UNIVERSIDADE FEDERAL DE LAVRAS

JOSÉ FERREIRA LUSTOSA FILHO

BIOCHAR-BASED PHOSPHATE FERTILIZER AS AN ALTERNATIVE TO IMPROVE PHOSPHORUS USE EFFICIENCY IN TROPICAL SOILS

LAVRAS-MG
2018

JOSÉ FERREIRA LUSTOSA FILHO

BIOCHAR-BASED PHOSPHATE FERTILIZER AS AN ALTERNATIVE TO IMPROVE PHOSPHORUS USE EFFICIENCY IN TROPICAL SOILS

Thesis presented to the Federal University of Lavras, as part of the requirements of the graduate program in Soil Science, area of concentration in Soil Fertility and Plant Nutrition, to earn the title of Doctor.

Advisor
Dr. Leônidas Carrijo Azevedo Melo

Co-advisor
Dr. Carlos Alberto Silva

LAVRAS-MG
2018

JOSÉ FERREIRA LUSTOSA FILHO

BIOCHAR-BASED PHOSPHATE FERTILIZER AS AN ALTERNATIVE TO IMPROVE PHOSPHORUS USE EFFICIENCY IN TROPICAL SOILS

> Thesis presented to the Federal University of Lavras, as part of the requirements of the graduate program in Soil Science, area of concentration in Soil Fertility and Plant Nutrition, to earn the title of Doctor.

APPROVED in August 02, 2018.

Dr. Paulo Sergio Pavinato	ESALQ
Dr. Edson Marcio Mattiello	UFV
Dr. Teotonio Soares de Carvalho	UFLA
Dr. Yuri Lopes Zinn	UFLA

Advisor
Dr. Leônidas Carrijo Azevedo Melo

LAVRAS-MG
2018

ACKNOWLEDGMENTS

RESUMO GERAL

O fósforo (P) é rapidamente sorvido em solos tropicais altamente intemperizados. A maioria dos fertilizantes fosfatados utilizados no Brasil possuem alta solubilidade, proporcionando liberação rápida do P e maior susceptibilidade à fixação de P nos solos. Assim, buscou-se produzir um fertilizante organomineral à base de biocarvão com o objetivo de aumentar a eficiência de uso de P em solos tropicais ácidos. Para este propósito, fosfato monoamônico (MAP), superfosfato triplo (TSP) e ácido fosfórico (H_3PO_4) com e sem a adição de óxido de magnésio (MgO) foram misturados com cama de frango para produzir fertilizantes à base de biocarvão (BBFs) por meio da pirólise a 500 °C. Três estudos foram realizados para caracterizar e avaliar a eficiência agronômica dos BBFs. Na primeira parte do estudo, avaliou-se a composição mineral, difração de raios-X, espectroscopia de infravermelho por transformada de Fourier, cinética de liberação de P em água e um ensaio em casa de vegetação com milho cultivado em Latossolo argiloso. A adição de MgO reduziu drasticamente a cinética de liberação de P em água dos BBFs, devido à formação de compostos de baixa solubilidade. No entanto, estes BBFs promoveram produção de biomassa de milho próxima a obtida com TSP e também elevaram o pH e o teor de Mg do solo após o cultivo. Na segunda parte do estudo, foram avaliados dois BBFs (biocarvão cama de frango + TSP + MgO, identificado como BCF-TSP-MgO e biocarvão cama de frango + H_3PO_4 + MgO, identificado como BCF-H_3PO_4-MgO) em relação: (i) as frações solúveis, (ii) difusão de P no solo utilizando uma técnica de visualização ao longo do tempo e (iii) eficiência agronômica na forma granular e em pó na cultura do milho. A solubilidade do P em água dos BBFs foi drasticamente reduzida, mas a solubilidade no ácido cítrico e citrato neutro de amônio + água é semelhante a do TSP. O método de visualização mostrou que o processo de difusão de P no solo dos BBFs é mais lento que o do TSP, característico de fertilizantes de liberação lenta. Os BBFs possuem eficiência agronômica semelhante ao TSP quando aplicados em pó. O BCF-H_3PO_4-MgO, aplicado na forma de grânulo, promoveu produção de biomassa do milho equivalente a obtida com TSP, apesar da pequena proporção do grânulo que dissolveu durante o cultivo do milho (~ 16%, em contraposto a 40% do TSP), preservando o P disponível no grânulo para cultivos futuros. Na terceira parte do estudo, os BBFs foram aplicados em diferentes doses em um Latossolo Vermelho e incubados por um período antes do cultivo com *Urochloa brizantha* durante três ciclos de crescimento para avaliar a eficiência agronômica e, posteriormente, um procedimento de extração sequencial foi utilizado para determinar a distribuição de P entre as diferentes frações de P. O rendimento de matéria seca da parte aérea no primeiro ciclo de cultivo na dose mais elevada foi maior para o TSP$_{plantio}$ (sem incubação). No entanto, nos ciclos de cultivo subsequentes, todos os BBFs apresentaram maior rendimento de biomassa em

comparação com o $TSP_{plantio}$. A adição de BCF-TSP influenciou positivamente a dinâmica das frações de P no solo com aumento das frações lábeis e moderadamente lábeis de P no solo após o cultivo.

Palavras-chave: Sorção de fósforo. Latossolo. Fertilizantes à base de biocarvão. Fertilizante de libertação lenta. Eficiência de uso de P. Frações de fósforo.

GENERAL ABSTRACT

Phosphorus (P) is rapidly sorbed on highly weathered tropical soils. Most phosphate fertilizers used in Brazil have high solubility, providing fast P release and greater susceptibility to P fixation in soils. Thereby, we sought to produce a biochar-based organomineral fertilizer aiming to increase the P use efficiency in acidic tropical soils. For this purpose, monoammonium phosphate (MAP), triple superphosphate (TSP) and phosphoric acid (H_3PO_4) with and without the addition of magnesium oxide (MgO) were mixed with poultry litter to produce biochar-based fertilizers (BBFs) by pyrolysis at 500 °C. Three studies were carried out to characterize and evaluate the agronomic efficiency of the BBFs. In the first part of the study, it was evaluated mineral composition, X-ray diffraction, Fourier transform infrared spectroscopy, P release kinetics in water of the BBFs and a bioassay with maize in a greenhouse using a clayey Oxisol. The addition of MgO dramatically reduced the release kinetics of P in water from BBFs due to the formation of low solubility compounds. However, these BBFs promoted maize biomass production close to TSP and also raised the pH and soil Mg content after cultivation. In the second part of the study, it was evaluated two BBFs (biochar poultry litter + TSP + MgO, identified as PLB-TSP-MgO, and biochar poultry litter + H_3PO_4 + MgO, identified as PLB-H_3PO_4-MgO) in relation to (i) the soluble fractions, (ii) diffusion of P in the soil using a visualization technique over time, and (iii) the agronomic efficiency in granular and powder form in the maize crop. The P water solubility of BBFs was dramatically reduced, but the solubility of citric acid and neutral ammonium citrate + water is similar to the TSP. The method of visualization showed that the P diffusion process of BBFs in soil is slower than the TSP, characteristic of slow-release fertilizers. BBFs have agronomic efficiency similar to TSP when applied in powder. The PLB-H_3PO_4-MgO, applied as a granule, promoted maize biomass production equivalent to TSP, despite the smaller proportion of the granule that dissolved during maize cultivation (~ 16% versus 40% of TSP), preserving P available in the granule for future harvests. In the third part of the study, the BBFs were applied at different doses in an Oxisol and incubated for a period before cultivation of *Urochloa brizantha* for three growth cycles to evaluate the agronomic efficiency and thereafter, a sequential extraction procedure was used to determine the P distribution among different P pools. The shoot dry matter yield in the first cropping cycle was higher at the highest P rate for TSP$_{planting}$ (no incubation). However, in subsequent crop cycles, all BBFs showed higher biomass yield as compared to TSP$_{planting}$. The PLB-TSP addition positively influenced the dynamics of the P fractions in the soil with an increase in the labile and moderately labile P fractions in soil after cultivation.

Keywords: Phosphorus sorption. Oxisol. Biochar-based fertilizers. Slow-release fertilizer. P use efficiency. Phosphorus fractions.

SUMMARY

FIRST PART

1 GENERAL INTRODUCTION

Efficient utilization of soil phosphorus (P) has attracted worldwide attention due to its scarcity, essentiality and erratic global distribution (CHILDERS et al., 2011). Phosphate rock is the main source of P and is a finite resource with reserve estimates are quite variable, ranging from 50 to 400 years (CORDELL, DRANGERT, WHITE, 2009; REIJNDERS, 2014; VAN DIJK, LESSCHEN, OENEMA, 2016). According to Roy et al. (2016), Brazil accounts for approximately 25% of global cropland P-fixing soils, besides that there is an intensification of agriculture in these soils in the last decades, representing three quarters of the P-fixing soils currently being used for crop production globally. The authors also reported that the expansion of new croplands onto P-fixing soils could increase the global soil P 'tax' imposed, reaching 2-7 Tg P yr^{-1} by 2050.

An alternative to improve the efficiency and sustainability of P use in Brazil is to reuse (recover and/or recycle) secondary P sources aiming to replace partially the imports of highly soluble inorganic fertilizers (WITHERS et al., 2018). According to these authors, the use of secondary sources such as livestock manures, sugarcane processing residues, wastewater biosolids and legacy P remaining in the soil could potentially provide up to 20% of crop P demand by 2050, if further investments in P recovery technologies are applied. Additionally, the use of technologies that harmonizes crop demand and P released from fertilizers are promising to reduce phosphate fixation in soils and improve P use efficiency (SARKAR et al., 2018).

A significant part of agricultural soils in Brazil are highly weathered, rich in Fe and Al(hydr)oxides and poor in nutrients (LOPES, GUILHERME, 2016).

In these soils, P is one of the most limiting nutrients for plant production, due to very low levels of available P caused by its strong interaction with (hydr)oxides of Fe and Al (ABDALA et al., 2015; NOVAIS, SMYTH, 1999). In Brazil, mines provide limited amounts of P due the scarcity phosphate rocks and high production costs (WITHERS et al., 2018), and therefore, about 60% of the inorganic P fertilizer used in Brazilian agriculture is imported (ANDA, 2017). Thus, the most phosphate rock is used for production of fully acidulated phosphate fertilizer that have high water solubility (STEINER et al., 2015). However, ca. 20-30% of total P is wasted, and the production cost is high (MAO et al., 2017).

Approximately 95% of the phosphate fertilizers used in Brazil carry water-soluble P (SOUSA et al., 2010). After application, the P content in the soil solution is rapidly increased, favoring the uptake of P by plants. However, this P can also be rapidly transformed into non-labile forms. Therefore, P applied via fertilizers and absorbed by the crop in the first harvest is usually in the order of 10% to 20% of the total applied P (CHIEN et al., 2010; ROBERTS, JOHNSTON, 2015). Thus, there is a need of improving the current agricultural management practices aiming to increase P use efficiency in acidic tropical soils.

Biochar can be defined as a solid product obtained from thermal conversion of biomass to carbonized chemical compounds using high temperatures under absence or limited oxygen presence (LEHMANN, STEPHEN, 2015). Applying of biochar in agriculture to improve soil quality is an ancillary practice used by indigenous tribes in Amazonian, which resulted in a kind of soil known in Portuguese as Terra Preta de Indio (indian dark earth) (CHAN et al., 2007; GLASER et al., 2001; LEHMANN, STEPHEN, 2015). In the last decade, the conversion of residues into biochar for use as a soil conditioner got attention worldwide. The scientific community has indicated the benefits of biochar to improve chemical (CHAN et al., 2007; GLASER et al., 2002; PANDIT et al., 2018), physical (ARE et al., 2018; GLASER et al., 2002) and biological

(LEHMANN et al., 2011; ZHANG et al., 2018) soil conditions. Despite the likely benefits with the use of biochar in soils, its economic feasibility is still questionable, mainly due to large amounts recommended (VOCHOZKA et al., 2016).

Recently, the use of nutrient enriched biochars as composite fertilizers has increased (JOSEPH et al., 2013; SCHMIDT et al., 2017; WEN et al., 2017). It has been demonstrated a great potential of biochar to increase nutrient use efficiency. Zhao et al. (2014) observed that the mix of biomass (wheat straw) with different P sources (H_3PO_4, phosphate rock and triple superphosphate) reduced carbon loss during pyrolysis (7.7-31.4%), reduced the rate of microbial mineralization and increased stability to chemical oxidation of biochar. However, these authors reported that the low pH of biochars impregnated with acidulated phosphates could limit its application in acidic soils. Thus, mixing the biomass with an alkaline source (e.g., MgO) in addition to the acid source of phosphate prior to pyrolysis may be a viable alternative to elevate the pH and enrich this biochar with phosphate and magnesium, which has a synergistic effect on P acquisition, root development, and plant growth (GONZÁLEZ-PONCE, LÓPEZ-DE-SÁ, PLAZA, 2009; NIU et al., 2015).

Brazil is the second largest poultry producer in the world and it is estimated that the annual poultry litter volume is around 8-10 million tons/year (DALÓLIO et al., 2017). Usually, large amounts of poultry litter are generated in small areas, and that can have a negative impact on the environment (NUERNBERG et al., 2016). Biochar production and integrated energy have been pointed out as an alternative to add value to poultry litter and reduce environmental problems resulting from its "*in natura*" application (HUANG et al., 2015). In addition, the production of biochar from poultry litter showed potential to reduce the rapid release of P and to increase its efficiency as fertilizer P, due to the slow and constant release of this nutrient (WANG et al., 2015). Thus,

this enriched biochar is expected to generate slow-release fertilizer and increase P use efficiency compared to conventional sources. In addition, it is expected that the C added to the soil through these fertilizers has a high stability, contributing to soil C sequestration.

1.1 Aim of this thesis and research questions

The major purpose of this research was to develop a biochar with potential for use as an enhanced P fertilizer for tropical soils. In the work described in this thesis our aim was to answer the following research questions:

Do biochar-based fertilizers (BBFs) produced from poultry litter impregnated with monoammonium phosphate, triple superphosphate and phosphoric acid, with and without the addition of magnesium oxide (MgO), present desirable characteristics to be applied to soil as phosphate fertilizer?

Do BBFs produced from sources of P and MgO present high agronomic performance in annual crops as compared to the soluble source and also a residual effect for future harvests?

1.2 Dissertation outline

The above research questions have been addressed in three chapters.

In chapter 1, the mineral composition, X-ray diffraction, Fourier transform infrared spectroscopy, P-release kinetics in water of the biochar-based fertilizers (BBFs) were assessed, as well as a bioassay with maize in a greenhouse using a clayey Oxisol;

In chapter 2, two BBFs were investigated in relation to the soluble fractions, diffusion of P in the soil using a visualization technique over time and the agronomic efficiency in the granular and powder form in the maize crop; and

In chapter 3, the BBFs were applied at different doses to an Oxisol and incubated for a period before cultivation of *Urochloa brizantha* for three cycles to evaluate the agronomic efficiency and thereafter, a sequential extraction procedure was used to determine the P distribution among different P pools.

REFERÊNCES

ABDALA, D. B. et al. Surface loading effects on orthophosphate surface complexation at the goethite/water interface as examined by extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. **Journal of Colloid and Interface Science**, New York, v. 442, p. 15-21, March 2015.

ASSOCIAÇÃO NACIONAL PARA A DIFUSÃO DE ADUBOS – ANDA. **Estatísticas Indicadores: Principais Indicadores do Sector de Fertilizantes**. Disponível em:http://www.anda.org.br/index.php?mpg=03.00.00. Acesso 2 jun. 2018.

ARE, K. S. et al. Improving physical properties of degraded soil: Potential of poultry manure and biochar. **Agriculture and Natural Resources**, Bangkok, v. 51, n. 6, p. 454-462, December 2017.

CHAN, K. Y. et al. Agronomic values of green waste biochar as a soil amendment. **Australian Journal of Soil Research**, Collingwood, v. 45, n. 8, p. 629-634, January 2007.

CHIEN, S. H et al. Agronomic and environmental aspects of phosphate fertilizers varying in source and solubility: an update review. **Nutrient Cycling in Agroecosystems**, Dordrecht, v. 89, p.229-255, March 2011.

CHILDERS, D. L. et al. Sustainability Challenges of Phosphorus and Food: Solutions from Closing the Human Phosphorus Cycle. **BioScience**, Washingtonv. 61, n. 2, p. 117-124, February 2011.

CORDELL, D., DRANGERT, J. O., WHITE, S. The story of phosphorus: Global food security and food for thought. **Global Environmental Change**, Oxford, v. 19, n. 2, p. 292-305, May 2009.

DALÓLIO, F. S. et al. Poultry litter as biomass energy: A review and future perspectives. **Renewable and Sustainable Energy Reviews**, Colorado, v. 76, p. 941-949, September 2017.

Glaser, B. et al. The "Terra Preta" phenomenon: A model for sustainable agriculture in the humid tropics. **Naturwissenschaften**, Berlin, v. 88, n. 1, p. 37-41, January 2001.

GLASER, B., LEHMANN, J., ZECH, W. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal - A review. **Biology and Fertility of Soils**, Berlin, v. 35, n. 4, p. 219-230, June 2002.

GONZÁLEZ-PONCE, R., LÓPEZ-DE-SÁ, E. G., PLAZA, C. Lettuce response to phosphorus fertilization with struvite recovered from municipal wastewater. **HortScience**, Alexandria, v.44, p.426-430, April 2009.

HUANG, Y. et al. Biochar and renewable energy generation from poultry litter waste: A technical and economic analysis based on computational simulations. **Applied Energy**, Amsterdam, v. 160, p. 656-663, December 2015.

JOSEPH, S. et al. Shifting paradigms: development of high-efficiency biochar fertilizers based on nano-structures and soluble components. **Carbon Management**, [S.I.], v. 4, n. 3, April 2014.

Lehmann, J. et al. Biochar effects on soil biota - A review. **Soil Biology and Biochemistry**, Elmsford, v. 43, n. 9, p. 1812-1836, September 2011.

LEHMANN, J., STEPHEN, J. **Biochar for Environmental Management: Science, Technology and Implementation**, 2 ed. London: Routledge, 2015. 944 p.

LOPES, A. S.; GUIMARÃES GUILHERME, L. R. A. career perspective on soil management in the Cerrado region of Brazil. **Advances in Agronomy**, Newark, v. 137, n. 1, p. 1-72, 2016.

MAO, X. et al. Phosphorus Availability and Release Pattern from Activated Dolomite Phosphate Rock in Central Florida. **Journal of Agricultural and Food Chemistry**, Washington, v. 65, n. 23, p. 4589-4596, May 2017.

NIU, Y. et al. Phosphorus and magnesium interactively modulate the elongation and directional growth of primary roots in Arabidopsis thaliana (L.) Heynh. J **Journal of Experimental Botany**, Oxford, v. 66, n. 13, 1, p. 3841-3854, July 2015.

NOVAIS, R. F., SMYTH, T. J. **Fósforo em solo e planta em condições tropicais**. Viçosa, MG: UFV/DPS, 1999. 399 p.

NUERNBERG, G. B. et al. Efficiency of basalt zeolite and Cuban zeolite to adsorb ammonia released from poultry litter. **Journal of Environmental Management**, London, v. 183, p. 667-672, December 2016.

PANDIT, N. R. et al. Biochar improves maize growth by alleviation of nutrient stress in a moderately acidic low-input Nepalese soil. **Science of The Total Environment**, Amsterdam, v. 625, p. 1380-1389, June 2018.

REIJNDERS, L. Phosphorus resources, their depletion and conservation, a review. **Resources, Conservation and Recycling**, Amsterdam, v. 93, p. 32-49, December 2014.

ROBERTS, T. L., JOHNSTON, A. E. Phosphorus use efficiency and management in agriculture. **Resources, Conservation and Recycling**, Amsterdam, v. 105, p. 275-281, December 2015.

ROY, E. D. et al. The phosphorus cost of agricultural intensification in the tropics. **Nature Plants**, London, v. 2, n. 43, p. 1-6, April 2016.

SARKAR, A. et al. Polymer coated novel controlled release rock phosphate formulations for improving phosphorus use efficiency by wheat in an Inceptisol. **Soil and Tillage Research**, Amsterdam, v. 180, p. 48-62, August 2018.

SCHMIDT, H. P. et al. Biochar-Based Fertilization with Liquid Nutrient Enrichment: 21 Field Trials Covering 13 Crop Species in Nepal. **Land Degradation & Development**, Hoboken, v. 28, n. 8, p. 2324-2342, November 2017.

SOUSA, D. M. G.; REIN, T.A.; GOEDERT, W. J.; LOBATO, E.; NUNES, R. S. Fósforo. In: PROCHNOW, L.I.; CASARIN, V.; STIPP, S.R. (Ed.) **Boas práticas para uso eficiente de fertilizantes**, volume 1. Piracicaba: IPNI, 2010. p.71-126.

STEINER, G. et al. Efficiency developments in phosphate rock mining over the last three decades. **Resources, Conservation and Recycling**, Amsterdam, v. 105, p. 235-245, December 2015.

VAN DIJK, K. C., LESSCHEN, J. P., OENEMA, O. Phosphorus flows and balances of the European Union Member States. **Science of The Total Environment**, Amsterdam, v. 542, p. 1078-1093, January 2016.

VOCHOZKA, M. et al. Biochar pricing hampers biochar farming. **Clean Technologies and Environmental Policy**, Berlin, v. 18, n. 4, p. 1225-1231, April 2016.

WANG, Y. et al. Phosphorus release behaviors of poultry litter biochar as a soil amendment. **Science of The Total Environment**, Amsterdam, v. 512-513, p. 454-463, April 2015.

WEN, P. et al. Microwave-Assisted Synthesis of a Novel Biochar-Based Slow-Release Nitrogen Fertilizer with Enhanced Water-Retention Capacity. **ACS Sustainable Chemistry & Engineering**, Washington, v. 5, n. 8, p. 7374-7382, June 2017.

WITHERS, P. J. A. et al. Transitions to sustainable management of phosphorus in Brazilian agriculture. **Scientific Reports**, London, v. 8, p.2537, February 2018.

ZHANG, L. et al. Responses of soil microbial community structure changes and activities to biochar addition: A meta-analysis. **Science of The Total Environment**, Amsterdam, v. 643, p. 926-935, December 2018.

SECOND PART – ARTICLES

CHAPTER 1

Co-Pyrolysis of Poultry Litter and Phosphate and Magnesium Generates Alternative Slow-Release Fertilizer Suitable for Tropical Soils

José F. Lustosa Filho[*†], Evanise S. Penido[‡], Patrícia P. Castro[†], Carlos A. Silva[†], and Leônidas C. A. Melo[*†]

[†]Soil Science Department, Federal University of Lavras, Lavras, 37200000 Minas Gerais, Brazil

[‡]Chemistry Department, Federal University of Lavras, Lavras, 37200000 Minas Gerais, Brazil

ABSTRACT: Monoammonium phosphate (MAP), triple superphosphate (TSP), and phosphoric acid (H_3PO_4), with and without the addition of magnesium oxide (MgO), were mixed with poultry litter (PL) to produce biochar-based fertilizers (BBFs). This is a novel approach aiming to add value to PL residue and to increase P use efficiency in acidic tropical soils. Samples of BBFs were assessed by P-release kinetics in water, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and a bioassay with maize in a greenhouse using a clayey Oxisol. Addition of MgO reduced the kinetics of P released from BBFs impregnated with all P sources. XRD analysis showed the formation of low-solubility $Ca_2P_2O_7$ and $Mg_2P_2O_7$ compounds, which is supported by P-O-P or P=O stretching observed in the FTIR spectra. The MgO-treated BBFs increased shoot

dry matter production compared to the control, but were inferior when compared to TSP in the short term. The slow release of P and the alkaline reaction of the BBFs show great potential for these materials to be used as enhanced P fertilizers in tropical soils.

Keywords: Compound biochar; Impregnation; Oxisol; P use efficiency; P-release kinetics

Graphical abstract
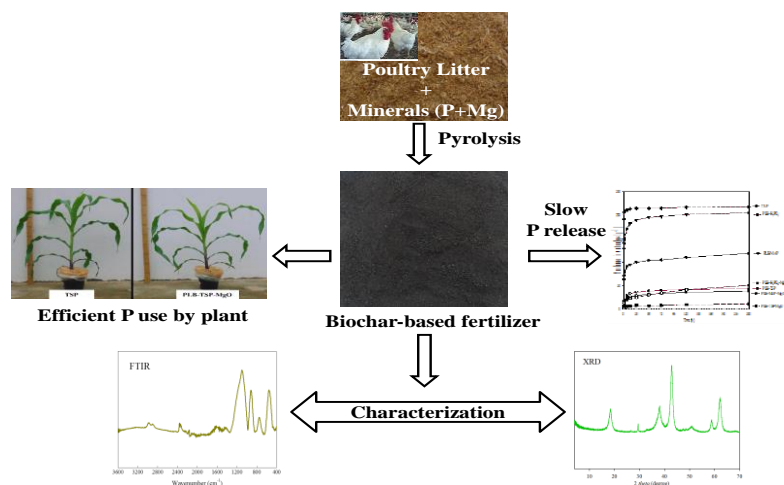
Synopsis: New approach to produce biochar-based fertilizers aiming to reduce water-soluble phosphorus (P) and increase P use efficiency in tropical soils.

INTRODUCTION

Phosphorus (P) is an essential, finite, and nonrenewable resource. The main source of P for phosphate fertilizer production is phosphate rock (PR). The vast majority of phosphate fertilizers used in Brazil and worldwide is acidified PR that generates highly water-soluble P.[1] After application of this type of fertilizer, the P content in the soil solution is rapidly increased, favoring P leaching in sandy soils[2]

and P fixation in acidic and highly weathered soils, such as those prevailing in Brazil and tropical regions.[3] Phosphorus fixation represents a problem in Brazil's soils due to intensive agriculture, and soils can impose a "P tax" to improve plant nutrition and increase yields.[4] Therefore, P applied via fertilizer and absorbed by the crop in the first growing cycle is usually in the order of 10-20% of the total applied P.[5] Since the efficiency of phosphate fertilizers is very low,[6] it is essential to search for alternatives aiming at optimizing the use of P sources or reducing P losses (precipitation, adsorption, and ultimately "fixation") in agricultural systems,[3,7] either by the development of more efficient P fertilizers or by the use of alternative P sources such as organic wastes. Among organic residues, poultry litter (PL) is produced in massive amounts in Brazil and worldwide and is not always properly disposed. Soil application of PL is the most common disposal practice, but its overapplication can cause P losses, posing a risk to the environment.[8] Therefore, recycling of P and other nutrients from PL is an alternative to prevent P losses and increase its fertilizer value.

