirect influence of biochar on soil properties and plant growth under no tillage system, field trials would be much better option in relation to the enhancement of the understanding real mechanism of biochar influence.
- In our experiments all biochars favored micronutrients uptake by both wheat and soybean crops, thus it must be evaluated in future experiments under field trials.

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11 APPENDICES

Figure 1. Materials collection for biochar preparation A) swine manure, B) poultry litter, C) cattle manure, D) rice straw, E) soybean straw and F) corn straw.

Figure 2. Biochar preparation in muffle furnace at 450 C for 1h. A) Putting raw material in ceramic crucibles, B) temperature setting, C) weighing end product for biochar production percentage, D) biochar.

Figure 3. Mineralization of biochars under incubation conditions A) weighing of soil, B) Air tight bottle (soil biochar mixture and NaOH for CO_2 capture), C) Titration against HCl to estimate CO_2 emission.

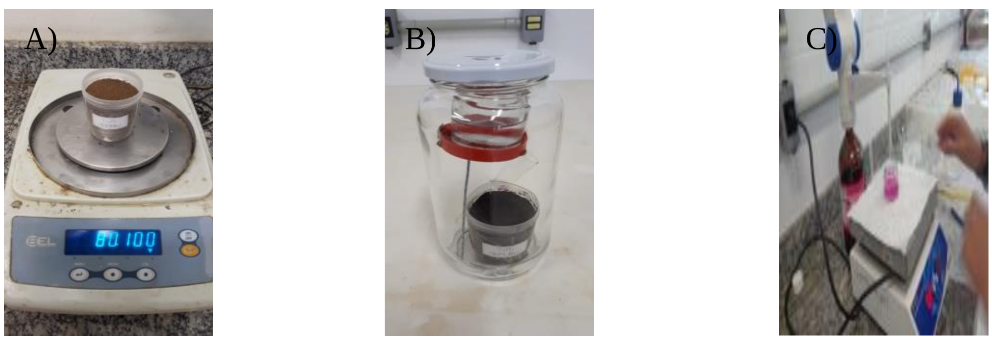

Figure 4. Direct and residual effect of biochars on wheat and soybean under no-tillage system. A) Wheat germination, B) Wheat crop, C) Soybean sowing, D) Soybean plants.