The production of biochar, which is the solid product obtained from pyrolysis of biomass under low or limited oxygen conditions,[9] can be a promising option for PL reuse and recycle. Soil application of biochar can store more carbon (C) and improve soil fertility, among other benefits.[10] However, high application rates are required when biochar is used as a soil conditioner, which makes biochar unfeasible from a large-scale perspective.[11] Therefore, enrichment of biomass (e.g., PL) with minerals is being proposed as an alternative to produce biochar-based products with potential to be used as slow-release and high-agronomic-performance fertilizers at feasible rates.[10] Phosphate impregnation in the biomass prior to pyrolysis has been shown to reduce C loss during pyrolysis, increase biochar yield, improve the oxidation stability, and reduce the microbial mineralization.[12] However, the low pH value of biochar impregnated with acidulated phosphates could limit its application in acidic soils.[12] Nevertheless,

mixing the feedstock with an alkaline source (e.g., MgO) in addition to the acid phosphate source prior to pyrolysis may be a viable alternative to raise the pH and enrich the biochar with phosphate and magnesium, which has a synergistic effect on P acquisition,[13] root development, and plant growth.[14]

Several researchers have shown the effect of pyrolysis on P transformations and P bioavailability in poultry litter and other feedstocks.[15-18] However, little is known on the pyrolysis of phosphate-impregnated materials.[10] Thus, the knowledge of the amount of available P in BBFs (biochar-based fertilizers) is essential for determining the doses of biochar to be applied, reaching the crop's requirements.[19] Kinetics studies have been used for evaluating P stability in BBFs and their possible slow-release of P to the soil.[10] In addition to kinetics, studies involving plant growth coupled with characterization techniques (e.g., FTIR and XRD) are essential to characterizing the surface functional groups,[20] crystallinity of minerals contained in biochars,[21] and the effectiveness of BBFs as P fertilizers. Moreover, the impregnation of acid phosphate sources with MgO aiming to produce an enhanced biochar to be used as a fertilizer for tropical soils is a novel and promising approach to increase P use efficiency by plants while at the same time incorporating stable C, increasing available Mg and correcting soil acidity.

In this study we aimed (i) to evaluate the effect of PL pretreatment with MAP, TSP, and H_3PO_4, with and without MgO addition, on the release of P from biochars; (ii) to investigate changes in P forms after conversion of feedstock into biochar; and (iii) to evaluate the BBF agronomic performance as compared to that of a soluble P fertilizer (TSP) supplied to maize grown in an Oxisol under greenhouse conditions.

MATERIALS AND METHODS

Feedstock and Mineral Additives

Poultry litter was collected from a farm near Lavras, Minas Gerais, Brazil (915 m altitude, 21°13′34″ S and 44°58′31″ W). Samples were air-dried at room temperature, ground to pass through a 20-mesh sieve (1.00 mm), and mixed with MAP ($NH_4H_2PO_4$), TSP [$Ca(H_2PO_4)_2$], and H_3PO_4, with and without MgO addition. All materials were mixed in powder form, except H_3PO_4, which was mixed as a solution. Thereafter, all mixtures were moistened to ensure greater uniformity. Phosphates and MgO were mixed to achieve a P/Mg molar ratio of 1:1, and the ratio of poultry litter/phosphate source was 1:0.5 (w/w), on the basis of previous studies[10, 12, 22] to ensure that P concentrations were high enough to increase the agronomic value of the produced fertilizer. After 16 h of resting in aqueous medium, the pretreated mixtures were oven-dried at 60 °C to a constant mass prior to pyrolysis.

Preparation and Production of Biochar-Based Fertilizers

The pretreated samples were placed in a top-opening muffle furnace, and pyrolysis was performed by raising the temperature up to 500 °C at a heating rate of 10 °C min^{-1}, maintaining the target temperature for 2 h to provide enough time for complete carbonization.[12] Figure S1 shows an illustration of the system. Briefly, the pretreated dry samples were placed into steel cylinders (10.6 cm diameter and 42 cm height), which was capped at both ends with a hole in the lid to enable the release of gases during pyrolysis. The cylinders were placed into an electrical muffle furnace, which was adapted to connect to the condenser through an iron tube. Noncondensable gases were released to the atmosphere, and volatiles were condensed as bio-oil. An air-free environment was achieved inside the cylinders during pyrolysis, as their lid and the furnace door were airtight, and the

continuous emission of pyrolysis volatiles prevented air from diffusing in through the hole in the lid.

The produced biochars were identified as follows: PLB-MAP = poultry litter biochar + MAP; PLB-TSP = poultry litter biochar + TSP; PLB-H_3PO_4 = poultry litter biochar + phosphoric acid; PLB-MAP-MgO = poultry litter biochar + MAP + MgO; PLB-TSP-MgO = poultry litter biochar + TSP + MgO; and PLB-H_3PO_4-MgO = poultry litter biochar + phosphoric acid + MgO.

Characterization of Biochar-Based Fertilizers

Electrical conductivity (EC) and pH were obtained in triplicate, using 1.0 g of biochar in 20 mL of deionized water.[23] The mixture was shaken for 1.5 h in an orbital shaker prior to pH measurement (S70 SevenMulti of Mettler Toledo, Columbus, OH) that was previously calibrated with standard solutions. The EC was determined in an S70 SevenMulti conductivity meter that was previously calibrated with standard solutions of EC equal to 1.4 dS m^{-1}.

The cation-exchange capacity (CEC) of the biochars was determined by the ammonium acetate displacement method modified in ref 24. Briefly, 0.2 g of biochar was weighed and placed in a suitable vacuum-filtering carrier containing a 0.45 μm filter. Biochar samples were then washed five times with 20 mL of deionized water to remove soluble ions. The samples were then washed five times with 20 mL of sodium acetate (1 mol L^{-1}, pH 7) to saturate the exchange sites with Na$^+$. Following the previous step, biochar samples were washed five times with ethanol to remove excess Na$^+$. Finally, Na$^+$ ions were displaced using five washes of 20 mL of ammonium acetate (1 mol L^{-1}, pH 7) and analyzed by flame photometry (Digimed DM 61, São Paulo, Brazil).

Biochar samples were analyzed for P colorimetrically,[25] and for Ca and Mg contents using ICP-OES after ashing for 8 h at 500 °C in a muffle furnace, followed by nitric acid digestion at 120 °C and H_2O_2 addition in the digestion final

step, to oxidize organic carbon.[26] Finally, the digested material was dissolved in 20 mL of 5% (v/v) HCl solution using sonication. This procedure ensures the highest recovery rate of nutrients in biochar samples.[26]

Kinetics of P Release from Biochars

The kinetics of P release was performed according to ref 21. Briefly, 1.0 g of biochar-based fertilizers sample was mixed with 200 mL of deionized water and then shaken in a reciprocating shaker at 120 rpm for up to 240 h at 25 °C. The suspensions (5 mL) were collected at 0.25, 0.5, 1, 6, 12, 24, 48, 72, 120, and 240 h. Since the solids in the suspension were rapidly separated from the liquid phase, the solid mass loss was negligible over sampling times. After passing through 0.45 mm Millipore filters, the solutions were analyzed for P, Ca, and Mg by ICP-OES (Spectro Analytical Instruments, Kleve, Germany). The kinetics of P release was determined as "changes in P concentrations" over time. The release of P as a function of sampling time was fitted using the following equations:[21, 27]

Parabolic diffusion model
$$\frac{K_t}{K\infty}=a\text{-}bt^{0.5} \quad (1)$$

Elovich equation
$$K_t=a\text{-}b\ln(t) \quad (2)$$

First order
$$\ln(K\infty\text{-}K_t)=a\text{-}b\,t \quad (3)$$

Linear model
$$K\infty\text{-}K_t=a\text{-}b\,t \quad (4)$$

Here, the terms are as follows: K_t is the cumulative P released at time t; a is P initially released; b is P-release constant; and $K\infty$ is the maximum P released. These mathematical models were tested and mathematically adjusted to a P kinetics data set on the basis of their coefficient of determination (R^2) and standard error of the estimate (SE), calculated by the following equation:

$$SE=\left[\frac{\sum(q\text{-}q^*)^2}{(n\text{-}2)}\right]^{1/2} \tag{5}$$

where q and q^* represent the measured and predicted amounts of released P at time t, respectively, and n is the number of data points evaluated.

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra were recorded on a Digilab Excalibur spectrometer with a spectral range 4000-400 cm^{-1}. Biochar samples were ground to a powder, and the FTIR spectra with a resolution of 4 cm^{-1} were collected over an average of 32 scans.

X-ray Diffraction (XRD)

For the identification of possible structural changes, the biochar samples (before and after kinetics trials) were characterized by XRD. Briefly, the samples were air-dried and ground to pass through a 100-mesh nylon sieve. The analyses were carried out on a Shimadzu XRD-6000 instrument, using a graphite crystal monochromator to select the Cu Kα1 radiation source at λ = 1.5406 Å, with a step size of 0.02 s^{-1}. The potential of the source was 40 kV, and the current was 40 mA. A scanning speed with a step of 0.01° 2θ every 10 s was employed. The X-ray diffraction patterns were recorded from 4° to 70° 2θ. The resulting diffractograms were interpreted with the aid of the Mineralienatlas and Webminerals databases.[28, 29]

Maize Growth Conditions

The experiment was carried out under greenhouse conditions aiming for evaluating the agronomic efficiency of the produced BBFs. Soil samples were collected from the botton layer (40-60 cm) of an Oxisol (Rhodic Hapludox-RH)

in Lavras, Minas Gerais, Brazil (915 m altitude, 21°13′34″ S and 44°58′31″ W). Samples were air-dried and passed through a 2 mm sieve for chemical and physical soil characterization. The Oxisol was characterized by a very low available P concentration (0.41 mg dm^{-3}, Mehlich-1 soil test), high clay content (64%), and pH_{water} of 4.8; Ca^{2+} and Mg^{2+} concentrations were 0.24 and 0.10 $cmol_c$ dm^{-3} ($cmol_c$ dm^{-3}, charge concentration units; KCl 1 mol L^{-1} extractor), respectively, and soil organic C was 11.8 g kg^{-1}.[30] Soil (1.5 dm^3) was placed into clean and sterilized plastic bags and mixed with $CaCO_3$ + $MgCO_3$ at a Ca/Mg molar ratio of 3:1, aiming to increase the soil base saturation to 70%. Soil was wetted to 80% of the field capacity (on the basis of previous tests) and incubated for 30 days. In sequence, soil was air-dried, homogenized, and fertilized with the following nutrients: N, K, S, Zn, Mn, Fe, Cu, B, and Mo, which were applied at the rates of 100, 100, 40, 4.0, 3.66, 1.55, 1.33, 0.81, and 0.15 mg dm^{-3}, respectively,[31] to ensure a proper fertility condition for optimum maize growth in pots. Soil and fertilizers were thoroughly mixed before maize sowing, aiming to achieve 200 mg dm^{-3} of P soluble in neutral ammonium citrate + water (NCA + H_2O), on the basis of the previous characterization of the BBFs.

The experiment was carried out in a randomized block design with four replicates. A control without P addition was included. Three seeds of maize (*Zea mays*) were planted in each pot containing 1.5 dm^3 of soil and thinned after 7 days to one plant, which was grown during 40 days. All of the pots received an additional application of N and K fertilizer (200 mg dm^{-3}) via fertigation at 10 and 25 days after planting. Maize shoot was harvested, washed with distilled water, dried at 65 °C until weight stabilization (≈72 h), weighed, and milled for chemical analysis. Approximately 150 cm^3 of soil was collected after homogenization for chemical analysis. Shoot tissues were digested in a block digestion system using concentrated nitric-perchloric acid solution, and P contents were measured by colorimetry, following analytical procedures described in ref 25. Accumulation of

P in the maize shoot was estimated by multiplying the P content with the respective dry mass yield. Soil-available P after maize cultivation was extracted using the anion-exchange resin,[32] followed by colorimetric determination.[25] The anion-exchange resin is a positively charged spherical polymer that is supposed to extract only plant-available P forms found in soil.

Statistical Analysis

The greenhouse experiment data were submitted to the analysis of variance (ANOVA), and the means were grouped by the Scott-Knott test ($P < 0.05$) using the SISVAR software.[33] Error bars were used to represent the standard deviations of the treatment mean replicates.

RESULTS AND DISCUSSION

Properties of Biochar-Based Fertilizers

The addition of different sources of phosphate (with and without MgO) in the process of biochar production changed BBF properties (Table 1). The pH value of unmodified PLB was 11.1, while PL impregnation with MAP, TSP, and H_3PO_4 reduced the BBF pH to 2.8, 4.6, and 2.0, respectively (Table 1). Addition of MgO increased the pH of BBFs to 6.9, 9.1, and 6.1 for MAP, TSP, and H_3PO_4, respectively. The acidic nature of phosphate sources (H_3PO_4 and MAP) without addition of MgO resulted in biochar fertilizers with low pH (2-2.8), which is in line with results previously reported.[12] The impregnation of PL with TSP, and mainly with MgO, decreased the EC, which was markedly increased when PL was mixed with H_3PO_4 before the BBF production, since EC was elevated from 5.5 dS m^{-1} with PLB to 14 dS m^{-1} with PLB-H_3PO_4 (Table 1). It must be highlighted that EC strongly decreased with the addition of MgO, mainly for PLB-H_3PO_4-MgO, which presented the lowest EC value (0.4 dS m^{-1}). EC estimates the amount of total dissolved salts or the total amount of dissolved ions in the water.[34] EC is also

regulated by the levels of H^+ and OH^- in the matrix evaluated. Therefore, the reduction of EC with the addition of MgO in the biochar samples is probably related to the decrease of the soluble salt content and reduced concentration of H^+.

Table 1. Selected Properties[a] of the Biochar-Based Fertilizers

fertilizer	pH	EC	CEC	C	P_{total}	Ca_{total}	Mg_{total}
		-dS m^{-1}-	cmol$_c$ kg^{-1}	----%----	-------------g kg^{-1}---------------		
PLB	11.1 ± 0.01	5.5 ± 0.40	16.3 ± 1.5	47.9 ± 0.01	24.4 ± 0.5	46.7 ± 0.8	13.7 ± 0.1
PLB-MAP	2.8 ± 0.01	5.1 ± 0.07	23.6 ± 2.2	31.4 ± 0.4	139 ± 16	30.0 ± 0.6	7.76 ± 0.3
PLB-TSP	4.6 ± 0.01	1.8 ± 0.04	12.4 ± 2.2	24.1 ± 0.2	118 ± 8.5	121 ± 0.5	8.09 ± 0.1
PLB-H$_3$PO$_4$	2.0 ± 0.03	14 ± 0.39	15.2 ± 0.6	27.1 ± 1.3	206 ± 17	25.0 ± 1.3	5.47 ± 0.0
PLB-MAP-MgO	6.9 ± 0.04	0.9 ± 0.27	23.3 ± 2.4	21.4 ± 0.9	135 ± 19	26.0 ± 0.3	72.6 ± 1.3
PLB-TSP-MgO	9.1 ± 0.04	1.1 ± 0.08	17.5 ± 3.5	21.2 ± 0.3	124 ± 5.6	102 ± 1.0	69.5 ± 0.9
PLB-H$_3$PO$_4$-MgO	6.1 ± 0.02	0.4 ± 0.02	21.6 ± 4.0	19.0 ± 0.1	162 ± 16	18.9 ± 0.3	98.0 ± 0.9

[a]Values are mean (n = 3) ± standard deviation; EC, electrical conductivity; CEC, cation-exchange capacity; PLB, poultry litter biochar.

Cation-exchange capacity of the biochars varied as a function of P sources mixed with PL. When MAP was added to PL, with or without MgO addition, CEC was increased from 16 cmol$_c$ kg^{-1} to nearly 23 cmol$_c$ kg^{-1}, while in the PLB-TSP CEC was slightly reduced to nearly 12 cmol$_c$ kg^{-1}. The formation of oxidized functional groups on biochar particles might increase CEC.[35] With the use of FTIR (discussed later), it was possible to observe the presence of C-O stretching and OH vibration for the PLB-MAP and PLB-MAP-MgO, respectively, which are most likely responsible for the increased CEC of these biochars. The presence of inorganic phosphate groups co-pyrolyzed with PL may also protect chemical organic groups and their negative charges from thermal degradation during the pyrolysis process.[22] The increase in CEC of some BBFs indicates that some P additives may be used to protect organic compounds during pyrolysis, and such compounds are responsible for the generation of negative charges.

The C content of the BBFs was relatively low (ranging from 19.0% to 31.4%), which may be explained by the dilution effect of mixing inorganic sources with PL (Table 1). The addition of phosphate significantly increased the P content in the biochars, reaching a maximum of 206 g kg^{-1} of P in sample PLB-H$_3$PO$_4$ (Table 1). This P content is equivalent to that obtained in the TSP, proving the phosphate

fertilizing potential of these BBFs. Contents of P found in the BBFs formulated in this study are higher than those verified in other biochar samples produced in ref 12 which also impregnated feedstock (wheat straw) with H_3PO_4 prior to pyrolysis and obtained a P content equal to 125 g kg^{-1}. Calcium contents were also increased in the biochars containing TSP (calcium monophosphate), and Mg content was increased up to 7 times when MgO was added (Table 1). The PLB-TSP-MgO has alkaline pH (9.1) and 102 g kg^{-1} of Ca, 69.5 g kg^{-1} of Mg, and 127 g kg^{-1} of P, showing the potential of this material as fertilizer and for soil acidity neutralization.

Kinetics of P Release

The results of P-release dynamics from the impregnated biochars as well as from TSP are shown in Figure 1. Overall, P release from BBFs increased over sampling time, but drastic differences were observed among the sources of P added to the feedstock, especially in samples treated with MgO. As expected, soluble TSP released more P when compared to all other BBFs. About 208 g kg^{-1} of P was leached from TSP after 1 h of agitation, which represents about 95.8% of the total P in the fertilizer. The kinetics of P released from TSP was better fitted to the Elovich equation ($R^2 = 0.77$; Table 2). However, such a fit does not provide enough information on the P-release mechanism of this fertilizer. The initially fast P release within the first hour for TSP was probably attributed to the ion desorption process and/or dissolution of some crystalline phosphates such as [$Ca(H_2PO_4)_2 \cdot H_2O$], as observed in the XRD pattern (Figure S3). Fast release of TSP is a signal that P from this source is readily available to plants. However, rapidly released phosphate may be strongly adsorbed by Fe and Al oxides, which causes the high P fixation capacity in tropical soils.[36]
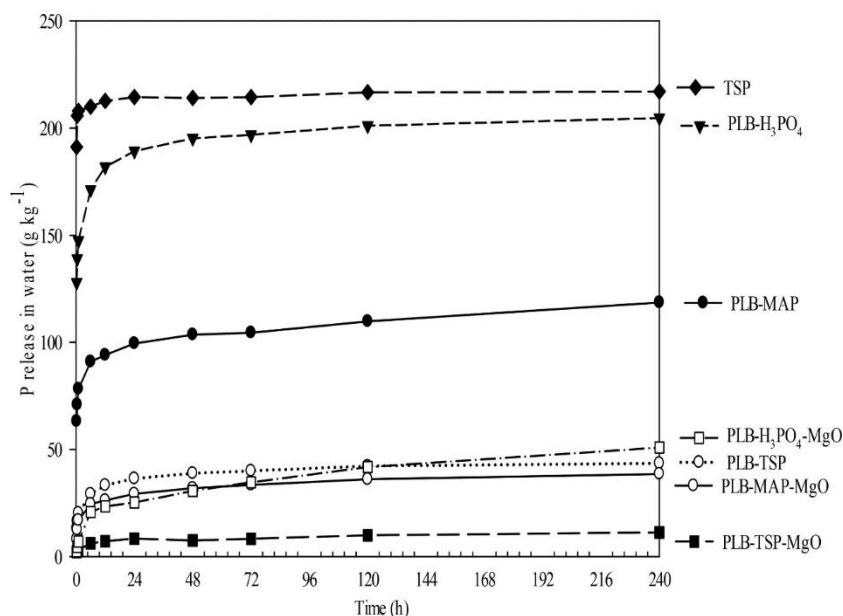
Figure 1. Kinetics of P release in water from biochar-based fertilizers and triple superphosphate (TSP).

The Elovich model was also the most suitable to describe and explain the P cumulative release over time by the BBFs. Overall, the kinetics parameters (R^2 and b) obtained from the Elovich model were higher when compared to those of the other tested models (Table 2). Despite releasing different amounts of P, BBFs exhibited similar P-release patterns. As shown in Figure 1, practically all water-extractable P was released in the first 24 h, and the accumulated amounts of released P were kept constant thereafter. High amounts of P from PLB-H_3PO_4 (147 g kg^{-1}) and PLB-MAP (78.2 g kg^{-1}) were released at the first hour, which represented 71.4% and 56.3% of the total P of each source, respectively. In fact, the kinetics of P release from PLB-H_3PO_4 is close to that of TSP regarding P release over time.

The Elovich model is an empirical equation based on the influences of P desorption from the sample.[37, 38] The constants a and b in the Elovich equation can

be regarded as the initial reaction rate and the desorption constant, respectively.[39] For PLB-H$_3$PO$_4$ and PLB-MAP, P release was initially controlled by a fast dissolution to form a high-concentration solution, while the other biochars were controlled by a slow diffusion process.

Table 2. Coefficient (R^2) of the Examined Models and the Rate Constant (b) for P-release Kinetics from the Biochar-Based Fertilizers and TSP

Fertilizer	Kinetic models							
	zero order		first order		parabolic diffusion		Elovich	
	R^2	b	R^2	b	R^2	b	R^2	B
PLB-MAP[a]	0.60	-0.18	0.95	-0.01	0.82	0.03	0.99	7.36
PLB-TSP	0.48	-0.10	0.79	-0.01	0.75	0.04	0.99	4.60
PLB-H$_3$PO$_4$	0.45	-0.24	0.88	-0.02	0.71	0.02	0.98	11.5
PLB-MAP-MgO	0.55	-0.10	0.90	-0.01	0.79	0.05	0.99	4.27
PLB-TSP-MgO	0.62	-0.03	0.79	-0.01	0.83	0.05	0.96	1.28
PLB-H$_3$PO$_4$-MgO	0.74	-0.18	0.98	-0.01	0.93	0.06	0.96	6.60
TSP	0.30	-0.30	0.57	-0.01	0.49	0.01	0.77	2.82

[a]PLB, poultry litter biochar.

A slower rate constant indicates gradual release of a nutrient. Clearly, P release from biochar impregnated with MgO was significantly lower than those from biochars not treated with MgO (Table 2). The P-release pattern already mentioned confirms that the formulated biochars are fertilizers with the main function of gradually releasing P into soil. Ideally, BBFs would have a longer P-release time and slower release rate within the expected time frame than general soluble phosphate fertilizer.[37] This slow-release characteristic may result in more efficient uptake of P by plants if they meet crop demands. On the other hand, highly water-soluble P fertilizers when incorporated into the soil release most P at once, which if not absorbed by plants might rapidly be adsorbed onto soil particle surfaces[3] causing a low residual effect. In this sense, the more gradual release of P from the BBFs could provide a longer-term source of P for crop growth as compared to the soluble forms of P. The potential of modified biochar to be used as a slow-release

fertilizer was also observed when bone meal was impregnated with TSP.[10] According to these authors, the release of P from TSP- and BM-composite biochars within 120 h was about 20.0 and 0.30 mg g^{-1}, respectively, which was much lower than the kinetics of P release verified for TSP and BM alone.

The percentage of the total P release of each BBF after 240 h is shown in Figure 2. Samples of PLB-H$_3$PO$_4$, PLB-MAP, and PLB-TSP released 99.8%, 86.0%, and 37.0% of total P to water, respectively. In contrast, when MgO was mixed with PL and P sources, P released over time was drastically reduced to 31.6%, 28.9%, and 9.1% from PLB-H$_3$PO$_4$-MgO, PLB-MAP-MgO, and PLB-TSP-MgO, respectively. This reduction in the release of P, mainly after the addition of MgO, is due to the formation of less-soluble phosphorus compounds, for example, magnesium pyrophosphate (Mg$_2$P$_2$O$_7$) in PLB-H$_3$PO$_4$-MgO and hydroxyapatite [Ca$_{10}$(OH)$_2$(PO$_4$)$_6$] in PLB-TSP-MgO, as can be seen in Figure 3b. According to ref 40, the gradual precipitation of Mg$_2$P$_2$O$_7$ on the biochar surface causes a decrease in the release of phosphate.
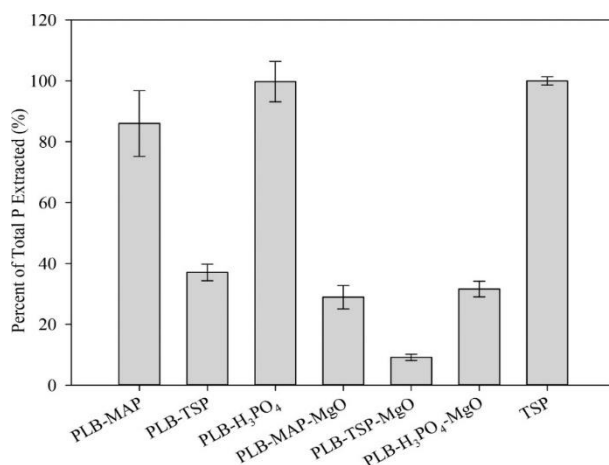

Figure 2. Released phosphate as a percentage of the total phosphorus mass in biochar-based fertilizers and TSP extracted by water. Values refer to the mean (n = 3) ± standard deviation.

The cumulative release kinetics of Ca and Mg were similar to the behavior of P (Figure S2). The samples of PLB-MAP and PLB-H$_3$PO$_4$ released the highest

amounts of Ca, reaching 90% and 84% of total Ca, respectively, while for PLB-TSP only 9.4% of the total Ca was released. With the addition of MgO, there was a reduction in Ca release, as was also observed for P. Regarding the kinetics of Mg release, 100%, 61.5%, and 48.8% of total Mg was released from PLB-H_3PO_4, PLB-MAP, and PLB-TSP in water, respectively. In the BBFs impregnated with MgO, the release of Mg was less than 30% of the total Mg. Decrease in the release of Mg as well as P confirms the formation of low-solubility P compounds such as magnesium pyrophosphate as observed in the XRD spectrum (Figure 3b), which are of low water solubility but are proton-releasable,[37] reinforcing the claim that these biochars formulated in this study have a high potential to act as slow P-release fertilizers.

X-ray Diffraction Characterization

XRD analysis of the mineral additives, PLB, and BBFs before and after release kinetics of P is shown in Figure 3a,b and Figure S3. Sylvite (KCl) and Calcite ($CaCO_3$) were identified in PLB at 28.5° and 29.5° 2θ, respectively. The XRD spectra of MgO showed several peaks (Figure S3), indicating the presence of mineral crystals such as periclase (MgO) and brucite (MgO·H_2O). For MAP, all peaks corresponded to biphosphammite [$(NH_4, K)H_2PO_4$]. The differences in peak amplitude can be attributed to the different sizes and orientation of the powdered grains. In the case of TSP fertilizer before kinetics, peaks of brushite [$Ca(H_2PO_4)_2·(H_2O)$], garronit [$Ca_3(Si, Al)_{16}O_{32}·13H_2O$], crandallite [$CaAl_3(PO_4)_{1.5}(OH)_5·H_2O$], and fluorapatite [$Ca_5(PO_4)_3F$] were observed at 2θ angles of 7.6°, 28.1°, 30.5°, and 31.6° (Figure 3b). After kinetics, it was still possible to observe the presence of all the mentioned minerals, with the inclusion of berlinite ($AlPO_4$; 2θ angles of 27.7°). However, brushite was dissolved in water, leaving insoluble forms such as fluorapatite.
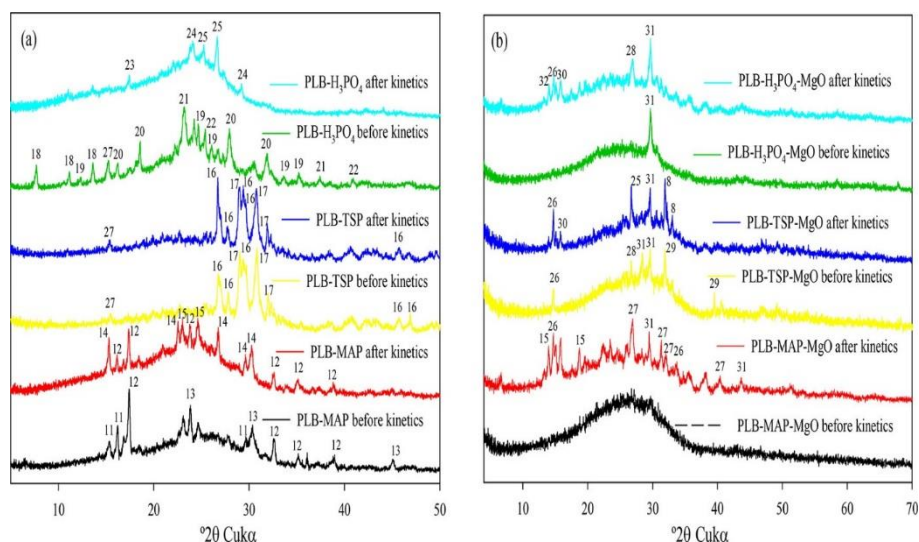
Figure 3. X-ray diffraction analysis of biochar-based fertilizers without MgO (a) and with MgO (b) before and after release kinetics of P. Labels are as follows: 8, fluorapatite; 11, ammonium imide phosphate hydrate; 12, struvite-K; 13, archerite; 14, tinticite; 15, variscite; 16, calcium pyrophosphate; 17, potassium phosphate hydrate; 18, heulandite; 19, althausite; 20, calcium hydrogen pyrophosphate; 21, farringtonite; 22, monetite; 23, ammonium fluoride phosphate; 24, silicon phosphate; 25, augelite; 26, bassanite; 27, phosphorrosslerite; 28, magniotriplite; 29, hydroxyapatite; 30, hydroxylwagnerite; 31, magnesium pyrophosphate; and 32, dypingite.

In the PLB-MAP samples before the kinetics study, the 2θ angle peaks of 15.3°, 17.4°, and 23.8° were recorded for ammonium imide phosphate hydrate $[(NH_4)_4P_2O_6NH\cdot 3H_2O]$, struvite-K $[KMg(PO_3)_3]$, and archerite $[(K_{0.78}(NH_4)_{0.22})(H_2PO_4)]$, respectively (Figure 3a). After kinetics, tinticite $[Fe_4(PO_4)_3(OH)_3\cdot 5H_2O]$, variscite $[Al(PO_4)\cdot 2H_2O]$, and struvite-K were observed at 2θ angle peaks of 15.3°, 26.8°, and 17.4°, respectively. It is possible to observe that the struvite-K remains after the kinetics study, where samples were continuously shaken with deionized water, because of a slow-P-release-rate characteristic of this mineral.[41]

The 2θ angle peaks for bassanite ($CaSO_4 \cdot 0.5H_2O$) at 15.4°, calcium pyrophosphate ($Ca_2P_2O_7$) at 26.7°, and potassium phosphate hydrate ($K_5P_3O_{10}$)·$4H_2O$ at 29.0° were observed in PLB-TSP before and after release kinetics of P, as shown in Figure 3a. Impregnated pine tree sawdust and switchgrass with TSP also showed by XRD analysis that $Ca(H_2PO_4)_2$, which is the main component of TSP, decomposed into insoluble calcium pyrophosphate ($Ca_2P_2O_7$).[10] Formation of insoluble P compounds explains the low percentage of phosphorus released in PLB-TSP, as shown in Figure 1. The peaks at 7.7°, 12.3°, 12.3°, 23.2°, 27.9°, and 30.6° were observed for heulandite [$Ca_{4.52}Al_{9.04}Si_{26.96}O_{72} \cdot (13.4H_2O)$], althausite [$Mg_4(PO_4)_2(OH)_{0.37}F_{0.25}O_{0.19}$], farringtonite [$Mg_3(PO_4)_2$], calcium hydrogen pyrophosphate [$Ca_3(HP_2O_7)_2$], and monetite ($CaHPO_4$) in PLB-H_3PO_4 before kinetics, respectively (Figure 3a). After kinetics, the soluble forms of P (althausite, farringtonite, and monetite) were not detected in the PLB-H_3PO_4, possibly because of their complete dissolution, as shown in Figure 1. The 2θ angle peaks of ammonium fluoride phosphate [$(NH_4)_2P_2O_5F_2$] at 17.4°, silicon phosphate ($SiO_2P_2O_5$) at 24.1°, and augelite [$Al_2(PO_4)(OH)_3$] at 25.3° were observed after the PLB-H_3PO_4 kinetics (Figure 3a).

The XRD spectrum of PLB-MAP-MgO before kinetics did not present a regular and continuous background line, probably because of unidentified minerals or impurities found in samples.[42] Thus, it was not possible to identify some peaks (Figure 3b). After kinetics, the angles of 14.7°, 18.7°, 29.7°, and 31.4° were observed for bassanite, variscite, magnesium pyrophosphate ($Mg_2P_2O_7$), and phosphorrosslerite ($MgHPO_4 \cdot 7H_2O$), respectively (Figure 3b). For PLB-TSP-MgO before the kinetics, the 2θ angle peaks of bassanite at 14.7°, magniotriplite [$Mg_2(PO_4)F$] at 26.7°, magnesium pyrophosphate at 29.7°, and hydroxyapatite [$Ca_{10}(OH)_2(PO_4)_6$] at 31.9° were observed, as shown in Figure 3b. After kinetics, new peaks of bassanite, hydroxylwagnerite [$Mg_2(PO_4)(OH)$], augelite, magnesium pyrophosphate, and fluorapatite were observed at 2θ angles of 14.7°,

15.8°, 26.7°, 29.7°, and 31.9°, respectively (Figure 3b). In particular, PLB-H_3PO_4-MgO before kinetics showed only one peak that was identified as magnesium pyrophosphate (29.7°, 2θ), while after kinetics dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$], bassanite, hydroxylwagnerite, magniotriplite, and magnesium pyrophosphate at 2θ angle peaks of 14°, 14.7°, 15.8°, 26.9°, and 29.7° were identified, respectively.

The impregnation of poultry litter with MgO promoted the formation of insoluble P compounds, such as magnesium pyrophosphate. This explains the reduced P release observed in Figures 1 and 2. Thereby, the primary reason for the decrease in P release is the precipitation of P with Ca and Mg that were added by the sources of P and MgO such as $Ca_2P_2O_7$ and $Mg_2P_2O_7$, which are less soluble minerals than monocalcium phosphate ($Ca(H_2PO_4)2 \cdot H_2O$).[40, 43]

FTIR Spectrum Features

The FTIR spectra of raw poultry litter, PLB, and BBFs are shown in Figure 4. The broad region at 3330 cm^{-1} observed in the poultry litter probably corresponds to H_2O stretching since it disappeared in the biochars, while in many cases it also may correspond to the N-H stretching vibration in amino compounds.[44, 45] An intense peak at 2979 cm^{-1} was observed in the PLB, PLB-MAP-MgO, and PLB-TSP-MgO, which is an indicator of aliphatic C-H stretching.[46] The peaks at 2920 cm^{-1} correspond to asymmetric C-H stretching vibrations in aliphatic compounds.[47] The P-H organophosphorus (2353 cm^{-1})[48] peak remains almost unchanged in all samples, while the peak around 1645 cm^{-1}, which corresponds to the C-C stretching vibration in aromatic compounds,[49] and at 1620 cm^{-1}, aromatics, COO[-], ketones, and N-H,[45] disappears in PLB and in their based fertilizers. Such losses of chemical groups at 1620-1645 cm^{-1} are expected because of thermal degradation of chemical groups in raw feedstock during the pyrolysis process at 500 °C.
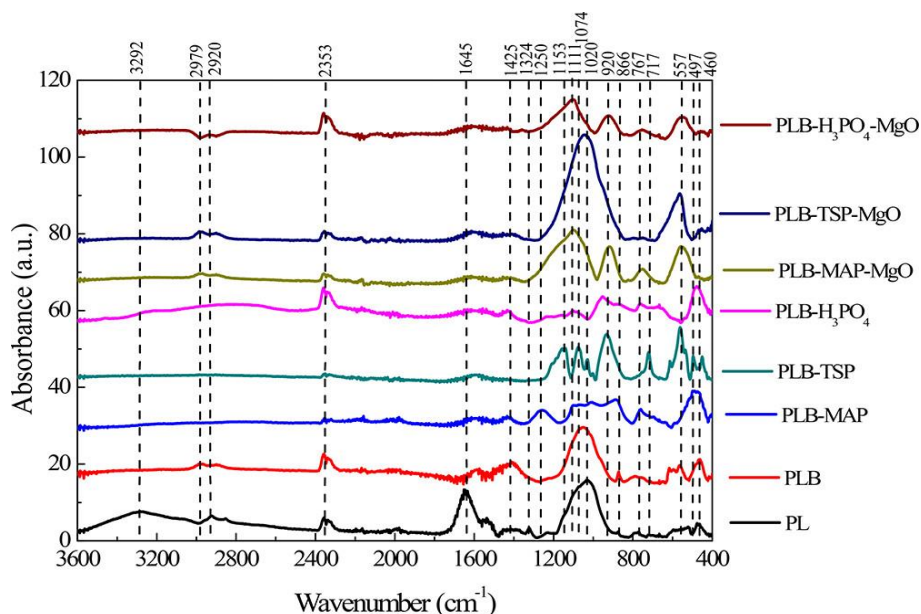
Figure 4. Fourier transform infrared spectroscopy (FTIR) spectra and key spectral bands in poultry litter (PL), poultry litter biochar (PLB), and biochar-based fertilizers.

The strong peak for PLB at 1435 cm^{-1} can be attributed to carbonates CO_3^{2-}[50] which is in accordance with the XRD spectrum in Figure S3, where $CaCO_3$ was found in PLB. No carbonate spectral bands were identified in the spectra of biochars impregnated with MgO. The peak around 1324 cm^{-1} corresponds to aromatic amines [C-N stretching], and assignments at 1250 and 1153 cm^{-1} are linked to C-O stretching.[47] The peak at 1111 cm^{-1}, which was observed only in PLB-MAP-MgO and PLB-H$_3$PO$_4$-MgO, corresponds to OH vibration.[51] On the other hand, the peak at around 1000 cm^{-1} is attributed to the stretching and bending vibration of Mg-OH.[52] The spectral region of 1150-1010 cm^{-1} peaks is attributed to polysaccharides, alcohols, and phosphates.[45]

Compounds of phosphates were observed in the region below 1100 cm^{-1} where band intensities become more evident. The peak at 1066 cm^{-1} (ionic bond P$^+$-O$^-$ in acid phosphate esters)[53] was only observed in PLB-TSP, which is possibly a

way to protect the organic matrix against thermal degradation,[12] since after pyrolysis there are still peaks at 1060 cm^{-1}. The peaks at 920, 866, 767, and 717 cm^{-1} were attributed to P-O-P stretching.[47] The peak at 557 cm^{-1} can be attributed to P-O or P=O stretching[47] and was dominant for PLB, PLB-TSP, and biochars treated with MgO. Finally, the peaks around 497-460 cm^{-1} were attributed to P-O[-] (PO_4^{3-}).[54] The peaks attributed to P-O-P and P=O stretching support the existence of $Ca_2P_2O_7$,[10] mainly for PLB-TSP as observed in the XRD spectrum (Figure 3a).

Maize Nutrition and Growth

After 40 days of growth, soil pH was significantly altered by the different materials (Figure 5a). The BBFs that were impregnated with MgO caused the greatest increase in soil pH because of their high pH values (Table 1). The highest increases in soil pH were observed in pots treated with PLB-H_3PO_4-MgO and PLB-TSP-MgO, which were increased by 1.15 and 1.25 units, respectively, as compared to the control (Figure 5a). In addition, soil treated with PLB-TSP-MgO showed a pH increase slightly higher than the pH of soil fertilized with TSP.

The combined use of organic ligand with P fertilizers is a modern strategy to decrease P adsorption in tropical soils, since organic ligands contribute to maintaining a negatively charged soil matrix and decrease the adsorption of anions such as phosphates,[55] increasing their longevity in the soil solution. We hypothesize that the BBFs impregnated with MgO are able to increase P diffusion in soils because of the residual basicity of these fertilizers. Therefore, these fertilizers also change the soil pH value, creating a microsite where P adsorption by the soil is decreased. Certainly this has a potential to increase the efficiency of P use for perennial crops when these fertilizers are added to tropical soils as a response to slow P-release rate throughout the growth season. Thus, plant P nutritional requirements may be directly coupled to the P kinetics release of BBFs, which may increase the efficiency of P use in Brazilian crop fields.
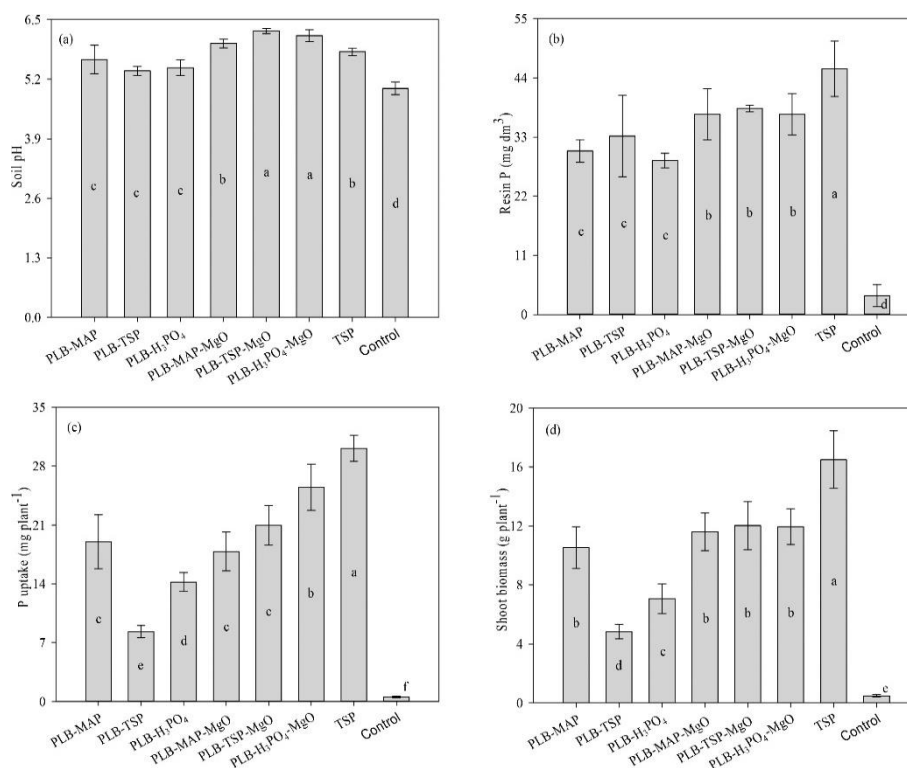
Figure 5. Soil pH (a), soil resin P after maize cultivation (b), plant P uptake (c), and maize shoot biomass (d).

Levels of resin P after maize cultivation were significantly higher in the soil treated with TSP compared to the other P sources and control (Figure 5b). The BBFs impregnated with MgO had low resin P values, and samples without MgO addition presented even lower soil-available P content as compared to TSP-treated soils. According to the kinetics of P release, these fertilizers have low solubility in water, and thus it is believed that the cultivation time (40 days) was not enough for the total release of P from these sources. The highest total P uptake by maize (30.1 mg plant^{-1}) was recorded for TSP (Figure 5c) because of the presence of high amounts of water-soluble P in the respective TSP-treated soil. Among the BBFs, the PLB-H$_3$PO$_4$-MgO showed the highest P uptake most probably induced by the highest Mg uptake in this treatment (Figure S4b), which confirms the

synergistic effect between these nutrients.[14] Although the PLB-MAP has a much lower Mg content, it also showed similar P uptake (Figure 5c) and yield (Figure 5d). Maize shoot dry matter production is shown in Figure 5d. Shoot dry matter production was significantly increased in the soil treated with TSP. For BBFs, treatments containing MgO promoted satisfactory shoot dry matter production that was statistically equivalent to that verified for PLB-MAP. The treatment that caused the lowest P uptake and shoot dry matter production was PLB-TSP. In addition to releasing P more gradually, MgO-treated biochars also caused soil pH to increase up to nearly 6.0, which is a suitable pH level to completely eliminate exchangeable Al^{3+} in the soil solution that may prevent maize growth. In contrast, samples PLB-TSP and PLB-H_3PO_4 reduced soil pH after cultivation to nearly 5.4, which represents an acidity degree that might solubilize Al^{3+} chemical species[56] that can precipitate soluble P forms released by BBFs. Moreover, MgO-treated biochars increased the residual level of exchangeable Mg^{2+} in soil (Figure S4a), and interestingly, the PLB-H_3PO_4-MgO caused an increase in Mg uptake (Figure S4b), reaching the same level as that of the TSP treatment despite the lower shoot biomass production.

The search for more efficient sources of P has driven the academia and fertilizer industries to invest in new products.[57] This study shows that maize cultivation with BBFs, especially those impregnated with MgO, can be used as slow-release fertilizers. Maize is a fast-growing crop that requires high levels of P in the beginning of its cycle. Therefore, it was already expected that TSP (highly water-soluble P source) would perform better as compared to the other P sources. Even so, we decided to use this crop for testing these slow-release P fertilizers to show that they are able to supply P in the short term as well. However, mainly alkaline sources (MgO-impregnated) need soil acidity to be solubilized and release most of the P. Future studies should be focused on testing the BBFs in perennial crops, which may reveal the real potential of these phosphate sources.

Furthermore, studies should focus on understanding in more detail the interaction of P from these sources with soil minerals in the long term (aging process).

CONCLUSIONS

The addition of MgO markedly decreased water-soluble P released over time from BBFs impregnated with MAP, TSP, and H_3PO_4. The P release is mainly controlled by a slow diffusion process because of the formation of low-solubility $Ca_2P_2O_7$ and $Mg_2P_2O_7$ compounds. Maize shoot biomass yield and P accumulated by plants are not regulated by the kinetics release of P by BBFs. MAP, TSP, and H_3PO_4 should be combined in use with MgO to correct the acidity of these phosphate sources and generate slow-release P fertilizers with a high potential to increase P uptake and maize growth. The slow release of P and alkaline reaction of the BBFs impregnated with MgO show great potential for these materials to be used as enhanced P fertilizers in highly weathered tropical soils.

AUTHOR INFORMATION

Corresponding Authors

*Phone: +55-35-3829-1256. Fax: +55-35-3829-1256. E-mail: filhoze04@hotmail.com. *Phone: +55-35-3829-1541. Fax: +55-35-3829-1256. E-mail: leonidas.melo@dcs.ufla.br.

Notes

The authors declare no competing financial interest.

REFERENCES

[1] Chien, S. H.; Prochnow, L. I.; Cantarella, H. Recent Developments of Fertilizer Production and Use to Improve Nutrient Efficiency and Minimize Environmental Impacts *Adv. Agron.* **2009**, 102 (9) 267– 322 DOI: 10.1016/S0065-2113(09)01008-6.

[2] Kang, J.; Amoozegar, A.; Hesterberg, D.; Osmond, D. L. Phosphorus leaching in a sandy soil as affected by organic and inorganic fertilizer sources *Geoderma* **2011**, 161 (3–4) 194– 201 DOI: 10.1016/j.geoderma.2010.12.019.

[3] Abdala, D. B.; da Silva, I. R.; Vergütz, L.; Sparks, D. L. Long-term manure application effects on phosphorus speciation, kinetics and distribution in highly weathered agricultural soils *Chemosphere* **2015**, 119, 504– 514DOI: 10.1016/j.chemosphere.2014.07.029.

[4] Roy, E. D.; Richards, P. D.; Martinelli, L. A.; Coletta, L. D.; Lins, S. R. M.; Vazquez, F. F.; Willig, E.;Spera, S. A.; VanWey, L. K.; Porder, S. The phosphorus cost of agricultural intensification in the tropics *Nat. Plants* **2016**, 2 (5) 16043 DOI: 10.1038/nplants.2016.43.

[5] Chien, S. H.; Prochnow, L. I.; Tu, S.; Snyder, C. S. Agronomic and environmental aspects of phosphate fertilizers varying in source and solubility: an update review *Nutr. Cycling Agroecosyst.* **2011**, 89 (2) 229–255 DOI: 10.1007/s10705-010-9390-4.

[6] Edelstein, D. M.; Tonjes, D. J. Modeling an Improvement in Phosphorus Utilization in Tropical Agriculture *J. Sustain. Agric.* **2012**, 36 (1) 18– 35 DOI: 10.1080/10440046.2011.627993

[7] Simpson, R. J.; Oberson, A.; Culvenor, R. a.; Ryan, M. H.; Veneklaas, E. J.; Lambers, H.; Lynch, J. P.;Ryan, P. R.; Delhaize, E.; Smith, F. A.Strategies and agronomic interventions to improve the phosphorus-use efficiency of farming systems *Plant Soil* **2011**, 349 (1–2) 89– 120 DOI: 10.1007/s11104-011-0880-1.

[8] Abdala, D. B.; Ghosh, A. K.; da Silva, I. R.; de Novais, R. F.; Alvarez Venegas, V. H. Phosphorus saturation of a tropical soil and related P leaching caused by poultry litter addition *Agric., Ecosyst. Environ.* **2012**, 162,15– 23 DOI: 10.1016/j.agee.2012.08.004.

[9] Lehmann, J.; Stephen, J. *Biochar for Environmental Management: Science, Technology and Implementation*, 2nd ed.; Routledge: London, **2015**.

[10] Zhao, L.; Cao, X.; Zheng, W.; Scott, J. W.; Sharma, B. K.; Chen, X. Copyrolysis of Biomass with Phosphate Fertilizers To Improve Biochar Carbon Retention, Slow Nutrient Release, and Stabilize Heavy Metals in Soil*ACS Sustainable Chem. Eng.* **2016**, 4 (3) 1630– 1636 DOI: 10.1021/acssuschemeng.5b01570.

[11] Vochozka, M.; Maroušková, A.; Váchal, J.; Straková, J. Biochar pricing hampers biochar farming *Clean Technol. Environ. Policy* **2016**, 18 (4) 1225– 1231 DOI: 10.1007/s10098-016-1113-3.

[12] Zhao, L.; Cao, X.; Zheng, W.; Kan, Y. Phosphorus-Assisted Biomass Thermal Conversion: Reducing Carbon Loss and Improving Biochar Stability *PLoS One* **2014**, 9 (12) e115373 DOI: 10.1371/journal.pone.0115373.

[13] González-Ponce, R.; López-de-Sá, E. G.; Plaza, C. Lettuce response to phosphorus fertilization with struvite recovered from municipal wastewater *HortScience* **2009**, 44 (2) 426– 430.

[14] Niu, Y.; Jin, G.; Li, X.; Tang, C.; Zhang, Y.; Liang, Y.; Yu, J. Phosphorus and magnesium interactively modulate the elongation and directional growth of primary roots in Arabidopsis thaliana (L.) Heynh *J. Exp. Bot.* **2015**, 66 (13) 3841– 3854 DOI: 10.1093/jxb/erv181.

[15] Novak, J. M.; Cantrell, K. B.; Watts, D. W.; Busscher, W. J.; Johnson, M. G. Designing relevant biochars as soil amendments using lignocellulosic-based and manure-based feedstocks *J. Soils Sediments* **2014**, 14 (2)330– 343 DOI: 10.1007/s11368-013-0680-8.

[16] Uchimiya, M.; Hiradate, S. Pyrolysis Temperature-Dependent Changes in Dissolved Phosphorus Speciation of Plant and Manure Biochars *J. Agric. Food Chem.* **2014**, 62 (8) 1802– 1809 DOI: 10.1021/jf4053385.

[17]   Wang, Y.; Lin, Y.; Chiu, P.   C.; Imhoff, P.   T.; Guo, M. Phosphorus release behaviors of poultry litter biochar as a soil amendment *Sci. Total Environ.* **2015**, 512–513, 454– 463 DOI: 10.1016/j.scitotenv.2015.01.093.

[18]   Uchimiya, M.; Hiradate, S.; Antal, M.   J. Dissolved   Phosphorus Speciation of Flash Carbonization, Slow Pyrolysis, and Fast Pyrolysis Biochars *ACS   Sustainable   Chem.   Eng.* **2015**, 3 (7) 1642– 1649 DOI: 10.1021/acssuschemeng.5b00336.

[19]   Vaneeckhaute, C.; Janda, J.; Vanrolleghem, P.   A.; Tack, F.   M. G.; Meers, E. Phosphorus   Use   Efficiency   of   Bio-Based   Fertilizers: Bioavailability   and   Fractionation *Pedosphere* **2016**, 26 (3) 310– 325 DOI: 10.1016/S1002-0160(15)60045-5

[20]   Gai, X.; Wang, H.; Liu, J.; Zhai, L.; Liu, S.; Ren, T.; Liu, H. Effects   of Feedstock and Pyrolysis Temperature on Biochar Adsorption of Ammonium and   Nitrate *PLoS   One* **2014**, 9 (12) e113888 DOI: 10.1371/journal.pone.0113888.

[21]   Liang, Y.; Cao, X.; Zhao, L.; Xu, X.; Harris, W. Phosphorus   Release from Dairy Manure, the Manure-Derived Biochar, and Their Amended Soil: Effects   of   Phosphorus   Nature   and   Soil   Property *J.   Environ. Qual.* **2014**,43 (4) 1504 DOI: 10.2134/jeq2014.01.0021.

[22]   Li, F.; Cao, X.; Zhao, L.; Wang, J.; Ding, Z. Effects   of   Mineral Additives   on   Biochar   Formation: Carbon   Retention,   Stability,   and Properties *Environ.   Sci.   Technol.* **2014**, 48 (19) 11211– 11217 DOI: 10.1021/es501885n.

[23]   Rajkovich, S.; Enders, A.; Hanley, K.; Hyland, C.; Zimmerman, A. R.; Lehmann, J. Corn growth and nitrogen nutrition after additions of biochars with   varying   properties   to   a   temperate   soil *Biol.   Fertil. Soils* **2012**, 48 (3)271– 284 DOI: 10.1007/s00374-011-0624-7.

[24]   Gaskin, J.   W.; Steiner, C.; Harris, K.; Das, K.   C.; Bibens, B. Effect   of Low-Temperature   Pyrolysis   Conditions   on   Biochar   for   Agricultural Use *Trans. ASABE* **2008**, 51 (6) 2061– 2069 DOI: 10.13031/2013.25409.

[25]   Murphy, J.; Riley, J.   P. A modified single solution method for the determination   of   phosphate   in   natural   waters *Anal.   Chim. Acta* **1962**, 27 (C) 31– 36 DOI: 10.1016/S0003-2670(00)88444-5.

[26]   Enders, A.; Lehmann, J. Comparison of Wet-Digestion and Dry-Ashing Methods for Total Elemental Analysis of Biochar *Commun. Soil Sci. Plant Anal.* **2012**, 43 (7) 1042– 1052 DOI: 10.1080/00103624.2012.656167.

[27] Jalali, M.; Zinli, N. A. M. Kinetics of phosphorus release from calcareous soils under different land use in Iran *J. Plant Nutr. Soil Sci.* **2011**, 174 (1) 38– 46 DOI: 10.1002/jpln.200900108.

[28] Mineralienatlaswebsite. http://www.mineralienatlas.de/%0Alexikon/index.php/MineralData?mineral=Meixnerite (accessed Feb 2, 2017).

[29] Webmineral Mineralogy database website. http://www.webmineral.com (accessed Feb 2, 2017).

[30] Walkley, A.; Black, I. A. An examination of the degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method *Soil Sci.* **1934**, 37 (1) 29– 38 DOI: 10.1097/00010694-193401000-00003.

[31] Novais, R. F.; Neves, J. C. L.; Barros, N. F. Ensaio em ambiente controlado. In *Métodos de pesquisa em fertilidade do solo*; Oliveira, A. J.; Garrido, W. E.; Araújo, J. D.; Lourenço, S., Eds.; Embrapa-SEA: Brasília,**1991**; pp 189– 253.

[32] van Raij, B.; Quaggio, J. A.; da Silva, N. M. Extraction of phosphorus, potassium, calcium, and magnesium from soils by an ion-exchange resin procedure *Commun. Soil Sci. Plant Anal.* **1986**, 17 (5) 547– 566 DOI: 10.1080/00103628609367733.

[33] Ferreira, D. F. Sisvar: a Guide for its Bootstrap procedures in multiple comparisons *Cienc. Agrotecnol.* **2014**,38 (2) 109– 112 DOI: 10.1590/S1413-70542014000200001.

[34] Ding, Y.; Liu, Y.-X.; Wu, W.-X.; Shi, D.-Z.; Yang, M.; Zhong, Z.-K. Evaluation of Biochar Effects on Nitrogen Retention and Leaching in Multi-Layered Soil Columns *Water, Air, Soil Pollut.* **2010**, 213 (1–4) 47– 55 DOI: 10.1007/s11270-010-0366-4.

[35] Wu, W.; Li, J.; Lan, T.; Müller, K.; Niazi, N.K.; Chen, X.; Xu, S.; Zheng, L.; Chu, Y.; Li, J.Unraveling sorption of lead in aqueous solutions by chemically modified biochar derived from coconut fiber: A microscopic and spectroscopic investigation *Sci. Total Environ.* **2017**, 576, 766– 774 DOI: 10.1016/j.scitotenv.2016.10.163.

[36] Abdala, D. B.; Northrup, P. A.; Arai, Y.; Sparks, D. L. Surface loading effects on orthophosphate surface complexation at the goethite/water interface as examined by extended X-ray Absorption Fine Structure (EXAFS) spectroscopy *J. Colloid Interface Sci.* **2015**, 437, 297– 303 DOI: 10.1016/j.jcis.2014.09.057.

[37]   Wang, Y.; Lin, Y.; Chiu, P.   C.; Imhoff, P.   T.; Guo, M. Phosphorus release behaviors of poultry litter biochar as a soil amendment *Sci. Total Environ.* **2015**, 512–513, 454– 463 DOI: 10.1016/j.scitotenv.2015.01.093.

[38]   Yao, Y.; Gao, B.; Chen, J.; Zhang, M.; Inyang, M.; Li, Y.; Alva, A.; Yang, L. Engineered carbon (biochar) prepared by direct pyrolysis of Mg-accumulated tomato tissues: Characterization and phosphate removal potential *Bioresour.   Technol.* **2013**, 138, 8– 13 DOI: 10.1016/j.biortech.2013.03.057.

[39]   Gerente, C.; Lee, V. K. C.; Le Cloirec, P.; McKay, G. Application of Chitosan for the Removal of Metals From Wastewaters by Adsorption— Mechanisms   and   Models   Review *Crit.   Rev.   Environ.   Sci. Technol.* **2007**, 37 (1)41– 127 DOI: 10.1080/10643380600729089.

[40]   Qian, T.; Zhang, X.; Hu, J.; Jiang, H. Effects   of   environmental conditions   on   the   release   of   phosphorus   from biochar *Chemosphere* **2013**, 93 (9) 2069– 2075 DOI: 10.1016/j.chemosphere.2013.07.041.

[41]   Talboys, P.   J.; Heppell, J.; Roose, T.; Healey, J.   R.; Jones, D. L.; Withers, P. J. A. Struvite: a slow-release fertiliser for sustainable phosphorus   management? *Plant   Soil* **2016**, 401 (1–2) 109– 123 DOI: 10.1007/s11104-015-2747-3.

[42]   Zhang, C.; Song, Z.; Shi, H.; Fu, J.; Qiao, Y.; He, C. The Effects of Pre-treatments and Low-temperature Pyrolysis on Surface Properties of Biochar from   Sunflower   Straw   as   Adsorption Material *BioResources***2016**, 12 (1) 1041– 1051 DOI: 10.15376/biores.12.1.1041-1051.

[43]   Park, J. H.; Ok, Y. S.; Kim, S. H.; Cho, J. S.; Heo, J. S.; Delaune, R. D.; Seo, D. C. Evaluation of phosphorus adsorption capacity of sesame straw biochar on aqueous solution: influence of activation methods and pyrolysis temperatures *Environ.   Geochem.   Health* **2015**, 37 (6) 969– 983 DOI: 10.1007/s10653-015-9709-9.

[44]   Movasaghi, Z.; Rehman, S. ur Rehman, D. I. Fourier Transform Infrared (FTIR)   Spectroscopy   of   Biological   Tissues *Appl.   Spectrosc. Rev.* **2008**, 43 (2) 134– 179 DOI: 10.1080/05704920701829043.

[45]   He, Z.; Waldrip, H. M. Composition of Whole and Water-Extractable Organic Matter of Cattle Manure Affected by Management Practices *Labile Organic Matter-Chemical Compositions, Function, and Significance in Soil and the Environment* **2015**, 23– 40 DOI: 10.2136/sssaspecpub62.2014.0034.

[46] Kaudal, B. B.; Chen, D.; Madhavan, D. B.; Downie, A.; Weatherley, A. An examination of physical and chemical properties of urban biochar for use as growing media substrate *Biomass Bioenergy* **2016**, 84, 49–58 DOI: 10.1016/j.biombioe.2015.11.012.

[47] Bekiaris, G.; Peltre, C.; Jensen, L. S.; Bruun, S. Using FTIR-photoacoustic spectroscopy for phosphorus speciation analysis of biochars *Spectrochim. Acta, Part A* **2016**, 168, 29– 36 DOI: 10.1016/j.saa.2016.05.049.

[48] Wang, Y.; Yin, R.; Liu, R. Characterization of biochar from fast pyrolysis and its effect on chemical properties of the tea garden soil *J. Anal. Appl. Pyrolysis* **2014**, 110 (1) 375– 381 DOI: 10.1016/j.jaap.2014.10.006.

[49] Farah Nadia, O.; Xiang, L. Y.; Lie, L. Y.; Chairil Anuar, D.; Mohd Afandi, M. P.; Azhari Baharuddin, S.Investigation of physico-chemical properties and microbial community during poultry manure co-composting process *J. Environ. Sci.* **2015**, 28, 81– 94 DOI: 10.1016/j.jes.2014.07.023.

[50] Iriarte-Velasco, U.; Sierra, I.; Zudaire, L.; Ayastuy, J. L. Preparation of a porous biochar from the acid activation of pork bones *Food Bioprod. Process.* **2016**, 98, 341– 353 DOI: 10.1016/j.fbp.2016.03.003.

[51] Wang, X.; Lü, S.; Gao, C.; Feng, C.; Xu, X.; Bai, X.; Gao, N.; Yang, J.; Liu, M.; Wu, L. Recovery of Ammonium and Phosphate from Wastewater by Wheat Straw-based Amphoteric Adsorbent and Reusing as a Multifunctional Slow-Release Compound Fertilizer *ACS Sustainable Chem. Eng.* **2016**, 4 (4) 2068– 2079DOI: 10.1021/acssuschemeng.5b01494.

[52] Li, R.; Wang, J. J.; Zhou, B.; Awasthi, M. K.; Ali, A.; Zhang, Z.; Lahori, A. H.; Mahar, A. Recovery of phosphate from aqueous solution by magnesium oxide decorated magnetic biochar and its potential as phosphate-based fertilizer substitute *Bioresour. Technol.* **2016**, 215, 209– 214 DOI: 10.1016/j.biortech.2016.02.125.

[53] Kennedy, L. J.; Vijaya, J. J.; Sekaran, G. Effect of Two-Stage Process on the Preparation and Characterization of Porous Carbon Composite from Rice Husk by Phosphoric Acid Activation *Ind. Eng. Chem. Res.* **2004**, 43 (8) 1832– 1838 DOI: 10.1021/ie034093f .

[54] Assaaoudi, H.; Fang, Z.; Butler, I. S.; Ryan, D. H.; Kozinski, J. A. Characterization of a new magnesium hydrogen orthophosphate salt, Mg3.5H2(PO4)3, synthesized in supercritical water *Solid State Sci.* **2007**, 9(5) 385– 393 DOI: 10.1016/j.solidstatesciences.2007.03.015.

[55]   Jiang, J.; Yuan, M.; Xu, R.; Bish, D. L. Mobilization of phosphate in variable-charge soils amended with biochars derived from crop straws *Soil Tillage Res.* **2015**, 146, 139– 147 DOI: 10.1016/j.still.2014.10.009.

[56]   Mulder, J.; Stein, A. The solubility of aluminium in acidic forest soils: Long-term changes due to acidic deposition *Geochim. Cosmochim. Acta* **1994**, 58, 85– 94 DOI: 10.1016/0016-7037(94)90448-0.

[57]   Benício, L.   P.   F.; Constantino, V.   R.   L.; Pinto, F. G.; Vergütz, L.; Tronto, J.; da Costa, L. M. da. Layered Double Hydroxides: New Technology in Phosphate Fertilizers Based on Nanostructured Materials *ACS   Sustainable   Chem.   Eng*. **2017**, 5 (1) 399– 409 DOI: 10.1021/acssuschemeng.6b01784 .

Supplementary Material for

Co-Pyrolysis of Poultry Litter and Phosphate and Magnesium Generates Alternative Slow Release Fertilizer Suitable for Tropical Soils

José F. Lustosa Filho[a], Evanise S. Penido[b], Patrícia P. Castro[a], Carlos A. Silva[a], Leônidas C. A. Melo[a*]*

[a]Soil Science Department, Federal University of Lavras, 37200000, Lavras, Minas Gerais, Brazil.

[b]Chemistry Department, Federal University of Lavras, 37200000, Lavras, Minas Gerais, Brazil.

Corresponding Authors

[*]Phone: +55-35-3829-1256. Fax: +55-35-3829-1256. E-mail: filhoze04@hotmail.com.

[*]Phone: +55-35-3829-1541. Fax: +55-35-3829-1256. E-mail: leonidas.melo@dcs.ufla.br.

• Number of pages: 7

• Number of figures: 4

• Number of tables: 2

1. Muffle furnace
2. Cylinders
3. Non-condensable gases (syngas)
4. Fume hood
5. Condenser
6. Bio-oil collection
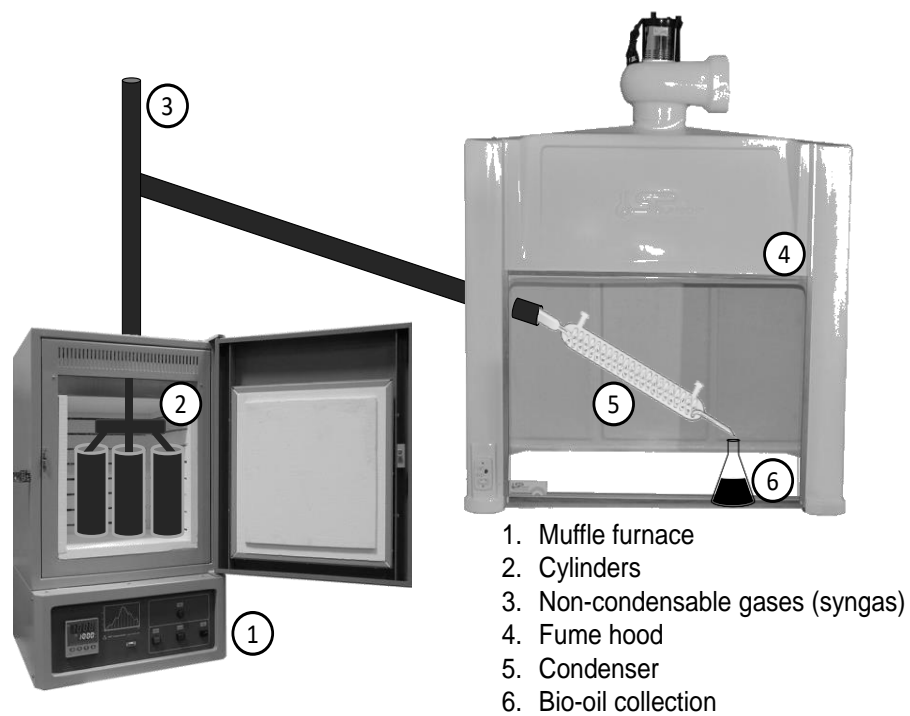
Figure S1. Scheme of the adapted muffle furnace used for the production of the Biochar-based fertilizers.
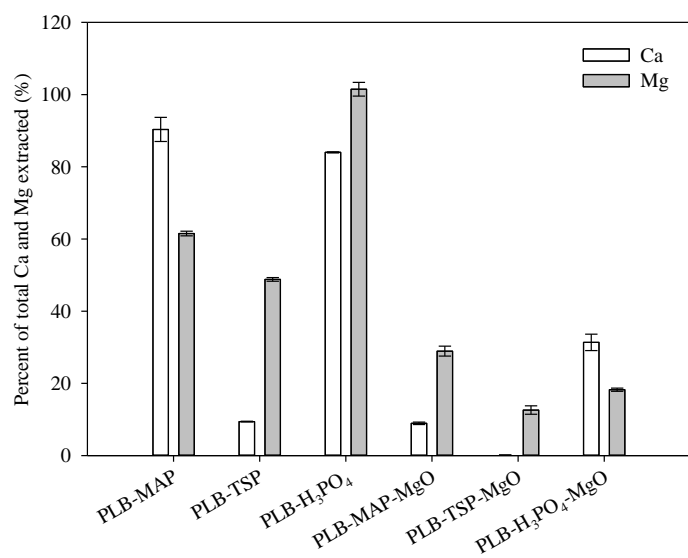
Figure S2. Released calcium (Ca) and magnesium (Mg) as a percentage of the total Ca and Mg mass in biochar-based fertilizers by water extraction. Values are mean (n = 3) ± standard deviation.
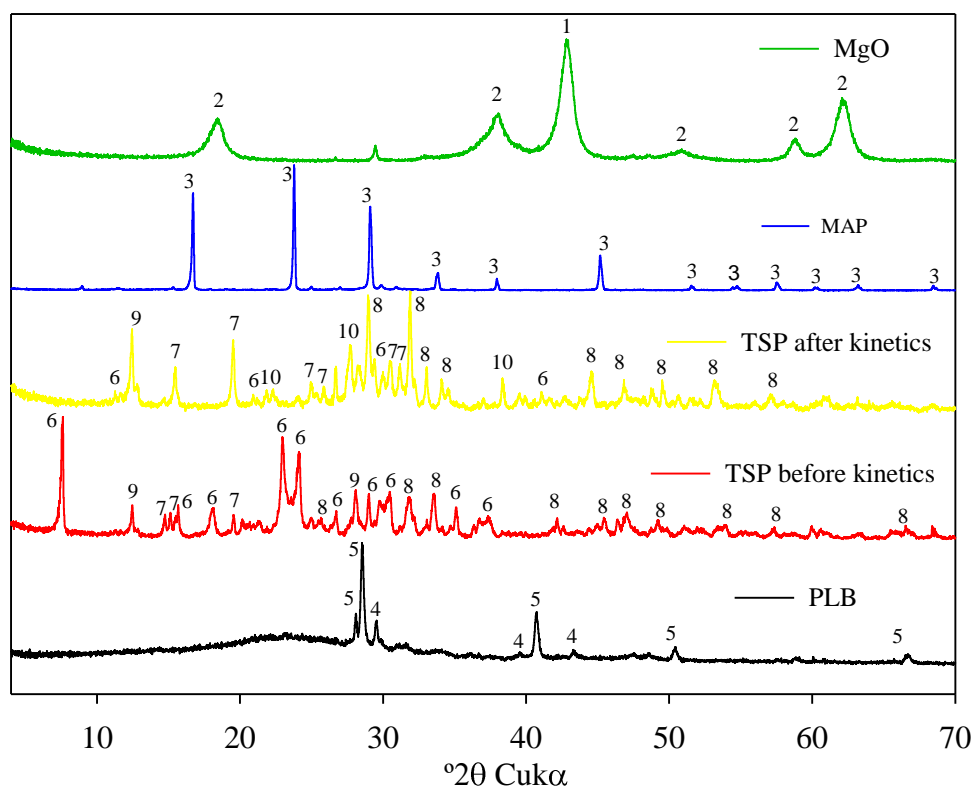
Figure S3. X-ray diffraction analysis of the additives and PLB. 1-brucite, 2-periclase, 3-piphosphammite, 4-calcite, 5-sylvite, 6-brushite, 7-crandallite, 8-fluorapatite, 9-garronit, 10-berlinite.
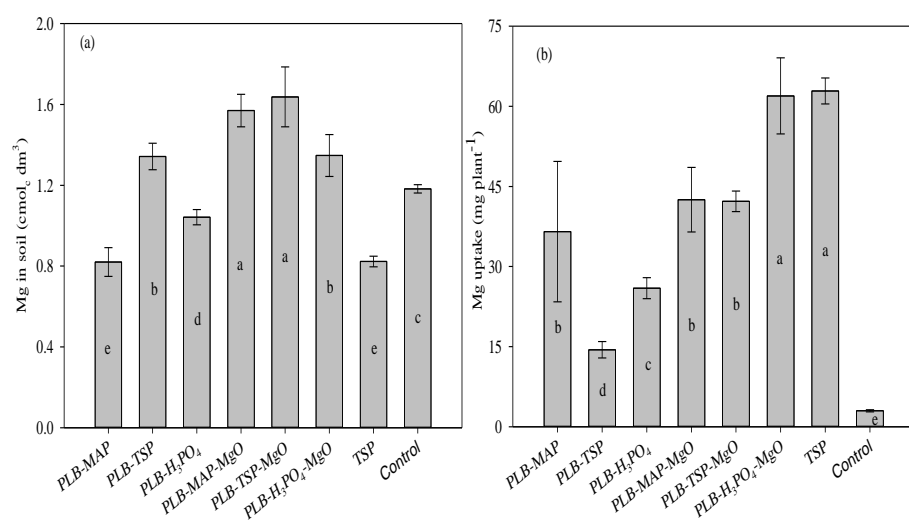
Figure S4. Available Mg in soil after maize cultivation (a) and plant Mg uptake (b).

Table S1. Chemical formulas of predominant crystalline phases in mineral additives, PLB and biochar-based fertilizers before and after release kinetics of P.

| ID[1]	Mineral name	Chemical formula
1	Brucite	$MgO \cdot H_2O$
2	Periclase	MgO
3	Biphosphammite	$(NH_4, K)H_2PO_4$
4	Calcite	$CaCO_3$
5	Sylvite	KCl
6	Brushite	$Ca(H_2PO_4)_2(H_2O)$
7	Crandallite	$CaAl_3(PO_4)_{1.5}(OH)_5 \cdot H_2O$
8	Fluorapatite	$Ca_5(PO_4)_3F$
9	Garronit	$Ca_3(Si, Al)_{16}O_{32} \cdot 13H_2O$
10	Berlinite	$AlPO_4$
11	Ammonium Imide	$(NH_4)_4P_2O_6NH \cdot 3H_2O$
12	Struvite-K	$KMg(PO_3)_3$
13	Archerite	$(K_{0.78}(NH_4)_{0.22})(H_2PO_4)$
14	Tinticite	$Fe_4(PO_4)_3(OH)_3 \cdot 5H_2O$
15	Variscite	$Al(PO_4) \cdot 2H_2O$
16	Calcium	$Ca_2P_2O_7$
17	Potassium	$K_5P_3O_{10} \cdot 4H_2O$
18	Heulandite	$Ca_{4.52}Al_{9.04}Si_{26.96}O_{72}(H_2O)_{13.4}$
19	Althausite	$Mg_4(PO_4)_2(OH)_{.37}F_{.25}O_{.19}$
20	Calcium Hydrogen	$Ca_3(HP_2O_7)_2$
21	Farringtonite	$Mg_3(PO_4)_2$
22	Monetite	$CaHPO_4$
23	Ammonium	$(NH_4)_2P_2O_5F_2$
24	Silicon Phosphate	$SiO_2 \cdot P_2O_5$
25	Augelite	$Al_2(PO_4)(OH)_3$
26	Bassanite	$CaSO_4 \cdot 0.5H_2O$
27	Phosphorrosslerite	$MgHPO_4 \cdot 7H_2O$
28	Magniotriplite	$Mg_2(PO_4)F$
29	Hydroxyapatite	$Ca_{10}(OH)_2(PO_4)_6$
30	Hydroxylwagnerite	$Mg_2(PO_4)(OH)$
31	Magnesium	$Mg_2P_2O_7$
32	Dypingite	$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$

[1]Identification of crystalline phases used in Figure 2 and S3.

Table S2. FTIR spectra band assignments presented in Figure 3.

Band, cm^{-1}	Assignment	References
3292	H$_2$O stretching or N-H stretching vibration in amino compounds	[1]
2979	Aliphatic C-H stretching	[2]
2920	Asymmetric C-H stretching vibrations in aliphatic compounds	[3]
2353	P–H organophosphorus	[4]
1645	C-C stretching vibration in aromatic compound	[5]
1425	Carbonates -CO$_3^{2-}$	[6]
1324	Aromatic amines [C-N stretching]	[3]
1250, 1153	C–O stretching	[3]
1111	Stretching and bending vibration of Mg-OH	[7]
1074	Ionic bond P$^+$-O$^-$ in acid phosphate esters)	[8]
920, 866, 767, 717	P-O-P stretching	[3]
557	P-O or P=O stretching	[3]
497, 460	P-O$^-$ (PO$_4^{3-}$)	[9]

References

(1)   Movasaghi, Z.; Rehman, S.; ur Rehman, D. I. Fourier Transform Infrared (FTIR) Spectroscopy of Biological Tissues. *Appl. Spectrosc. Rev.* **2008**, *43* (2), 134–179.

(2)   Kaudal, B. B.; Chen, D.; Madhavan, D. B.; Downie, A.; Weatherley, A. An examination of physical and chemical properties of urban biochar for

use as growing media substrate. *Biomass and Bioenergy* **2016**, *84*, 49–58.

(3)   Bekiaris, G.; Peltre, C.; Jensen, L. S.; Bruun, S. Spectrochimica Acta Part A : Molecular and Biomolecular Spectroscopy Using FTIR-photoacoustic spectroscopy for phosphorus speciation analysis of biochars. **2016**, *168*, 29–36.

(4)   Wang, Y.; Yin, R.; Liu, R. Characterization of biochar from fast pyrolysis and its effect on chemical properties of the tea garden soil. *J. Anal. Appl. Pyrolysis* **2014**, *110* (1), 375–381.

(5)   Nadia, F. O.; Xiang, L. Y.; Lie, L. Y.; Chairil Anuar, D.; Mohd Afandi, M. P.; Azhari Baharuddin, S. Investigation of physico-chemical properties and microbial community during poultry manure co-composting process. *J. Environ. Sci.* **2015**, *28*, 81–94.

(6)   Iriarte-Velasco, U.; Sierra, I.; Zudaire, L.; Ayastuy, J. L. Preparation of a porous biochar from the acid activation of pork bones. *Food Bioprod. Process.* **2016**, *98*, 341–353.

(7)   Li, R.; Wang, J. J.; Zhou, B.; Awasthi, M. K.; Ali, A.; Zhang, Z.; Lahori, A. H.; Mahar, A. Recovery of phosphate from aqueous solution by magnesium oxide decorated magnetic biochar and its potential as phosphate-based fertilizer substitute. *Bioresour. Technol.* **2016**, *215*, 209–214.

(8)   Kennedy, L. J.; Vijaya, J. J.; Sekaran, G. Effect of Two-Stage Process on the Preparation and Characterization of Porous Carbon Composite from Rice Husk by Phosphoric Acid Activation. *Ind. Eng. Chem. Res.* **2004**, *43* (8), 1832–1838.

(9)   Assaaoudi, H.; Fang, Z.; Butler, I. S.; Ryan, D. H.; Kozinski, J. A. Characterization of a new magnesium hydrogen orthophosphate salt, Mg3.5H2(PO4)3, synthesized in supercritical water. *Solid State Sci.* **2007**, *9* (5), 385–393.

CHAPTER 2

Article prepared according to guidelines of the journal Soil & Tillage Research (Current status: Under review).

Diffusion and phosphorus solubility of biochar-based fertilizer: visualization, chemical assessment and availability to plants

José Ferreira Lustosa Filho[a*], Cristiane Francisca Barbosa[a], Jefferson Santana da Silva Carneiro[a], Leônidas Carrijo Azevedo Melo[a*]

[a] Soil Science Department, Federal University of Lavras, 37200-000, Lavras, MG, Brazil;

* Corresponding author at: Soil Science Department, Federal University of Lavras, 37200-000, Lavras, MG, Brazil.
E-mail address: leonidas.melo@dcs.ufla.br (Leônidas C. A. Melo), filhoze04@hotmail.com (José F. Lustosa Filho).

ABSTRACT

Developing slow-release phosphate sources more synchronized with the crop cycle is needed to increase phosphorus (P) use efficiency in highly weathered tropical soils. We hypothesized that impregnation of biomass with phosphate and magnesium prior to biochar production will generate slow-release P fertilizer and increase P use efficiency by plants. In this study, triple superphosphate (TSP) or phosphoric acid (H_3PO_4) were mixed with magnesium oxide (MgO) and poultry litter (PL) to produce slow-release P biochar-based fertilizers (BBFs). The P fractions of the BBFs soluble in water, citric acid and neutral ammonium citrate + water were analyzed. Phosphorus diffusion in soil was determined using a visualization technique over time and chemical analyses, and the agronomic efficiency of the BBFs was compared with soluble fertilizer (TSP) in both granular and powder form for maize grown in an Oxisol under greenhouse conditions. Results showed that BBFs strongly decreased water-soluble P, which

caused a slow-release of P in soil as demonstrated by the diffusion visualization technique. When applied as powder mixed through the soil, BBFs improved soil pH and Mg and were able to provide P to plants similarly to TSP. The granular form of PLB-H$_3$PO$_4$-MgO was equivalent to TSP for P release during early growth of maize and preserved higher amounts of P from in the granule, which can be used for plants in future harvests. Pyrolysis of biomass with phosphate and magnesium is an option to generate enhanced P fertilizers, especially for on high P-fixing soils.

Keywords: Slow-release fertilizer, Fertilizer granulation, Phosphorus use efficiency.

Graphical abstract
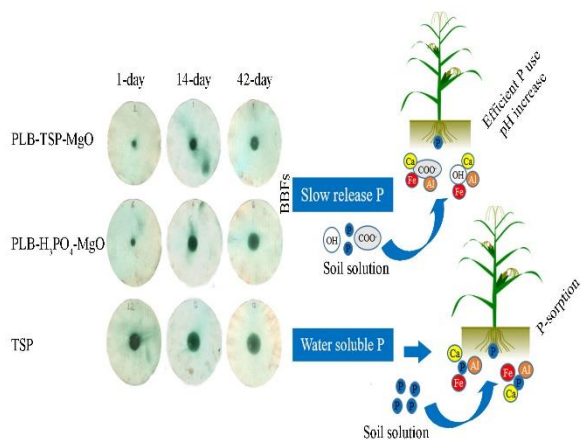
Highlights

• Phosphate sources and MgO with poultry litter produce biochar-based slow-release P fertilizers.

• The granular form of PLB-H$_3$PO$_4$-MgO promotes maize growth equivalent to conventional fertilizer.

• Biochar-based fertilizer preserves greater amount of phosphate in the granule after cultivation.

• Biochar-based fertilizer has great potential as P fertilizer in tropical soils.

1. Introduction

Phosphorus supply to crops planted on soils is a major constraint on the quantity and quality of food production. Conventional mineral P fertilizers are manufactured from finite reserves of phosphate rock (Sarkar et al., 2018). The reserves of high-grade phosphate rock might be depleted within 50 to 400 years, depending on P supply and demand dynamics (van Dijk et al., 2016), with a few countries concentrating the majority of these phosphate reserves (Cordell et al., 2009). This scenario increases the pressure for P recycling and use efficiency. In highly weathered soils, such as those prevailing in Brazil and tropical regions, irreversible P fixation is favored by high contents of (hydr)oxides of Fe and Al (Abdala et al., 2015; Novais and Smyth, 1999). Currently, most commercial P fertilizers, such as monoammonium phosphate (MAP) or TSP, are water-soluble and P sorbs rapidly onto soil minerals, causing low P use efficiency and low residual values of these fertilizations (Everaert et al., 2017, 2016). However, in Brazil, the application of P fertilizers in medium to large-scale farms has been performed as a pre-planting operation by broadcasting, in order to optimize the seeding process (Teixeira et al., 2016). Due to increased surface and contact time of P fertilizer with oxidic soils, P availability is reduced and might affect P supply to crops (Guedes et al., 2016).

Developing new technologies to reduce P losses and increase its effectiveness is necessary to improve P management in tropical soil. There are a number of potential options to improve P fertilizer use efficiency by plants, including polymer-coating, liquid products for soil application, bioinoculants, seed dressings, foliar applications and organomineral fertilizers (McLaughlin et

al., 2011; Withers et al., 2014). Recently, our research group synthesized biochar-based fertilizers (BBFs) by co-pyrolysis of biomass with phosphate and magnesium (Lustosa Filho et al., 2017). We found that impregnation of poultry litter with TSP and H_3PO_4 combined with MgO eliminated the acidity of these phosphate sources and generate BBFs of slow-release P with a high potential to increase P uptake and maize growth. In addition to releasing P more gradually, the BBFs also changed the soil pH value, creating microsites where P adsorption by the soil is decreased (Lustosa Filho et al., 2017). Zhao et al. (2016) also impregnated two feedstocks (sawdust and switchgrass) with bone meal (BM) and TSP, and found that release of P from TSP- and BM-composite biochars was much lower than the kinetics of P release verified for TSP and BM alone, showing the potential of the modified biochars as slow-release P fertilizers.

In general, sources low in water soluble P show higher agronomic efficiency when compared to water-soluble P fertilizers only when the fertilizer is ground and mixed through the soil. For instance, Degryse et al. (2017) observed that ground struvite ($MgNH_4PO_4.6H_2O$) mixed with the soil dissolves quickly and supply P to plants similarly to water-soluble P fertilizer applied at the same P rate, but when applied in granular form it dissolves much slower and its agronomic effectiveness is lower than water-soluble P fertilizer. Talboys et al. (2016) carried out a pot trial with spring wheat to compare P availability of granular struvite and diammonium phosphate (DAP) in a soil with pH 6.0, and found that after 30 days the P uptake for struvite treatment was only 30% as compared to a positive control the control (DAP). However, after 90 days, they observed similar yield and P uptake by spring wheat for struvite and TSP, although only 26% of the struvite had dissolved as determined by the recovery of the residual struvite granules at the end of the experiment. Thereby, it is evident that granular struvite is slow to dissolve and does not provide sufficient P for early crop growth (Talboys et al., 2016). Granulation can have large effects on the effectiveness of fertilizers,

considering that powdered fertilizers are generally impractical for application at large-scale given the current fertilizer delivery systems (Everaert et al., 2017). Hence granulation or pelletization of BBFs can provide a more suitable fertilizer use in conventional agricultural practices. However, so far the P release dynamics in this type of material in different forms (granular or powder) has not been studied.

In this study we aimed (i) to evaluate the effect of poultry litter impregnation with P sources (TSP and H_3PO_4) and MgO on the P solubility of the BBFs; (ii) to evaluate the diffusion of P from granular BBFs applied to slightly acidic and high-P fixing soil, by using a simple and quick visualization technique and soil chemical analysis to assess P release and (iii) to investigate the use of BBFs in both granular and powder forms and compare them with conventional TSP on maize growth in an Oxisol under greenhouse conditions.

2. Materials and methods

2.1. Preparation, Production and Granulation of Biochar-Based Fertilizers

Detailed information concerning feedstock and process for biochar production and characterization can be found elsewhere (Lustosa Filho et al., 2017). Briefly, poultry litter was air-dried at room temperature, ground to pass through a 20-mesh sieve (1.00 mm), and separately mixed with TSP [$Ca(H_2PO_4)_2$] and H_3PO_4, with addition of MgO in both mixtures. Phosphates and MgO were mixed to achieve a P:Mg molar ratio of 1:1, and the ratio of poultry litter:phosphate source was 1:0.5 (w/w). After 16 h of resting as moistened sample, the pretreated mixtures were oven-dried at 60 °C to a constant mass prior to pyrolysis. Thereafter, samples were placed in a muffle furnace in sealed cylinders to avoid air flow and gaseous biomass. Pyrolysis was performed by raising the temperature up to 500 °C at a heating rate of 10 °C min^{-1}, maintaining the target temperature for 2 h to provide enough time for complete carbonization

(Zhao et al., 2014). The produced biochars were identified as follows: PLB-TSP-MgO = poultry litter biochar + TSP + MgO; and PLB-H_3PO_4-MgO = poultry litter biochar + phosphoric acid + MgO.

The PLB-H_3PO_4-MgO, PLB-TSP-MgO and TSP were ground and sieved to 60-mesh before granulation. Cassava starch and liquid glue (water-based polyvinyl acetate) were used as binding agents to promote the granulation of the fertilizers. The fertilizers were homogenized in the proportion of 70% (BBF), 25% (liquid glue) and 5% (Cassava starch). Deionized water was added to the mixture for homogenization until it had pasty consistency (moldable). Samples were then manually accommodated in a stainless steel pastillator with circular holes (300 total) of 5.0 mm in diameter and 3.0 mm in height (Figure S1). Subsequently, the wet granules were suspended out of the pastillator and the set was placed in an oven to dry at 65 °C until constant weight. The contents of total and soluble P in neutral ammonium citrate + water (NAC+H_2O) were determined after granulation, according to the official methods described in (Brasil, 2014).

2.2. Solubility of the P Fertilizers

Water-soluble P contents were determined in samples of fertilizers after successive washings with deionized water in 1.0 g of material until a final volume of 250 mL was reached, being the washing process completed within 1.0 h. Citric acid-soluble P was extracted by stirring the mixtures with a 2% citric acid solution for 30 min, in a fertilizer:solution ratio of 1:100 (w/v). Neutral ammonium citrate solution (pH 7) was used to extract NAC+H_2O-soluble P by boiling the sample, using a fertilizer:solution ratio of 1:50 (w/v). These analytical procedures were performed according to the official methods for P fertilizers described in Brasil (2014). The P fractions in fertilizers were quantified by inductively coupled plasma optical emission spectrometry (ICP-OES, Spectro Blue, Spectro

Analytical Instruments, Germany). Contents of water-soluble P, citric acid-soluble P and NAC+H_2O-soluble P of each fertilizer were converted to P_2O_5.

2.3. Maize Growth Conditions

A pot trial with maize (*Zea mays*) grown for five weeks was carried out under greenhouse conditions. Samples of an Oxisol (Rhodic Hapludox) were collected from the subsurface layer (40-60 cm), aiming to reduce the organic matter content, in Lavras, Minas Gerais, Brazil (915 m altitude, 21°13′34″ S and 44°58′31″ W). Samples were air dried and passed through a 2-mm sieve. The soil has very low available P concentration (0.41 mg dm^{-3}, Mehlich-1), high clay content (640 g kg^{-1}) and pH_{water} of 4.8; Ca^{2+} and Mg^{2+} concentrations were 0.24 and 0.10 $cmol_c$ dm^{-3} (KCl 1 mol L^{-1} extractor), respectively, and soil organic C was 11.8 g kg^{-1} (Walkley and Black, 1934).

A total of 1.5 dm^3 of soil was placed into plastic bags and mixed with $CaCO_3$ + $MgCO_3$ at a Ca:Mg molar ratio of 3:1, aiming to increase the soil base saturation to 70%, which was then moistened to field capacity. After 30 days of incubation, the soil samples were fertilized with a basal fertilizer solution of macronutrients (100 mg kg^{-1} N, 100 mg kg^{-1} K, and 40 mg kg^{-1} S) and micronutrients (4.0 mg kg^{-1} Zn, 3.66 mg kg^{-1} Mn, 1.55 mg kg^{-1} Fe, 1.33 mg kg^{-1} Cu, 0.81 mg kg^{-1} B and 0.15 mg kg^{-1} Mo), following recommendations for pot experiments (Novais et al., 1991).

The experiment was conducted in a completely randomized factorial design ($3 \times 2 \times 2 + 1$). Three P sources (PLB-H_3PO_4-MgO, PLB-TSP-MgO and TSP) at two P rates (150 and 300 mg kg^{-1}, NAC+H_2O-soluble P), applied both as granular and powder form, besides control pots without P addition were replicated three times, totaling 39 experimental units. Both the granules and the powder fertilizers were mixed with only 0.5 dm^3 of soil and distributed at the middle tier of the pot. Three seeds of maize (*Zea mays*) were sown in each pot and thinned to one

seedling after 7 days, which was grown during five weeks. All pots received an additional application of N and K fertilizer (100 mg kg^{-1}) via fertigation at 20 days after sowing.

After 35 days, maize shoot was harvested, washed with distilled water, dried at 65 °C for 72 h, weighed, and milled for chemical analysis. Shoot tissues were digested in a block digestion system using concentrated nitric and perchloric acids, and P contents were measured colorimetrically, following analytical procedures described in Murphy and Riley (1962). P uptake by maize shoot was estimated by multiplying the P content with the respective dry mass yield. Approximately 200 cm^3 of soil was collected from each pot after homogenization for chemical analysis. The soil-available P after maize cultivation was extracted by anion-exchange resin (van Raij et al., 1986), followed by colorimetric determination (Murphy and Riley, 1962). After cultivation, the fertilizer granules were isolated from the soil sample (only for dose 300 mg kg^{-1}) and analyzed for total and NAC+H$_2$O-soluble P contents, according to the official methods described in Brasil (2014).

The relative agronomic effectiveness (RAE), which shows the increase in production due to each unit of applied P, was calculated by the following equation:

$$RAE\ (\%) = \frac{(Pi - P0)}{\left(P_{tsp} - P0\right)}\ x\ 100$$

in which Pi is the dry matter production by plants in a given treatment (g plant^{-1}); P0 is the dry matter production by plants in the control treatment without P application; P$_{tsp}$ is the dry matter production by plants in the reference treatment (TSP).

2.4. Petri Dish Experiment - Granular Fertilizers

Before the experiment, soil acidity was corrected and the pH (water) was raised to 6.0 by applying CaCO$_3$ + MgCO$_3$ at a Ca:Mg molar ratio of 3:1,

considering that in highly weathered tropical soils the availability of P is optimized in this pH range (Novais and Smyth, 1999). The pH, organic C, P, Ca^{2+}, Mg^{2+} and clay content were analyzed after correction as previously described. The cation exchange capacity (CEC) at pH 7.0 (ammonium acetate) and oxalate-extractable Al and Fe concentrations were determined (Schwertmann, 1964) and P total content was determined after sulfuric acid digestion (Embrapa, 2011). The soil characteristics are shown in Table 1.

Table 1. Selected soil properties describing the conditions for the petri dish experiment.

pH	Organic C	Total P	Available P	Ca^{2+}	Mg^{2+}	CEC	Clay	Fe_2O_3ox	Al_2O_3ox
water	---g kg^{-1}---	--------mg kg^{-1}--------		-------cmol$_c$ dm^{-3}-------			%	---------mg kg^{-1}---------	
5.7	11.8	71.2	0.73	1.70	1.06	6.4	64	400	1200

The soil was added to petri dishes (diameter 9.0 cm) and wetted to 90% field capacity. Single fertilizer granules of either PLB-TSP-MgO, PLB-H_3PO_4-MgO or TSP, each containing 8.0 mg of total P, were carefully inserted in the center of the petri dishes, 5 mm below the soil surface. The mean weight of each granule was 73.0 mg for PLB-TSP-MgO, 52.3 mg for PLB-H_3PO_4-MgO, and 42.9 mg for TSP and each treatment was replicated four times. The petri dishes were incubated at 25 °C and P diffusion was visualized at 1, 3, 7, 14, 28 and 42 days after fertilizer application using the method developed by Degryse and McLaughlin (2014). Briefly, an Fe oxide impregnated paper was exposed to the soil surface for a contact time ranging from 5 to 30 min (5 minutes for 1-day incubation; 10 minutes for 3-7-day incubation; 30 minutes for > 7-day incubation). The P captured by the Fe oxides on the paper was colored using a modified malachite green method, and the dried papers were scanned and analyzed with an image processing free software (GIMP 2) to determine the radius of high-P diffusion zone around the granule. At 42 days, the soils were concentrically sampled (0-8.0 mm and >8.0 mm from the granule). The soil

samples were oven-dried at 60 °C for 48 h, homogenized and analyzed for pH (water) (soil:water ratio, 1:10) and available P by the resin method, as described by van Raij et al. (1986). The granules in the petri dish were isolated from the soil sample, digested in HNO_3 20% (v/v) overnight and analyzed for P content by ICP-OES (Everaert et al., 2017).

2.5. Statistical Analysis

Statistical analyses were performed with the statistical software package R (R core Team, 2016). A one-way analysis of variance was run to test the significance of the fertilizers, application form and doses. The Shapiro-Wilk test was performed to test the residuals for normal distribution. Multiple comparisons were made using the Tukey's Test (P < 0.05)

3. Results and discussion

3.1. Solubility of biochar-based fertilizers

The relative percentages of total P in soluble fractions are shown in Figure 1. Addition of P sources and MgO strongly decreased the water-soluble P_2O_5 of BBFs to 2% and 1% of the total P_2O_5, when impregnated with TSP and H_3PO_4, respectively. In contrast, the relative amount of citric acid and NAC+H_2O soluble P_2O_5 were similar to TSP, showing that mineral additives added to the feedstock for BBF production promoted change only for the fertilizers P water solubility.
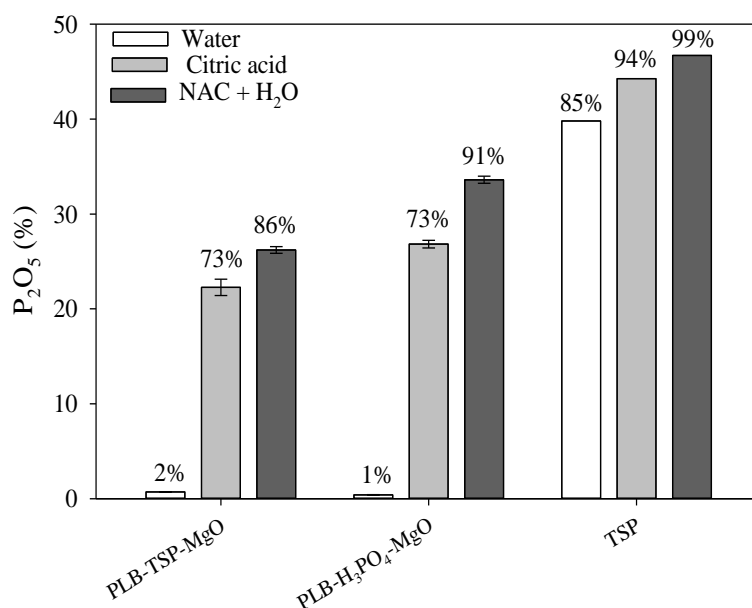
Figure 1. Water, citric acid and neutral ammonium citrate + water (NAC + H_2O) soluble P_2O_5 contents from the biochar-based fertilizers and TSP. The error bars present the standard error of the mean (n = 3). Each of the contents related to the soluble P fractions were relativized individually in relation to total P according to equation: Soluble P index (%) = ($\frac{\text{soluble P content}}{\text{total P content}}$) x 100. Total P of the fertilizers were adapted from Lustosa Filho et al. (Lustosa Filho et al., 2017).

The formation of water-insoluble P compounds, such as calcium pyrophosphate ($Ca_2P_2O_7$) and magnesium pyrophosphate ($Mg_2P_2O_7$) might explain the low water-soluble P percentage for the BBFs (Lustosa Filho et al., 2017). Low solubility of P in water, it not decreasing the solubility in NAC+H_2O for BBFs, is an effective strategy for avoiding rapid P sorption and the low reversibility of P bonding to Al and Fe(hydr)oxides), especially in acidic and highly weathered soils, such as those prevailing in Brazil and tropical regions (Abdala et al., 2015; Novais and Smyth, 1999; Teixeira et al., 2016). This effect of reducing P solubility in water might be particularly beneficial for Brazilian tropical soils (Maluf et al., 2018), where P sorption can be as high as 2,000 mg

kg^{-1} at the 0.20 m soil layer (Novais and Smyth, 1999). Therefore, use of BBFs with lower P water solubility might increase P use efficiency by plants when applied to soils of high P sorption capacity (Prochnow et al., 2006), mainly for perennial crops due to the response to slow P-release rate throughout the growth season (Lustosa Filho et al., 2017).

3.2. Phosphorus diffusion

Phosphorus diffusion assessed by the visualization test showed large differences among treatments (Figures 2 and 3). The visualization technique clearly distinguished the fast P release of TSP from the slow P release from PLB-H$_3$PO$_4$-MgO and PLB-TSP-MgO. In the TSP treatment, P diffusion stabilizes after 1 day, as observed from the initial radius of the P diffusion zone (Figure 2), which can be attributed to saturation of the sorption sites that limits further movement of P in soil (Degryse et al., 2017). In this diffusion zone, P concentration in soil solution exceeds a threshold value estimated to be around 0.3 mg L^{-1} (Degryse and McLaughlin, 2014). In contrast, the diffusion for the PLB-H$_3$PO$_4$-MgO and PLB-TSP-MgO treatments was slower and proceeded more gradually. However, the radius of P diffusion zone for PLB-H$_3$PO$_4$-MgO was similar to TSP after 28 days, while for PLB-TSP-MgO, it was always smaller as compared to the other fertilizers up to 42 days (Figure 2).

The relative color intensity decreased over time for TSP and this effect was not observed for TSP-PLB-MgO and TSP-H$_3$PO$_4$-MgO probably due to the gradual and constant release of P (Figure 3). Everaert et al. (2017) evaluated the agronomic effectiveness of granulated and powdered layered double hydroxides (LDH) relative to struvite and MAP and also observed a decrease in color intensity over time of the visualized P diffusion zone, which was attributed to a decrease in P concentration in the solution due to the ongoing diffusion and fixation reactions (Degryse and McLaughlin, 2014; Everaert et al., 2017).
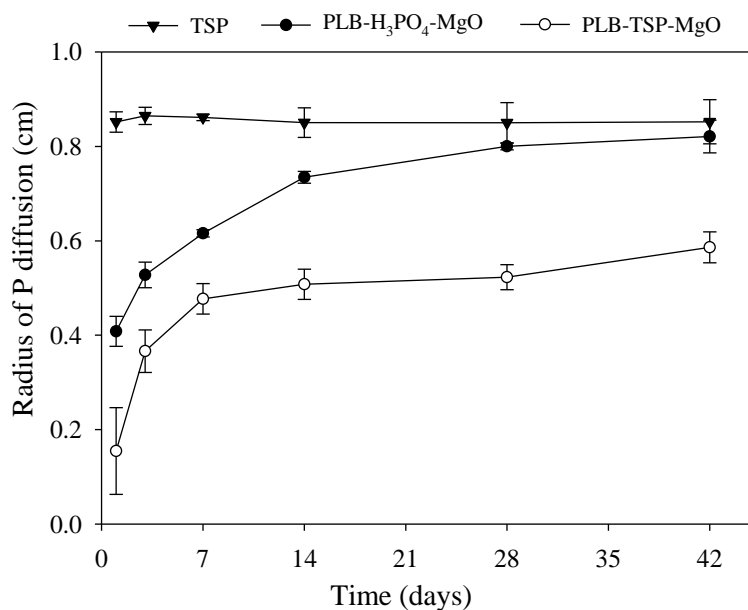
Figure 2. Radius of the P diffusion zone as a function of incubation time for the granular TSP, PLB-H$_3$PO$_4$-MgO and PLB-TSP-MgO fertilizers. The error bars present the standard error of the mean (n = 4).

The reactions that occur when a highly water-soluble fertilizer granule (e.g. TSP) is applied to soil are summarized by Hedley and McLaughlin (2005). The first reaction is hydration of the granule through water transfer from the soil or atmosphere. The dissolution of the hygroscopic granule form a P-saturated zone immediately adjacent to the granule, in which the P sorption capacity of the soil is exceeded and precipitates of P form with the metal ions (Khatiwada et al., 2012; Teixeira et al., 2016). In acidic soils, in addition to Fe-P and Al-P precipitates, Ca-P can also be formed, which limits P fertilizer availability (Khatiwada et al., 2012; McLaughlin et al., 2011). Further away from the fertilizer granule, a P-unsaturated zone exists in which the soil P sorption capacity is not exceeded. In this P-unsaturated zone, P adsorption by soil minerals is dominant, thus the increase of contact time with Fe and Al (hydr)oxides drastically reduce the desorption (Guedes et al., 2016). Therefore, slow-release P sources, such as BBFs, are less

prone to this problem due to the continuous release of P, which can better meet plant demands and avoid soil P sorption.
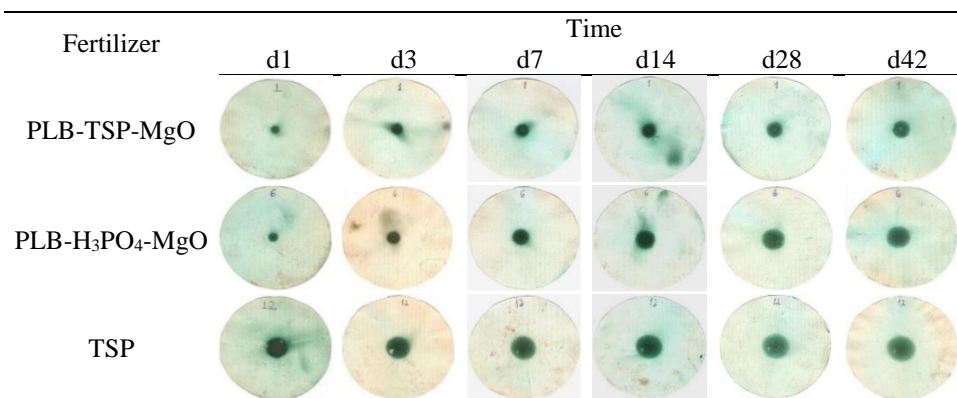

Figure 3. P diffusion zone visualized at 1, 3, 7, 14, 28 and 42 days after the application of granular fertilizers.

The pH and resin P results of soil sampled at two distances around the application site of the granule after 42 days of incubation are presented in Table 2. The BBFs caused significant increase in soil pH around the granules (< 8 mm). The highest increase in soil pH was observed for the PLB-TSP-MgO treatment, which was statistically equivalent to that verified for PLB-H_3PO_4-MgO. There was no significant difference between the TSP and PLB-H_3PO_4-MgO treatment. The soil pH measured out of the diffusion zone (> 8 mm) did not differ among treatments. Changes of pH in the soil around the application point of the fertilizer granule have been previously reported (Degryse et al., 2017; Everaert et al., 2017; Montalvo et al., 2014). The decrease of soil pH has been attributed to the acidity of the TSP fertilizer (Degryse et al., 2013; Lustosa Filho et al., 2017) and the increase of soil pH occurs due to the alkaline nature of the fertilizers (Benício et al., 2017; Everaert et al., 2017). In addition, in soils rich in variable charge minerals, such as in the present study (Oxisol), sorption of P on hydroxide groups of Al and Fe can cause release of hydroxyls and hence an increase in soil pH (Stoop, 1983). In the present study, most likely the alkaline nature of BBFs has

directly contributed to increased soil pH around the application point, mainly in the soil incubated with PLB-TSP-MgO granules.

Table 2. Soil pH and resin P concentrations at the end of the 42-day incubation period with granular fertilizer applications.

Fertilizer	pH		Resin P (mg kg^{-1})	
	<8 mm	>8 mm	<8 mm	>8 mm
PLB-H$_3$PO$_4$-MgO	5.7 ± 0.13 [ab]	5.5 ± 0.05 [a]	439 ± 14 [b]	12.2 ± 1.1 [b]
PLB-TSP-MgO	6.0 ± 0.21 [a]	5.4 ± 0.26 [a]	302 ± 12 [c]	13.9 ± 0.5 [b]
TSP	5.3 ± 0.04 [b]	5.5 ± 0.14 [a]	667 ± 20 [a]	19.8 ± 1.3 [a]

Values are mean (n = 4) ± standard error. Mean values followed by the same letter in the column do not differ significantly (Tukey's test, p<0.05).

Levels of resin P after 42 days of incubation were in the following order: TSP > PLB-H$_3$PO$_4$-MgO > PLB-TSP-MgO in the diffusion zone (<8 mm) and were much higher than out of the diffusion zone (>8 mm) (Table 2), which shows the limited diffusion of P in clayey and weathered soils such as the one of the present study. Considering only the diffusion zone, for each mg kg^{-1} of available P by resin, 4.3, 2.7 and 1.1 μg P were released from the granules for TSP, PLB-H$_3$PO$_4$-MgO and PLB-TSP-MgO, respectively. The soil of this study has high clay and high content of Fe and Al oxides, which are key factors in controlling P sorption and diffusion in soils (Freese et al., 1992; Montalvo et al., 2014). Therefore, the fast release of P from TSP followed by the increase in the contact time may reduce P availability due to rapid sorption and low reversibility of the bonding of phosphate ions with Al and Fe (oxy)hydroxides.

After 42 days of incubation, the residual P in the fertilizers granules were 64%, 85% and 96% for TSP, PLB-H$_3$PO$_4$-MgO and PLB-TSP-MgO, respectively (Figure S2), which is a result of the slow-release process of the BBFs that might increase P use efficiency by crops in high P-fixing capacity soils (Lustosa Filho et al., 2017).

3.3. Plant experiment

The analysis of variance shows that fertilizers sources, application form, and P dose of BBFs affected plant responses and soil conditions after cultivation ($P < 0.01$) (Table S1). The interaction among fertilizers, application form and P dose was only significant ($P < 0.05$) for resin P and Mg^{2+} in soil after maize cultivation (Figure 4a and b). The BBFs applied in powder form caused an increase in soil pH after cultivation as compared to the pH of soil fertilized with TSP (Figure 4a). When the fertilizers were applied in granular form, there was a slight increase in soil pH cultivated with PLB-TSP-MgO and TSP. For TSP, there was no significant difference in soil pH between powder and granular form (Figure 4a), as well as for P doses (Figure 4b). In contrast, for BBFs, soil pH was higher for the powder than for granule treatments (Figure 4a) and increased with increasing P doses (Figure 4b). This capacity of BBFs to increase soil pH is especially significant in acid tropical soils, since phosphate sorption is reduced and availability to crops is enhanced (Bernardo et al., 2018; Jiang et al., 2015; Lustosa Filho et al., 2017). Moreover, an increase in soil pH might release phosphate anions that still are weakly bound to goethite and kaolinite (Devau et al., 2010).
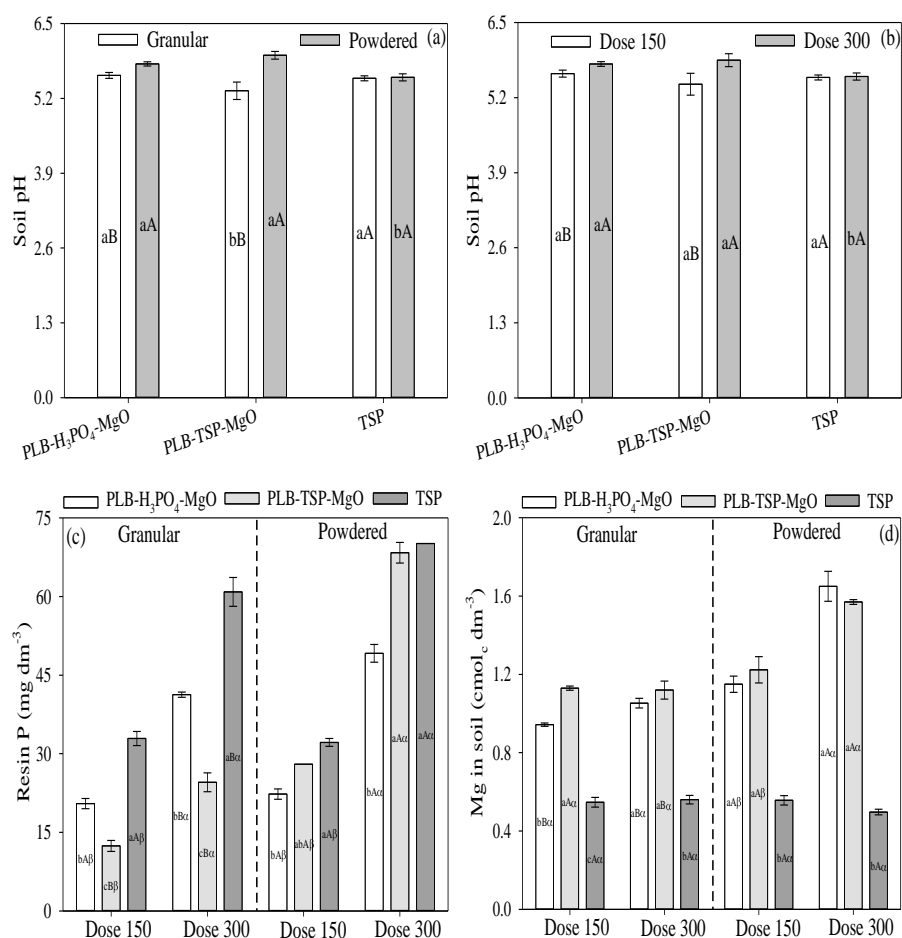
Figure 4. Soil pH (a and b), soil resin P (c) and available Mg in soil (d) after maize cultivation in response to different phosphate fertilizer type, doses and application form (powdered or granule) in an Oxisol. Means followed by the same letter are not statistically different (Tukey's Test, P < 0.05); figure a and b: lower case letters compare the fertilizers within each application form or dose; upper case letters compare the application form or dose within each fertilizer; the error bars present the standard error of the mean (n = 6). Figure c and d: lower case letters compare the fertilizers within each application form and dose; upper case letters compare each fertilizer within the same dose under different forms of application; greek letters compare each fertilizer within the same form of application in the different doses; the error bars present the standard error of the mean (n = 3).

There was a significant increase in resin P in soil with increasing doses of all fertilizers applied in both granular or powder form (Figure 4c). Over time, however, these values decrease due to P sorption by minerals of the clay fraction, especially Fe and Al (hydr)oxides (Guedes et al., 2016; Novais and Smyth, 1999). There was no significant difference ($P < 0.05$) in resin P between the powdered TSP and PLB-TSP-MgO treatments in any dose (Figure 4c). At dose 150 mg kg^{-1} P, when PLB-TSP-MgO was applied in powder form, resin P was higher than in the granular form, while for dose 300 mg kg^{-1}, the resin P was higher when the fertilizers were applied in powdered form when compared to granular form. Regardless of the application form, there was an increase in resin P with increasing P doses. The differences in soil P resin between PLB-TSP-MgO and TSP fertilizers applied in powdered form were lower when compared to the differences observed for granular treatments, which is attributed to the higher contact area between soil and powdered materials, facilitating dissolution and ion-exchange processes (Everaert et al., 2017). Additionally, the high P availability by resin for powdered PLB-TSP-MgO might be primarily related to the liming effect of this material (Figure 4a).

The anion exchange resin was proposed as a potentially useful test for characterizing P bioavailability in soils fertilized with P-rich biochars (T. Wang et al., 2014). However, investigations in a wider range of modified biochars and soils conditions are needed to confirm its effectiveness. Anionic resin can underestimate available P to plants, particularly for perennials, for not solubilizing forms of P-Ca, which can be solubilized by some plants due to rhizosphere acidification or by high Ca-absorption (Freitas et al., 2013). Our BBFs have low solubility P compounds, such as $Mg_2P_2O_7$ in PLB-H$_3$PO$_4$-MgO and hydroxyapatite [$Ca_{10}(OH)_2(PO_4)_6$] in PLB-TSP-MgO, which might be solubilized by plants and not accessed by the anionic resin.

In general, there was a significant ($P < 0.05$) increase in available Mg^{2+} in soil after cultivation when BBFs were applied compared to TSP, regardless of the P dose or application form (Figure 4d). Among the BBFs, PLB-TSP-MgO showed the highest level of available Mg^{2+} in soil at dose 150 mg kg^{-1} applied in the granular form, probably due to low biomass yield in this treatment (discussed later) and the lowest Mg uptake (Figure S3). When the BBFs were applied in the granular form there was no significant difference ($P < 0.05$) between doses for available Mg^{2+} in soil, however, when applied in powder form there was a higher level of available Mg^{2+} at 300 mg kg^{-1} P (Figure 4d). Likewise, at 300 mg kg^{-1} P, Mg uptake in powdered BBFs was higher than the TSP treatment (Figure S3a). In our previous study, we also observed that MgO-treated BBFs increased the residual level of exchangeable Mg^{2+} in soil (Lustosa Filho et al., 2017). This residual Mg^{2+} content can be extremely important for subsequent cultivations in strongly weathered soils from Brazil, since 90% of Cerrado soils has low levels (<0.5 $cmol_c$ dm^{-3}) and 55% extremely low levels (<0.1 $cmol_c$ dm^{-3}) of exchangeable Mg^{2+} (Lopes and Guilherme, 2016).

The shoot dry matter yield and P uptake for all treatments are shown in Figure 5. Regardless of the P source, dose or application form, the biomass yield was much higher in all treatments when compared to the control without P (0.5 g $plant^{-1}$) due to very low soil available P (0.41 mg dm^{-3}). The BBFs showed shoot dry matter yield equivalent to TSP treatments, except for PLB-TSP-MgO applied in granular form (Figure 5a) which was lower. For BBFs, powdered treatment showed higher shoot dry matter yield when compared to the granular form (Figure 5a). P uptake was higher in powder treatments when compared to granular treatments regardless of the P source or dose (Figure 5c and d).
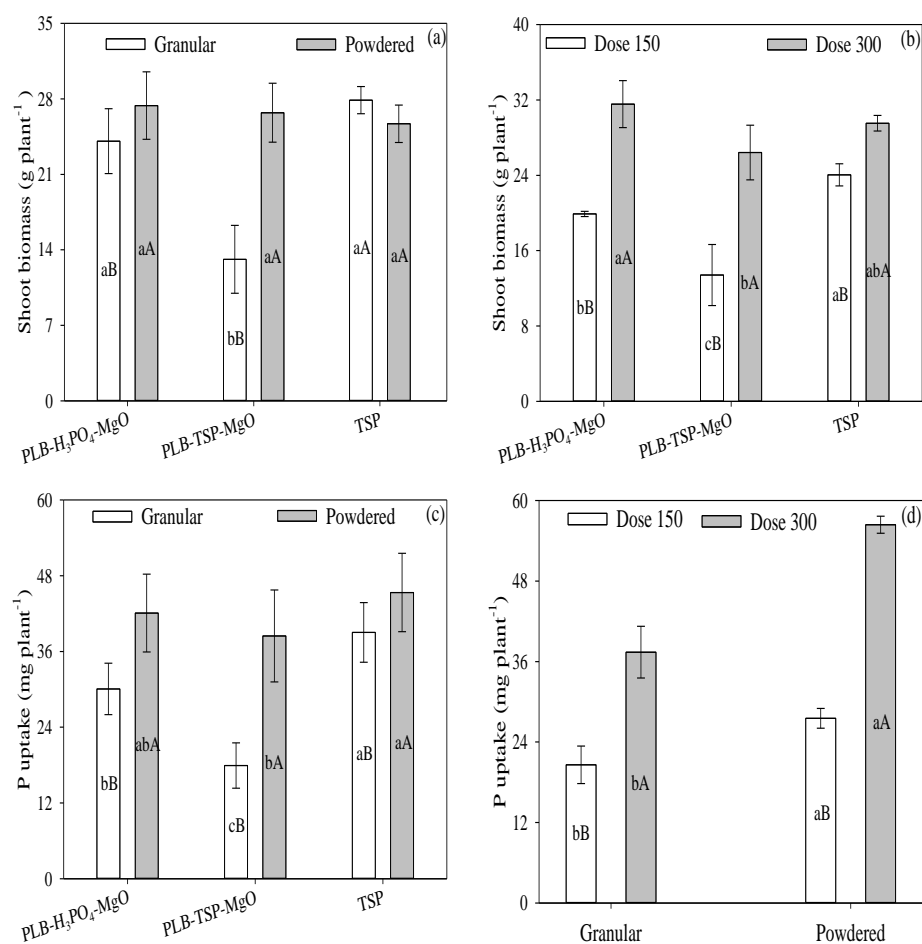
Figure 5. Shoot biomass yield (a and b) and P uptake by maize (c and d) in response to different P sources, doses and application form (powder or granule) in an Oxisol. Means followed by the same letter are not statistically different (Tukey's test, $P < 0.05$); lower case letters compare the fertilizers within each application form or dose; upper case letters compare the application form or dose within each fertilizer; the error bars present the standard error of the mean (n = 6).

These results demonstrated that BBFs applied in powder form were able to supply P to maize in a short time similarly to a soluble P fertilizer (TSP). Additionally, BBFs applied in powder form showed relative agronomic effectiveness higher than TSP in 12% and 18% for PLB-TSP-MgO and PLB-

H_3PO_4-MgO, respectively, at a dose of 300 mg kg^{-1} P (Figure 6a). However, when the BBFs were used in granular form, only PLB-H_3PO_4-MgO had an relative agronomic effectiveness equivalent to TSP at 300 mg kg^{-1} P dose and showed much lower relative agronomic effectiveness (especially PLB-TSP-MgO) at 150 mg kg^{-1} P dose. This low relative agronomic effectiveness occurred due to the slow-release characteristic of BBFs and the high P demand of maize. The fertilizers granules did not dissolve during the 35-day pot experiment and showed total remaining P of 84% and 86% for PLB-H_3PO_4-MgO and PLB-TSP-MgO, respectively, which were greater than for TSP (60%), considering the P dose 300 mg kg^{-1} (Figure 6). This result suggests that BBFs has a higher potential P residual value for succeeding crops than soluble fertilizers.
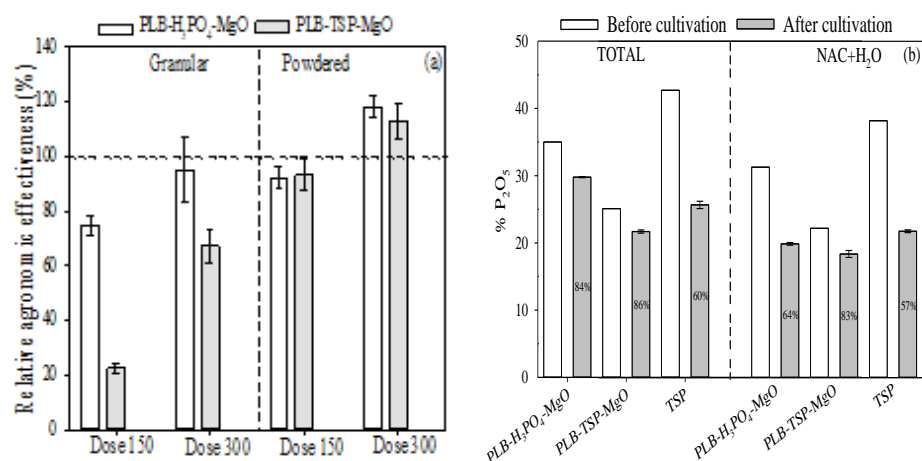
Figure 6. Relative agronomic effectiveness (a) and total and soluble phosphorus content in neutral ammonium citrate + water (NAC+H_2O) remaining in the granule (b) after five weeks of growth maize. Percentage in the bars indicates how much of the total P remained in the granule after cultivation. The error bars present the standard error of the mean (n = 3).

The results demonstrated that the release profile shown by granular PLB-H_3PO_4-MgO is desirable for a smart fertilizer, since the shoot dry matter yield was equivalent to TSP and maintained a significant fraction of P protected from

interactions with the soil (40% more of P in the granule compared to TSP). The PLB-H_3PO_4-MgO granule was able to preserve phosphate, enabling a release of P to the soil over longer periods and hence, available for future harvests. This pot trial data need confirmation with long-term field data. However, if BBFs are proved of higher efficiency, they might be an alternative for organomineral fertilizer production, which help to recycle and add value to organic residues (e.g. poultry litter) and reduce the pressure on finite reserves of phosphate rock.

4. Conclusions

A biochar-based slow-release P fertilizer was developed and its patterns of solubility, diffusion in soil and P uptake and efficiency of use by maize were assessed and compared to a soluble P fertilizer. The addition of P sources and MgO to poultry litter prior to pyrolysis had a drastic effect in reducing P water solubility of BBFs (without compromising the solubility in NAC+H_2O), enabling potential P availability in a high P-fixing soil over longer periods. The visualization method showed that the P diffusion process of BBFs in soil is slower than TSP, which is a characteristic of slow-release fertilizers. The soil application of BBFs in powder form has similar agronomic effectiveness as soluble fertilizer, probably due to fast dissolution and the liming effect, being the recommended for PLB-TSP-MgO. The slow release behavior of granular PLB-H_3PO_4-MgO did not compromise P uptake during early growth of maize, which performed equivalent to TSP. Positive impacts on fertilizer P recovery by maize were obtained when calculating the relative small proportion (up to 16%) of granular PLB-H_3PO_4-MgO that actually dissolved during the growing season of the crop, leaving P available for future harvests and thus contributing to increased crop P use efficiency.

Acknowledgment

The authors are grateful to Eduardo Lopes Cancellier for technical assistance for the P diffusion visualization analysis. We are also grateful to Carlos Alberto Silva from Federal University of Lavras for helpful discussions on experimental design.

Conflict of interest

The authors have declared no conflict of interest.

Appendix A. Supplementary data

Supplementary information regarding production of the biochar-based fertilizers granules, phosphorus content remaining in the granule after incubation, Mg plant uptake and summary of analysis of variance can be found in the online version.

REFERENCES

Abdala, D.B., Northrup, P.A., Arai, Y., Sparks, D.L., 2015. Surface loading effects on orthophosphate surface complexation at the goethite/water interface as examined by extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. J. Colloid Interface Sci. 437, 297–303. doi:10.1016/j.jcis.2014.09.057

Assaaoudi, H., Fang, Z., Butler, I.S., Ryan, D.H., Kozinski, J.A., 2007. Characterization of a new magnesium hydrogen orthophosphate salt, Mg3.5H2(PO4)3, synthesized in supercritical water. Solid State Sci. 9, 385–393. doi:10.1016/j.solidstatesciences.2007.03.015

Bekiaris, G., Peltre, C., Jensen, L.S., Bruun, S., 2016. Spectrochimica Acta Part A : Molecular and Biomolecular Spectroscopy Using FTIR-photoacoustic spectroscopy for phosphorus speciation analysis of biochars 168, 29–36. doi:http://dx.doi.org/10.1016/j.saa.2016.05.049

Benício, L.P.F., Constantino, V.R.L., Pinto, F.G., Vergütz, L., Tronto, J., da Costa, L.M., 2017. Layered Double Hydroxides: New Technology in Phosphate Fertilizers Based on Nanostructured Materials. ACS Sustain. Chem. Eng. 5, 399–409. doi:10.1021/acssuschemeng.6b01784

Bernardo, M.P., Guimarães, G.G.F., Majaron, V.F., Ribeiro, C., 2018. Controlled Release of Phosphate from Layered Double Hydroxide Structures: Dynamics in Soil and Application as Smart Fertilizer. ACS Sustain. Chem. Eng. 6, 5152–5161. doi:10.1021/acssuschemeng.7b04806

Brasil, 2014. Ministério da Agricultura, Pecuária e Abastecimento. Manual de métodos analíticos oficiais para fertilizantes e corretivos. (Org.), Murilo Carlos Muniz Veras. MAPA/SDA/CGAL, Brasília- DF.

Cordell, D., Drangert, J.O., White, S., 2009. The story of phosphorus: Global food security and food for thought. Glob. Environ. Chang. 19, 292–305. doi:10.1016/j.gloenvcha.2008.10.009

Degryse, F., Ajiboye, B., Armstrong, R.D., McLaughlin, M.J., 2013. Sequestration of Phosphorus-Binding Cations by Complexing Compounds is not a Viable Mechanism to Increase Phosphorus Efficiency. Soil Sci. Soc. Am. J. 77, 2050–2059. doi:10.2136/sssaj2013.05.0165

Degryse, F., Baird, R., da Silva, R.C., McLaughlin, M.J., 2017. Dissolution rate and agronomic effectiveness of struvite fertilizers – effect of soil pH, granulation and base excess. Plant Soil 410, 139–152. doi:10.1007/s11104-016-2990-2

Degryse, F., McLaughlin, M.J., 2014. Phosphorus Diffusion from Fertilizer: Visualization, Chemical Measurements, and Modeling. Soil Sci. Soc. Am. J. 78, 832–842. doi:10.2136/sssaj2013.07.0293

Devau, N., Le Cadre, E., Hinsinger, P., Gérard, F., 2010. A mechanistic model for understanding root-induced chemical changes controlling phosphorus availability. Ann. Bot. 105, 1183–1197. doi:10.1093/aob/mcq098

Embrapa, 2011. Manual de métodos de análise de solo, 2 edição. ed. Rio de Janeiro.

Everaert, M., Degryse, F., McLaughlin, M.J., De Vos, D., Smolders, E., 2017. Agronomic Effectiveness of Granulated and Powdered P-Exchanged Mg-Al LDH Relative to Struvite and MAP. J. Agric. Food Chem. 65, 6736–6744.

doi:10.1021/acs.jafc.7b01031

Everaert, M., Warrinnier, R., Baken, S., Gustafsson, J.P., De Vos, D., Smolders, E., 2016. Phosphate-Exchanged Mg-Al Layered Double Hydroxides: A New Slow Release Phosphate Fertilizer. ACS Sustain. Chem. Eng. 4, 4280–4287. doi:10.1021/acssuschemeng.6b00778

Freese, D., Zee, S.E. van der, Riemsdijk, W. Van, 1992. Comparison of different models for phosphate sorption as a function of the iron and aluminium oxides of soils. J. Soil Sci. 43, 729–738. doi:10.1111/j.1365-2389.1992.tb00172.x

Freitas, I.F. de, Novais, R.F., Villani, E.M. de A., Novais, S.V., 2013. Phosphorus Extracted By Ion Exchange Resins and Mehlich-1 From Oxisols (Latosols) Treated With Different Phosphorus Rates and Sources for Varied Soil-Source Contact Periods. Rev. Bras. Ciência do Solo 37, 667–677. doi:http://dx.doi.org/10.1590/S0100-06832013000300013

Guedes, R.S., Melo, L.C.A., Vergütz, L., Rodríguez-Vila, A., Covelo, E.F., Fernandes, A.R., 2016. Adsorption and desorption kinetics and phosphorus hysteresis in highly weathered soil by stirred flow chamber experiments. Soil Tillage Res. 162, 46–54. doi:10.1016/j.still.2016.04.018

Hedley, M., McLaughlin, M., 2005. Reactions of Phosphate Fertilizers and By-Products in Soils, in: Sims, J.T., Sharpley, A.N. (Eds.), Phosphorus: Agriculture and the Environment. Agronomy Monograph Publisher, Madison, pp. 181–252. doi:10.2134/1980.roleofphosphorus.c12

Iriarte-Velasco, U., Sierra, I., Zudaire, L., Ayastuy, J.L., 2016. Preparation of a porous biochar from the acid activation of pork bones. Food Bioprod. Process. 98, 341–353. doi:10.1016/j.fbp.2016.03.003

Jiang, J., Yuan, M., Xu, R., Bish, D.L., 2015. Mobilization of phosphate in variable-charge soils amended with biochars derived from crop straws. Soil Tillage Res. 146, 139–147. doi:10.1016/j.still.2014.10.009

Kaudal, B.B., Chen, D., Madhavan, D.B., Downie, A., Weatherley, A., 2016. An examination of physical and chemical properties of urban biochar for use as growing media substrate. Biomass and Bioenergy 84, 49–58. doi:10.1016/j.biombioe.2015.11.012

Kennedy, L.J., Vijaya, J.J., Sekaran, G., 2004. Effect of Two-Stage Process on the Preparation and Characterization of Porous Carbon Composite from Rice Husk by Phosphoric Acid Activation. Ind. Eng. Chem. Res. 43, 1832–1838. doi:10.1021/ie034093f

Khatiwada, R., Hettiarachchi, G.M., Mengel, D.B., Fei, M., 2012. Speciation of Phosphorus in a Fertilized, Reduced-Till Soil System: In-Field Treatment

Incubation Study. Soil Sci. Soc. Am. J. 76, 2006–2018. doi:10.2136/sssaj2011.0299

Li, R., Wang, J.J., Zhou, B., Awasthi, M.K., Ali, A., Zhang, Z., Lahori, A.H., Mahar, A., 2016. Recovery of phosphate from aqueous solution by magnesium oxide decorated magnetic biochar and its potential as phosphate-based fertilizer substitute. Bioresour. Technol. 215, 209–214. doi:10.1016/j.biortech.2016.02.125

Lopes, A.S., Guilherme, L.R.G., 2016. A Career Perspective on Soil Management in the Cerrado Region of Brazil. Adv. Agron. 137, 1–72. doi:10.1016/bs.agron.2015.12.004

Lustosa Filho, J.F., Penido, E.S., Castro, P.P., Silva, C.A., Melo, L.C.A., 2017. Co-Pyrolysis of Poultry Litter and Phosphate and Magnesium Generates Alternative Slow-Release Fertilizer Suitable for Tropical Soils. ACS Sustain. Chem. Eng. 5, 9043–9052. doi:10.1021/acssuschemeng.7b01935

Maluf, H.J.G.M., Silva, C.A., Morais, E.G. de, Paula, L.H.D. de, 2018. Is Composting a Route to Solubilize Low-Grade Phosphate Rocks and Improve MAP-Based Composts? Rev. Bras. Ciência do Solo 42, 1–17. doi:http://dx.doi.org/10.1590/18069657rbcs20170079

McLaughlin, M.J., McBeath, T.M., Smernik, R., Stacey, S.P., Ajiboye, B., Guppy, C., 2011. The chemical nature of P accumulation in agricultural soils-implications for fertiliser management and design: An Australian perspective. Plant Soil 349, 69–87. doi:10.1007/s11104-011-0907-7

Montalvo, D., Degryse, F., McLaughlin, M.J., 2014. Fluid Fertilizers Improve Phosphorus Diffusion but not Lability in Andisols and Oxisols. Soil Sci. Soc. Am. J. 78, 214–224. doi:10.2136/sssaj2013.02.0075

Movasaghi, Z., Rehman, S., ur Rehman, D.I., 2008. Fourier Transform Infrared (FTIR) Spectroscopy of Biological Tissues. Appl. Spectrosc. Rev. 43, 134–179. doi:10.1080/05704920701829043

Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27, 31–36. doi:10.1016/S0003-2670(00)88444-5

Nadia, F.O., Xiang, L.Y., Lie, L.Y., Chairil Anuar, D., Mohd Afandi, M.P., Azhari Baharuddin, S., 2015. Investigation of physico-chemical properties and microbial community during poultry manure co-composting process. J. Environ. Sci. 28, 81–94. doi:10.1016/j.jes.2014.07.023

Novais, R.F., Neves, J.C.L., Barros, N.F., 1991. Ensaio em ambiente controlado, in: Oliveira, A.J., Garrido, W.E., Araújo, J.D., Lourenço, S. (Eds.), Métodos

de Pesquisa Em Fertilidade Do Solo. Embrapa-SEA, Brasília, pp. 189–253.

Novais, R.F., Smyth, T.J., 1999. Fósforo em solo e planta em condições tropicais. Universidade Federal de Viçosa, Viçosa.

Prochnow, L.I., Quispe, J.F.S., Francisco, E.A.B., Braga, G., 2006. Effectiveness of phosphate fertilizers of diffrent water solubilities in relation to soil phophorus adsorption. Sci. Agric. 63, 333–340. doi:10.1590/S0103-90162006000400004

R core Team, 2016. R: A language and environment for statistical computing.

Sakadevan, K., Bavor, H.J., 1998. Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems. Water Res. 32, 393–399. doi:10.1016/S0043-1354(97)00271-6

Sarkar, A., Biswas, D.R., Datta, S.C., Roy, T., Moharana, P.C., Biswas, S.S., Ghosh, A., 2018. Polymer coated novel controlled release rock phosphate formulations for improving phosphorus use efficiency by wheat in an Inceptisol. Soil Tillage Res. 180, 48–62. doi:10.1016/j.still.2018.02.009

Schwertmann, U., 1964. Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung. Zeitschrift für Pflanzenernährung, Düngung, Bodenkd. 105, 194–202. doi:10.1002/jpln.3591050303

Stoop, W.A., 1983. Phosphate adsorption mechanisms in oxidic soils: implications for P-availability to plants. Geoderma 31, 57–69. doi:https://doi.org/10.1016/0016-7061(83)90083-6

Talboys, P.J., Heppell, J., Roose, T., Healey, J.R., Jones, D.L., Withers, P.J.A., 2016. Struvite: a slow-release fertiliser for sustainable phosphorus management? Plant Soil 401, 109–123. doi:10.1007/s11104-015-2747-3

Teixeira, R. da S., Silva, I.R. da, Sousa, R.N. de, Mattiello, E.M., Soares, E.M.B., 2016. Organic acid coated-slow-release phosphorus fertilizers improve P availability and maize growth in a tropical soil. J. soil Sci. plant Nutr. 16, 1097–1112. doi:10.4067/S0718-95162016005000081

van Dijk, K.C., Lesschen, J.P., Oenema, O., 2016. Phosphorus flows and balances of the European Union Member States. Sci. Total Environ. 542, 1078–1093. doi:10.1016/j.scitotenv.2015.08.048

van Raij, B., Quaggio, J.A., da Silva, N.M., 1986. Extraction of phosphorus, potassium, calcium, and magnesium from soils by an ion-exchange resin procedure. Commun. Soil Sci. Plant Anal. 17, 547–566. doi:10.1080/00103628609367733

Walkley, A., Black, I.A., 1934. An examination of the degtjareff method for

determining soil organic matter, and a proposed modification of the chromic acid titration method. Soil Sci. 37, 29–38. doi:10.1097/00010694-193401000-00003

Wang, T., Camps-Arbestain, M., Hedley, M., 2014. The fate of phosphorus of ash-rich biochars in a soil-plant system. Plant Soil 375, 61–74. doi:10.1007/s11104-013-1938-z

Wang, Y., Yin, R., Liu, R., 2014. Characterization of biochar from fast pyrolysis and its effect on chemical properties of the tea garden soil. J. Anal. Appl. Pyrolysis 110, 375–381. doi:10.1016/j.jaap.2014.10.006

Warren, G.P., 1994. Influence of soil properties on the response to phosphorus in some tropical soils: I. Initial response to fertilizer. Eur. J. Soil Sci. 45, 337–344. doi:10.1111/j.1365-2389.1994.tb00517.x

Withers, P.J.A., Sylvester-Bradley, R., Jones, D.L., Healey, J.R., Talboys, P.J., 2014. Feed the Crop Not the Soil: Rethinking Phosphorus Management in the Food Chain. Environ. Sci. Technol. 48, 6523–6530. doi:10.1021/es501670j

Zhao, L., Cao, X., Zheng, W., Kan, Y., 2014. Phosphorus-Assisted Biomass Thermal Conversion: Reducing Carbon Loss and Improving Biochar Stability. PLoS One 9, e115373. doi:10.1371/journal.pone.0115373

Zhao, L., Cao, X., Zheng, W., Scott, J.W., Sharma, B.K., Chen, X., 2016. Copyrolysis of Biomass with Phosphate Fertilizers To Improve Biochar Carbon Retention, Slow Nutrient Release, and Stabilize Heavy Metals in Soil. ACS Sustain. Chem. Eng. 4, 1630–1636. doi:10.1021/acssuschemeng.5b01570

Supplementary Material

Diffusion and phosphorus solubility of biochar-based fertilizer: visualization, chemical assessment and availability to plants

José Ferreira Lustosa Filho[a*], Cristiane Francisca Barbosa[a], Jefferson Santana da Silva Carneiro[a], Leônidas Carrijo Azevedo Melo[a*]

[a] Soil Science Department, Federal University of Lavras, 37200-000, Lavras, MG, Brazil;

[*] Corresponding author at: Soil Science Department, Federal University of Lavras, 37200-000, Lavras, MG, Brazil.
E-mail address: leonidas.melo@dcs.ufla.br (Leônidas C. A. Melo),
filhoze04@hotmail.com (José F. Lustosa Filho)

Figure S1. Stainless steel pastillator used for the production of the biochar-based fertilizer granules.
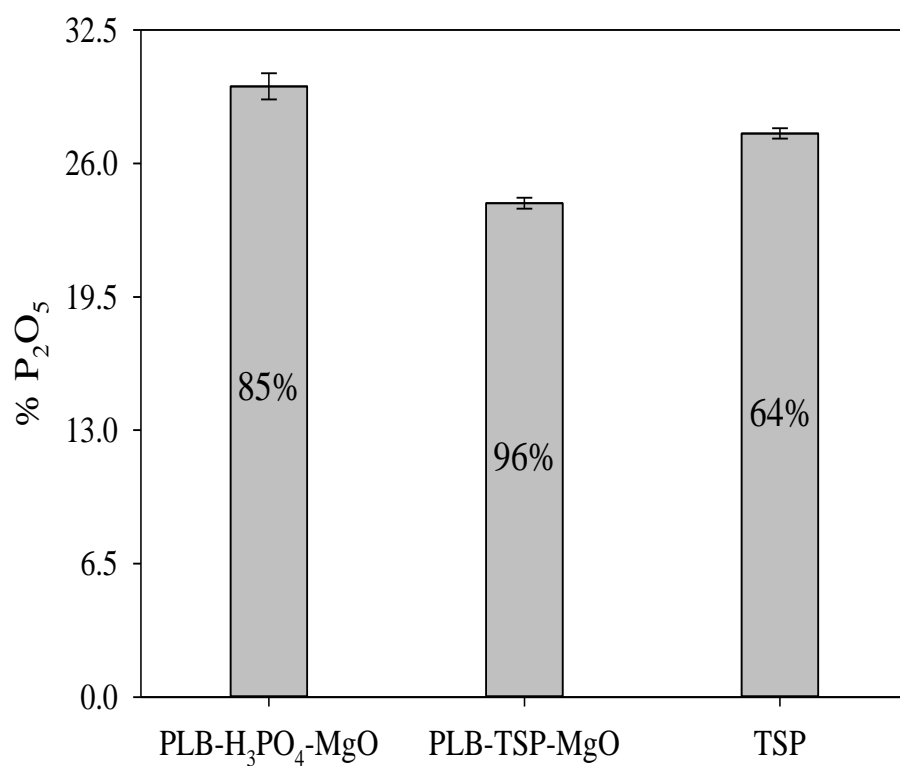
Figure S2. Remaining P_2O_5 content in the granule after 42-day incubation as related to initial P_2O_5 content. The error bars represent the standard error of the mean (n = 4).
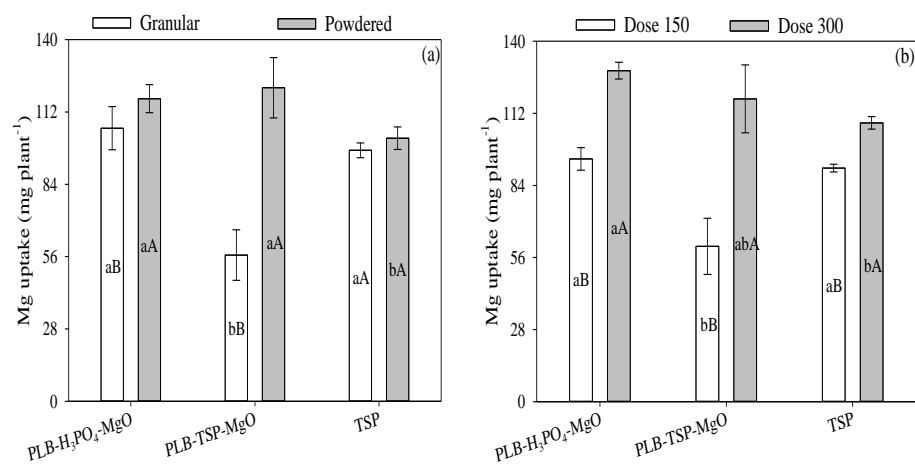
Figure S3. Mg uptake (a and b) by maize in response to different P sources, doses and application form (powder or granule) in an Oxisol. Means followed by the same letter are not statistically different (Tukey's test, p<0.05); lower case letters compare the fertilizers within each application form or dose; upper case letters compare the application form or dose within each fertilizer; the error bars present the standard error of the mean (n = 6).

Table S1. Summary of the analysis of variance.

Source of Variation	[1]DF	Shoot biomass	P uptake	Mg uptake	Soil pH	Resin P	Soil Mg
		---------------------------------- Mean Square ----------------------------------					
Fertilizer (F)	2	164.285*	590.362*	1514.824*	0.061**	986.380*	1.916*
Application form (AF)	1	216.482*	1512.562*	6548.046*	0.694*	1505.957*	0.418*
Dose (D)	1	909.022*	4690.652*	11905.720*	0.360*	6900.071*	0.202*
F x AF	2	192.785*	153.483*	3255.035*	0.284*	633.761*	0.145*
F x D	2	48.423*	8.024ns	1194.594*	0.122*	67.438*	0.082*
AF x D	1	7.821ns	327.429*	2.434ns	0.028ns	490.770*	0.113*
F x AF x D	2	7.830ns	19.856ns	124.035ns	0.042ns	104.884*	0.051*
Without P x factorial	1	1549.039*	3406.484*	26418.68*	1.111*	3434.654*	0.0368**

* 1% of significance; ** 5% of significance; ns: not significant by F test. [1]Degrees of freedom

CHAPTER 3

Article prepared according to guidelines of the journal Soil & Tillage Research (preliminary version)

Ageing of biochar-based fertilizers in soils: effects on phosphorus pools and availability to *Urochloa brizantha* grass

ABSTRACT

Water-soluble phosphate fertilizers swiftly release phosphorus (P) to soils, and this is typically fixed in oxide-rich, highly weathered tropical soils. The development of strategies to improve the use of this nutrient is necessary. In this study, triple superphosphate (TSP) and phosphoric acid (H_3PO_4) were pyrolyzed with and without magnesium oxide (MgO) and poultry litter to produce slow-release P biochar-based fertilizers (BBFs). A pot experiment under greenhouse conditions was performed to evaluate agronomic efficiency of BBFs compared with soluble fertilizer in an Oxisol. The treatments were incubated over a period of 100 days after the application of 25, 50, 100, and 200 mg kg^{-1} of P, plus TSP applied immediately before sowing and a control (without P) Marandu grass (*Urochloa brizantha* cv. Marandu) was cultivated in pots for three cycles of 40 days each. After the cultivation, a sequential extraction procedure was used to determine the P distribution among different P pools. The shoot dry matter yield in the first cropping cycle was, as expected, higher at the highest P rate for TSP$_{planting}$, not incubated. For the treatments that were incubated, higher shoot dry matter yield was observed in the treatment PLB-H_3PO_4-MgO, with 9% increase in the shoot dry matter when compared to TSP$_{incubation}$. In subsequent crop cycles, all BBFs promoted higher biomass yield as compared to TSP$_{planting}$. There was an increase in the labile and moderately labile P fractions in soil after cultivation with

PLB-TSP. The results suggest that BBFs can enhance P use efficiency in tropical soils in the middle- to long-term.

Keywords: Slow-release fertilizer, P use efficiency, Hedley phosphorus fractions.

1. Introduction

Phosphorus (P) is an essential nutrient for plant growth, and the relative scarcity of high-grade phosphate rock for fertilizer production it is expected to be a future constraint in agricultural systems (Gilbert, 2009; Koch et al., 2018). Brazil is one of the leading exporters of agricultural products, and consumed ca. 2.2 Tg of P as fertilizers in 2016, which represents around 10% of world consumption (Withers et al., 2018). Such large consumption of P fertilizers is needed due to the rapid immobilization of soluble inorganic P (Withers et al., 2018), in highly weathered soils rich in kaolinite and iron and aluminum (hydr)oxides that present high P sorption capacity and cause low P availability to plants (Novais e Smyth, 1999; Abdala et al., 2015; Roy et al., 2016). The phosphate rock reserves in Brazil are insufficient for the domestic fertilizer supply and, consequently there is a continued reliance on P imports. Therefore, a more efficient P use is necessary and alternative ways of P supply must be developed (Koch et al., 2018).

Alternative sources of P, such as biosolids, animal wastes and biochars have been experimented with increasing intensity over the last few decades (Wang et al., 2014; Waldrip et al., 2015; Lima et al., 2016). Brazil is the second largest producer of poultry in the world, and it is estimated that the annual volume of poultry litter generated is around 8-10 million tons/year (Dalólio et al., 2017). However, the use of poultry litter is limited to areas near to its production sites, due to the high transportation costs (Lima et al., 2016). Therefore, transformation of poultry litter is needed to facilitate recycling of nutrients, minimize environmental problems and as an alternative to prevent P losses and fixation,

increasing its fertilizer value (Lima et al., 2016; Lustosa Filho et al., 2017). Co-pyrolysis of biomass with P sources has been suggested as an alternative to obtain improved biochar-based fertilizers (BBFs) with stable C forms and slow-release P (Li et al., 2014; Zhao et al., 2014, 2016). Recently, we impregnated poultry litter with TSP and H_3PO_4 with and without magnesium oxide (MgO) aiming to produce (BBFs) (Lustosa Filho et al., 2017). We verified that maize plants fertilized with BBFs co-pyrolyzed with MgO showed high P uptake, and maize growth, and additionally the BBFs release P more gradually and increase the soil pH value (Lustosa Filho et al., 2017). Although the results were satisfactory, the comparison of this alternative P source with soluble mineral fertilizers in the long-term can result even in higher performance, since the BBFs release P more gradually during crop development and may show greater P use efficiency.

Plant P availability of low water-soluble P fertilizers, such as BBFs, is generally low in the short-term, but may increase over time due to the increased dissolution of the fertilizer (Degryse et al., 2017). In soluble fertilizers, P is released immediately upon application, but plant P availability generally decreases over time due to the conversion of soluble P to less soluble forms, as a result of reaction with soil constituents (Rivaie et al., 2008; Everaert et al., 2016), especially in acidic and highly weathered soils (Novais e Smyth, 1999; Abdala et al., 2015). The P dissolved from these fertilizers undergoes various reactions with the inorganic and organic constituents of the soil, resulting in products of varying solubility (Rivaie et al., 2008). However, the information obtained from sequential chemical fractionation developed by Hedley et al. (1982) to identify several soil Pi and Po fractions has been widely used to understand soil P transformations (Pavinato et al., 2009; Waldrip et al., 2015; Koch et al., 2018; Soltangheisi et al., 2018). Thus, the measurement of P forms in soil supplied with different fertilizers over time can provide information about P availability for future crops. However, the changes in soil P pools in weathered tropical soils following applications of

BBFs, especially the available P, after successive cropping cycles, has not been studied yet.

We hypothesized that the use of BBFs as compared to soluble P source could provide to long-term lasting P availability to plants. We aimed (i) to evaluate the effect of poultry litter impregnated with P sources (TSP and H_3PO_4) with and without MgO addition on P supply to cropping cycles of Marandu grass in a greenhouse experiment and (ii) to investigate the effect of incubation period and cropping cycles on the transformations of soil P pools (labile, moderately labile, and non-labile).

2. Materials and methods

2.1. Preparation and Production of Biochar-Based Fertilizers

Detailed information concerning biomass preparation and pyrolysis process for BBFs production and characterization can be found elsewhere (Lustosa Filho et al., 2017). Briefly, biomass was air-dried at room temperature, ground to pass through a 20-mesh sieve (1.00 mm), and mixed with TSP [$Ca(H_2PO_4)_2$] or H_3PO_4, with and without MgO addition. Phosphate sources and MgO were mixed to achieve a P/Mg molar ratio of 1:1, and the ratio of poultry litter/phosphate source was 1:0.5 (w/w) based on previous studies (Li et al., 2014; Zhao et al., 2014, 2016). After 16 h in contact with water the pretreated mixtures were oven-dried at 60 °C to a constant mass prior to pyrolysis. The treated biomass was pyrolysed at 500 °C for 2 h using a heating rate of 10 °C min^{-1} (Zhao et al., 2014). The produced BBFs were identified as follows: PLB-TSP= poultry litter biochar + TSP; PLB-TSP-MgO = poultry litter biochar + TSP + MgO; PLB-H_3PO_4= poultry litter biochar + phosphoric acid and PLB-H_3PO_4-MgO = poultry litter biochar + phosphoric acid + MgO. Selected characteristics of BBFs are provided in Table 1.

Table 1. Selected Properties of the Biochar-Based Fertilizers

Fertilizer	pH	EC	CEC	C	$P_{total,}$	Mg_{total}
		--dS m^{-1}--	cmol$_c$ kg^{-1}	-----%-----	--------g kg^{-1}--------	
PLB-TSP	4.6 ± 0.01	1.8 ± 0.04	12.4 ± 2.2	24.1 ± 0.2	118 ± 8.5	8.09 ± 0.1
PLB-H$_3$PO$_4$	2.0 ± 0.03	14 ± 0.39	15.2 ± 0.6	27.1 ± 1.3	206 ± 17	5.47 ± 0.0
PLB-TSP-MgO	9.1 ± 0.04	1.1 ± 0.08	17.5 ± 3.5	21.2 ± 0.3	124 ± 5.6	69.5 ± 0.9
PLB-H$_3$PO$_4$-MgO	6.1 ± 0.02	0.4 ± 0.02	21.6 ± 4.0	19.0 ± 0.1	162 ± 16	98.0 ± 0.9

Adapted from Lustosa Filho et al. 2017. Values are mean (n = 3) ± standard deviation; EC, electrical conductivity; CEC, cation-exchange capacity.

2.2. Greenhouse pot experiment

Phosphate fertilizers were evaluated in a greenhouse pot experiment with plants of *Urochloa* (*syn. Brachiaria) brizantha* (Hochst ex A. Rich.) Stapf cv. Marandu. Soil samples were collected from the subsurface layer (40-60 cm) of an Oxisol (Rhodic Hapludox) in Lavras, Minas Gerais, Brazil (915 m altitude, 21°13′34″ S and 44°58′31″ W), air dried and passed through a 2.0-mm sieve. The soil had very low available P concentration (0.41 mg dm^{-3}, Mehlich-1 soil test), high clay content (64%) and pH$_{water}$ of 4.8; Ca^{2+} and Mg^{2+} concentrations were 0.24 and 0.10 cmol$_c$ dm^{-3} (KCl 1 mol L^{-1} extractor), respectively. Soil organic C was 11.8 g kg^{-1} (Walkley e Black, 1934), and oxalate-extractable Fe and Al concentrations of 280 and 635 mg kg^{-1}, respectively, determined as described by Schwertmann (1964).

Three dm^3 of soil were placed into plastic bags and the soil acidity was corrected using a mixture of CaCO$_3$ and MgCO$_3$ at a Ca/Mg molar ratio of 3:1 aiming to elevate the base saturation to 70%. The samples were incubated with the carbonates for 30 days at a soil moisture content of ~ 80% of the field capacity water retention. After this period, the different P sources and doses were mixed with the whole soil volume that was again incubated for further 100 days.

The experiment was conducted in a completely randomized factorial design (6 × 5 + 1) with three replications. Six P sources (PLB-TSP, PLB-TSP-MgO,

PLB-H$_3$PO$_4$, PLB-H$_3$PO$_4$-MgO, TSP incubated and TSP applied immediately before sowing) at five P doses (25, 50, 100, 150 and 200 mg kg^{-1}), based on NAC+H$_2$O-soluble P contents and applied in powder form. Control pots without P addition were included. After the incubation, soil was air-dried, homogenized and basal nutrients were supplied for each pot at the following rates in mg kg^{-1} soil: macronutrients (100 N, 100 K, and 40 S) and micronutrients (4.0 Zn, 3.66 Mn, 1.55 Fe, 1.33 Cu, 0.81 B and 0.15 Mo), following recommendations for pot experiments (Novais et al., 1991).

Ten seeds of Marandu grass were sown in each pot and after germination the seedlings were thinned to three per pot. Plants were grown for three cropping cycles, and harvested at a height of 10 cm each 40 days, starting after the last thinning. All pots received an additional application of N and K fertilizer (100 mg kg^{-1}) via fertigation at 20 days before each cut. After harvest, grass shoots were washed with distilled water, placed into paper bags and dried at 65 °C until weight stabilization (≈72 h), weighed and milled for chemical analysis. Shoot tissues were digested using concentrated nitric and perchloric acids, and P contents were measured colorimetrically, following analytical procedures described in Murphy e Riley (1962). Phosphorus uptake by maize shoot was estimated by multiplying the P content by the respective dry mass yield.

2.3. Phosphorus Fractionation Procedure

To evaluate the influence of incubation and cultivation with Marandu grass in soil P dynamics we performed a sequential chemical fractionation as proposed by Hedley et al. (1982) and modified by Condron et al. (1985). In short, 1.5 g of soil sample was weighed into 50-mL centrifuge tubes and 30 mL of each extractant were added. The tubes were placed in a horizontal shaker and shaken at 110 rpm for 16 h. The P fractions were extracted in the following order: anion exchange resin membrane (resin-Pi fraction), 0.5 mol L^{-1} of sodium bicarbonate

(NaHCO$_3$) (NaHCO$_3$-Pi and NaHCO$_3$-Po fractions), 0.1 mol L^{-1} sodium hydroxide (NaOH) (0.1 mol L^{-1} NaOH-Pi and 0.1 mol L^{-1} NaOH-Po fractions), 1.0 mol L^{-1} of hydrochloric acid (HCl) (HCl-Pi fraction) and 0.5 mol L^{-1} of NaOH (0.5 mol L^{-1} NaOH-Pi and 0.5 mol L^{-1} NaOH-Po fractions). At each step, the suspension was centrifuged (20-30 min at 4000 rpm) and the supernatants stored for colorimetric analysis. The residues after each extraction step were washed with 30 mL of 0.5 mol L^{-1} NaCl solution to completely remove the extractant before the next fractionation step. To determine inorganic P (Pi), the organic matter was flocculated in a 10 mL subsample of the NaHCO$_3$ and NaOH extracts using 3.5 mL of 0.9 mol L^{-1} H$_2$SO$_4$. The samples were centrifuged for 15 min and the supernatant was decanted. Total P (Pt) in the alkali extracts (NaHCO$_3$-Po, 0.1 mol L^{-1} NaOH-Po and 0.5 mol L^{-1} NaOH-Po) was determined by digestion with H$_2$SO$_4$ 1:1 (acid:water) and ammonium persulfate 7.5% in an autoclave (103 kPa, 121 °C) for 2 h (USEPA - United States Environmental Protection Agency, 1971). The organic P (Po) was calculated as the difference between the concentration of Pt and Pi in each extract (Po = Pt - Pi). At the end of the sequential extraction, the remaining soil was dried at 50 °C, ground to homogenize, and digested with a mixture of concentrated H$_2$SO$_4$ + 30 % H$_2$O$_2$ and saturated magnesium chloride to extract residual P (residual-P fraction) (Brookes and Powlson, 1981). All P measurements were determined by the colorimetric method (Murphy and Riley, 1962), after pH adjustment using *p*-nitrophenol as an indicator.

Phosphorus fractions obtained by the Hedley fractionation were grouped into pools according to their plant availability as suggested by Cross and Schlesinger (1995): labile pool, including resin-Pi + NaHCO$_3$-Pi + NaHCO$_3$-Po; moderately labile pool, including 0.1 mol L^{-1} NaOH-Pi + 0.1 mol L^{-1} NaOH-Po + HCl-Pi; non-labile pool, including 0.5 mol L^{-1} NaOH-Pi + 0.5 mol L^{-1} NaOH-Po + residual-P.

2.4 Statistical Analysis

Statistical analyses were performed with the statistical software R (R core Team, 2016). Variance homogeneity and normality of data distribution were tested for each parameter before carrying out an analysis of variance (ANOVA). Data from the greenhouse experiment were analyzed for each cycle and when the interaction between P sources and doses was significant ($P < 0.05$), the effect of P doses was adjusted to linear or quadratic models for each source. Data of P fractionation were evaluated by ANOVA and the means were compared using the Tukey's Test ($P < 0.05$). Additionally, the data of the P fractionation variables and shoot dry matter yield for the higher dose of P applied were submitted to Principal Component Analysis (PCA).

3. Results and discussion

3.1 Shoots biomass and P uptake

Plant growth was very limited in the control treatment (1.5 and 4.6 g pot^{-1}, respectively in the second and third cropping cycles) due to very low soil available P (0.41 mg dm^{-3}). However, the shoot dry matter yield was significantly affected by the interaction among P doses and P sources for all cropping cycles (Figure 1A-C). In the first cropping cycle, the shoot dry matter response to P application dose was better described by a linear response for all treatments, except for TSP$_{planting}$, for which a quadratic model was the best fit (Figure 1A). The application of TSP immediately before planting resulted in the highest shoot dry matter yield (38.05 g pot^{-1}), obtained for the estimated dose of P of 172.1 mg kg^{-1}. These results reinforce the idea that increase in contact time of P fertilizer with oxidic soils contributes to P sorption, especially in soils with substantial amounts of low degree crystallinity Fe and Al oxide (280 and 635 mg kg^{-1}, respectively) (Freese et al., 1992; Montalvo et al., 2014; Sakadevan and Bavor, 1998; Warren,

1994). Among the treatments that were incubated, higher SDM yield was obtained in the treatment of PLB-H_3PO_4-MgO, which showed a 9% increase in the yield at the dose 200 mg kg^{-1} when compared to $TSP_{incubation}$ at the same dose.

In the second cropping cycle, all BBFs promoted higher shoot dry matter yield when compared to $TSP_{planting}$ and $TSP_{incubation}$ (Figure 1B), although the total shoot yield was generally lower the for first cycle. Shoot dry matter response to P doses from PLB-H_3PO_4, PLB-H_3PO_4-MgO and PLB-TSP treatments was best described by a linear response, while for PLB-TSP-MgO a quadratic response was the best fit. Additionally, it should be highlighted that the application of PLB-H_3PO_4-MgO, PLB-TSP and PLB-TSP-MgO at the highest P dose were responsible for an increment of about 40% in SDM yield in the second cropping cycle when compared to $TSP_{planting}$, while for the PLB-H_3PO_4 treatment the increase was 32%. During the third cropping cycle, the PLB-H_3PO_4-MgO, PLB-TSP, PLB-TSP-MgO and $TSP_{planting}$ treatments presented quadratic response to the application of P doses, while for the PLB-H_3PO_4 and $TSP_{incubation}$ treatments there was a linear increase as a function of the increased P dose (Figure 1C). In the third cropping cycle, all BBFs showed higher SDM yield at the highest dose as compared to $TSP_{planting}$ (Figure 1C).
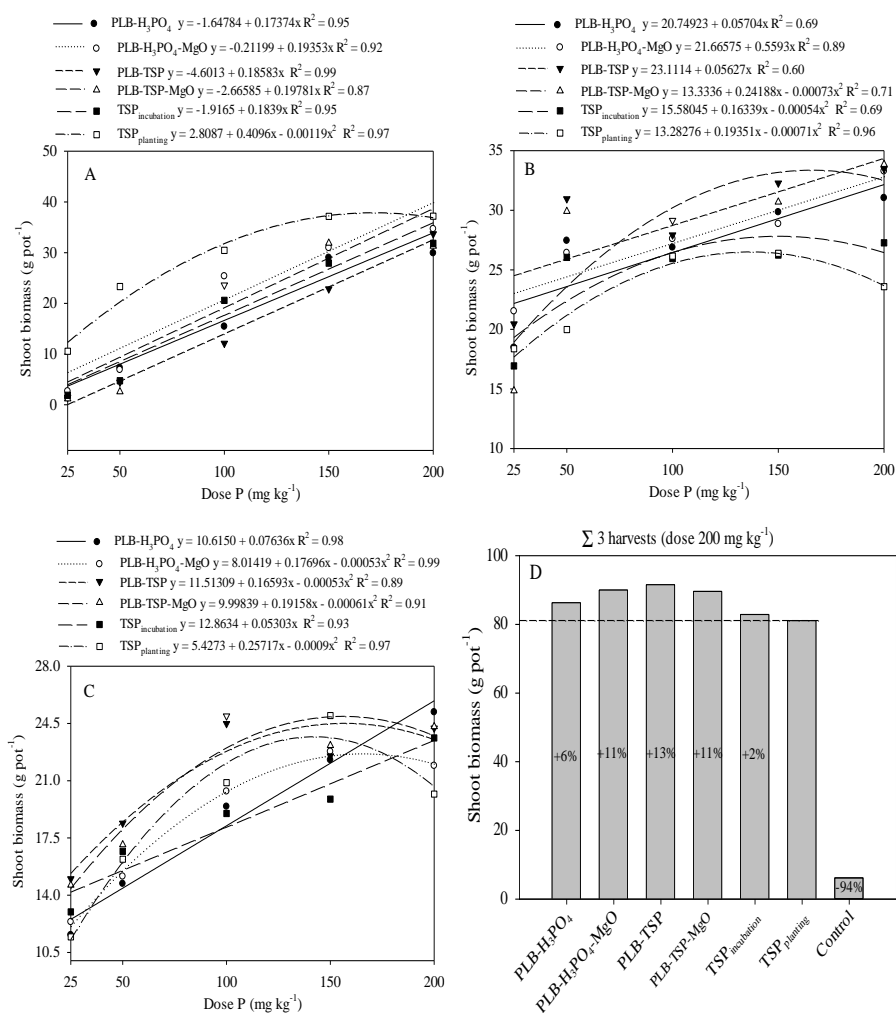
Figure 1. Shoot biomass yield of Marandu grass (*Urochloa brizantha* cv. Marandu) in first (A), second (B), third (C) cropping cycle and cumulative yield (D) as a function of P application using biochar-based-fertilizers and TSP.

Although the BBFs showed lower SDM yield in the first cultivation when compared to TSP$_{planting}$, when summing up all harvests together, the BBFs presented significant increase in SDM yield (Figure 1D). In fact, even though TSP$_{planting}$ caused a prompt and significant increase in SDM yield at the first cropping cycle for all doses, this effect diminished at the following harvests.

Therefore, considering the accumulated yield of the three harvests at the highest dose, there was an increase of 6%, 11%, 13% and 11% for the PLB-H_3PO_4, PLB-H_3PO_4-MgO, PLB-TSP and PLB-TSP-MgO, respectively, as compared TSP$_{Planting}$ (Figure 1D). The decreased SDM yield by Marandu grass plants, especially in the last cropping cycle (Figure 1A-C), can be attributed to the lower content of available P, due to the extraction of successive cultivations (Sá et al., 2017).

The addition of BBFs to the soil, except for the PLB-H_3PO_4 that show high P water solubility, increased the residual effect of phosphate fertilization through the gradual release of the nutrient into the soil (Lustosa Filho et al., 2017). Additionally, these BBFs have high CEC and a liming effect, which are especially significant in acidic tropical soils, since these attributes reduce phosphate sorption and increase its availability to crops is enhanced (Benício et al., 2017; Lustosa Filho et al., 2017; Maluf et al., 2018). Inorganic fertilizers such as TSP have almost 100% of P readily available to react with soil, and therefore, contact time of P fertilizer with oxidic soils could affect P bioavailability to plants (Guedes et al., 2016). An intriguing observation was that TSP$_{planting}$ showed higher SDM yield only in the first cultivation as compared to other treatments, which were incubated with soil. Possibly the high plant P uptake in first harvest (Figure 2A) reduced the available P amount for the other cropping cycles.

It appears that the amount of water-soluble P in the BBFs do not play a significant role in the amount of P that will be available for plant uptake, from the first to subsequent cropping cycles. In contrast, Lima et al. (2016) showed better performance of maize plants in four successive cropping cycles when cultivated with inorganic MAP-based fertilizer mix (80% of water-soluble P_2O_5) as compared with organomineral granulated with poultry litter and MAP (66% of water-soluble P_2O_5).
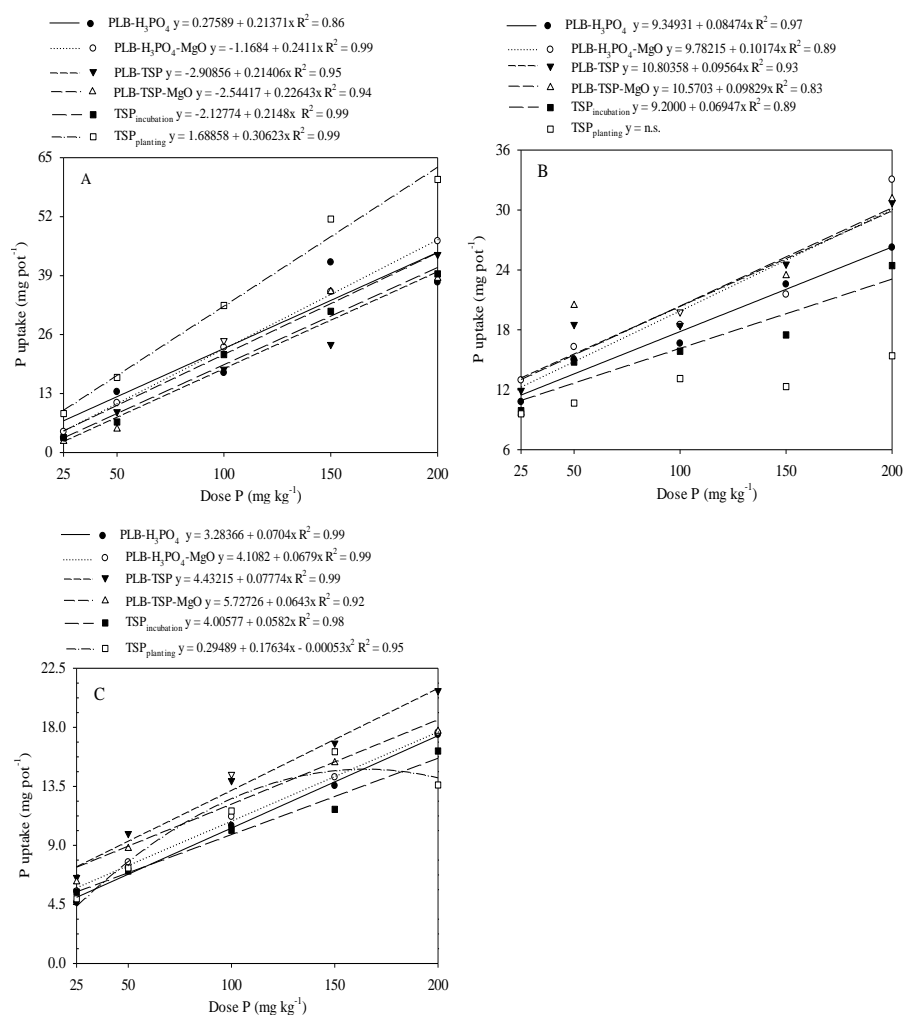
Figure 2. Phosphorus uptake by Marandu grass (*Urochloa brizantha* cv. Marandu as a function of P application using biochar-based-fertilizers and TSP during the (A) first, (B) second and (C) third cropping cycles.

Phosphorus uptake by Marandu grass in the three cropping cycles responded to the applied P doses following a linear model for all six sources (Figure 2A-C), except for the $TSP_{planting}$ in the second cropping cycle (not significant, $P > 0.05$) and in the third cropping cycle, in which P uptake was best described by a quadratic model. Regardless of the source, P uptake decreased

considerably at each subsequent cropping cycle. However, the reduction in P uptake was more intense in the soil that received the $TSP_{planting}$ (Figure 2A-C). In the first cropping cycle, the P uptake in the $TSP_{planting}$ treatment stood out and showed a 29% increase as compared to PLB-H_3PO_4-MgO (Figure 2A), which in turn reflected at only 7% increase in SDM yield. Similarly, Ramos et al. (2009) reported that the use of TSP resulted in higher available P to *Urochloa* and *Sorghum bicolor* plants in the first cropping cycle after the application, but this was not reflected in a higher P use efficiency. This means that immediate availability of P from highly water-soluble sources might not be the best P management strategy, especially in high P fixing soils.

Marandu grass P uptake in the second cropping cycle was highest (33.1 mg pot^{-1}) with PLB-H_3PO_4-MgO treatment, while for $TSP_{planting}$ only 15.4 mg pot^{-1} of P were accumulated (Figure 2B). In the third harvest, the PLB-TSP treatment had the highest P uptake (20.8 mg pot^{-1}), followed by the other BBFs which accumulated about 17.5 mg pot^{-1} of P, yet $TSP_{planting}$ and $TSP_{incubation}$ accumulated 15.0 and 16.2 mg pot^{-1}, respectively. The increase in P uptake by Marandu grass in the second and third harvests for the BBFs (PLB-H_3PO_4-MgO, PLB-TSP and PLB-TSP-MgO) as compared to the soluble source ($TSP_{planting}$) may be related to the characteristics of gradual P release of these sources (Lustosa Filho et al., 2017). Tahir et al. (2011) also observed that total P accumulated in wheat (*Triticum aestivum* L.) was lower when plants were treated with inorganic fertilizer (i.e., single superphosphate, SSP) as compared to an organomineral mix produced from poultry litter and SSP, pre-incubated by 21 days. These authors attributed this result to the release of native P as a result of acids produced during decomposition of poultry litter as well as the chelating effect of organic complex with P.

3.2. Phosphorus Pool Lability

The soil fractionation results measured after three harvests of Marandu grass showed that labile P (resin-Pi + NaHCO$_3$-Pi + NaHCO$_3$-Po) represented only 3.0-5.0% of the total P in the soil (Table 2), which is a typical result of P immobilization in cultivated tropical soils (Teles et al., 2017). The soil of this study has a high clay content with a portion of low degree crystallinity Fe and Al oxide, which are key factors in controlling P sorption in soils (Freese et al., 1992; Warren, 1994; Sakadevan e Bavor, 1998; Montalvo et al., 2014). The NaHCO$_3$-Po fraction was always the dominant fraction of labile P, except for PLB-H$_3$PO$_4$-MgO. In contrast, The PLB-H$_3$PO$_4$-MgO treatment showed significantly higher NaHCO$_3$-Pi content when compared to the other treatments.

The addition of PLB-TSP increased the resin-P pool in the soil more than other treatments (Table 2). A significant increase in labile P fraction was observed in both PLB-TSP and PLB-TSP-MgO treatments, the latter not statistically different from TSP$_{incubation}$ and TSP$_{planting}$ (Figure 3). The PLB-H$_3$PO$_4$ showed similar behavior of TSP in terms of P release, most probably due to its high residual acidity that resulted in a low pH (2.0) (Lustosa Filho et al., 2017). Thus, this source acts as a fast-release P source, increasing the contact time with Al and Fe (oxy)hydroxides, which can to explain to the low amount of P labile after cultivation (Figure 3).

Similarly to the labile fraction, concentrations of moderately labile P (0.1 M NaOH-Pi + 0.1 M NaOH-Po + HCl-Pi) were higher for PLB-TSP as compared to the other treatments (Figure 1). The determination of P fractions by the extractor NaOH 0.1 mol L^{-1} were affected by P sources. The highest contents of 0.1 M NaOH-Pi were detected for PLB-TSP and TSP$_{planting}$ treatments (Table 2). It should be noticed that the 0.1 M NaOH-Po was significantly greater for the soil cultivated with PLB-TSP, PLB-H$_3$PO$_4$, PLB-TSP-MgO and TSP$_{planting}$, although the last was statistically equivalent to the other treatments. Moderately labile P in

the soil was dominated by the NaOH-Pi fraction, except for the control (Table 2). This fraction represent inorganic P bound to oxides and silicates clay minerals with intermediate binding energy (Cross e Schlesinger, 1995; Caione et al., 2015; Rodrigues et al., 2016; Schneider e Haderlein, 2016)

Table 2. Distribution of sequentially extracted inorganic (Pi) and organic (Po) P fractions (mg kg^{-1}) in soils fertilized with biochar-based-fertilizer and TSP (200 mg P kg^{-1} soil) after three cultivation cycles of Marandu grass.

Fertilizers	Resin-P	NaHCO$_3$-P		0.1 M NaOH-P		HCl-P	0.5 M NaOH-P		Residual-P
	-	Pi	Po	Pi	Po	-	Pi	Po	-
PLB-TSP	24.4a	12.9cd	46.3a	119a	86.9a	7.40a	133a	90.7a	1160b
PLB-H$_3$PO$_4$	10.49b	11.6d	20.3c	88.2b	82.9ab	5.68a	55.8bc	47.5bc	1194b
PLB-TSP-MgO	12.7b	14.5cd	46.3a	96.8b	80.3ab	5.42a	61.5b	53.3bc	1163b
PLB-H$_3$PO$_4$-MgO	14.4b	21.7a	15.3c	96.1b	45.9c	5.52a	58.2bc	65.0b	1212b
TSP$_{incubation}$	13.0b	16.0bc	42.0a	101b	54.9bc	5.61a	61.4b	55.3bc	1766b
TSP$_{planting}$	11.4b	18.8ab	32.6b	103ab	70.9abc	5.78a	63.7b	57.8bc	1167b
Control	2.19c	4.67e	13.1c	27.3c	43.6c	6.05a	40.8c	38.7c	1290a

The P fraction extracted by NaOH 0.1 mol L^{-1} is considered a moderately labile fraction, and indeed some authors have reported that this P fraction contributes to P availability for plant uptake, mainly in highly weathered soils, since this fraction acts as a buffer for resin and NaHCO$_3$-extractable P (Pavinato et al., 2009; Olibone e Rosolem, 2010; Almeida et al., 2018). The HCl extractable fraction was the lowest P fraction in all treatments (~0.4%) and showed no difference among the treatments. The HCl 1.0 mol L^{-1} can extract mainly apatite-type minerals, other sparingly soluble Ca-P compounds or P bound to negatively charged oxide surfaces (Hedley et al., 1982; Soltangheisi et al., 2018). The BBFs have Ca-P compounds, such as Ca$_2$P$_2$O$_7$ in PLB-TSP and hydroxyapatite [Ca$_5$(PO$_4$)$_3$OH] in PLB-TSP-MgO (Lustosa Filho et al., 2017), which were possibly solubilized by plants.
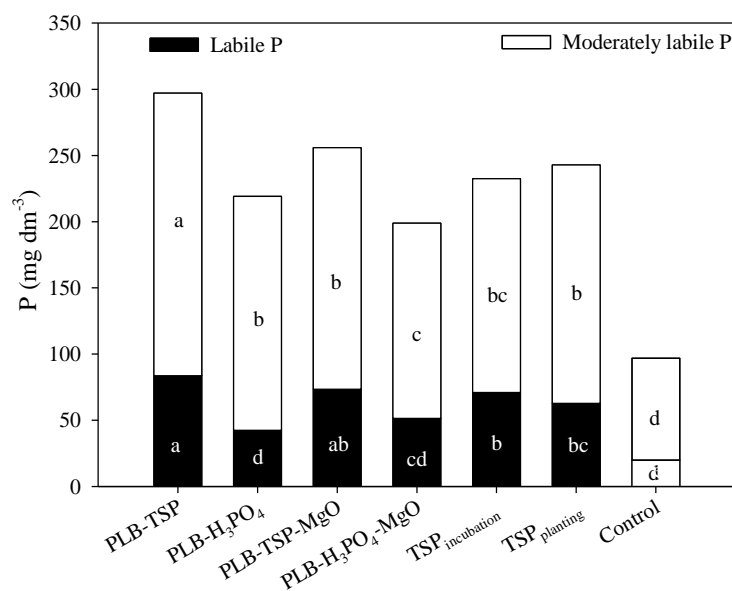
Figure 3. Labile and moderately labile P pool in soils fertilized with biochar-based-fertilizer and TSP (200 mg P kg^{-1} soil) after three cultivation cycles of Marandu grass.

For the P extracted by NaOH 0.5 mol L^{-1} (Table 2), both Pi and Po were higher in the soil cultivated with PLB-TSP as compared to the other treatments. The addition of fertilizers in soil decreased the concentration of residual-P as compared to the control. The increased residual-P depletion suggests that the added P by these fertilizers did not enter the residual-P pool, but rather plants have mobilized some of the residual-P, as observed by Rivaie e Tillman (2009). In addition, the use of these sources increased the total P, compared to the control, especially the PLB-TSP, ranging from 1466 to 1681 mg dm^{-3}. The increase in total P stocks is important, since the P extracted by NaHCO$_3$, NaOH, HCl and residual-P can be either bioavailable or transformed into available pools with cultivation of maize (Almeida et al., 2018).

A principal component analysis (PCA) was conducted to determine variations among the BBFs and TSP, considering the soil P fractionation after three harvests of Marandu grass and shoot dry matter yield for the highest P dose

(Figure 4). The two first principal components explained 75 % of the total variation (Figure 4). Reducing from fifteen original variables to the two main components simplified the analysis without loss of information. PCA revealed that $TSP_{planting}$ and $PLB-H_3PO_4-MgO$ were associated with higher SDM yield in the first cropping cycle (Figure 4). It was also observed that $PLB-H_3PO_4-MgO$ was associated with residual-P and $NaHCO_3$-Po as compared to the other treatments (Figure 4). The PLB-TSP addition was closely related with labile, moderately labile and non-labile P fractions, resin-P, $NaHCO_3$-Po, HCl-P, 0.1 M NaOH-Pi and 0.5 M NaOH-P (Figure 4), according to the observed results (Table 2 and Figure 1A).
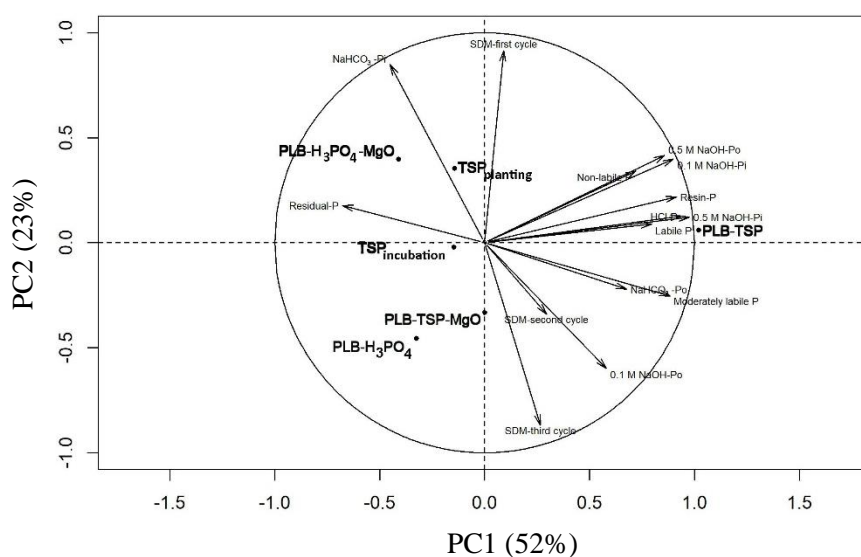

Figure 4. Biplot showing ordination of biochar-based-fertilizer and TSP (black text) based on PCA of variables of P fractionation and shoot dry matter yield (grey text). PC1 explains 50% of the variance in the data and PC2 explains 24% of the variance in the data.

Overall, the PCA enabled a combined evaluation of most of the studied variables, thus showing the PLB-TSP treatment influenced the dynamics of the P fractions in the soil, mainly labile and moderately labile P fractions, reinforce the

idea that this source have slow release, and hence, maintaining the P available for plants over longer periods. It is clear from our results that there is an initial and rapid redistribution of P after application of the fertilizers in the soil. Further research in the long-term is required to assess the residual effects of the BBFs in the pools of P and confirm the greater efficiency of P use observed in the three crop cycles with Marandu grass.

4. Conclusions

In the present study, we investigated the effect of the pre-incubation of biochar-based slow-release P fertilizers compared to a soluble P fertilizer (TSP) in Marandu grass cultivation over three cropping cycles, and also P fractionation in the soil. The results showed that although the TSP$_{planting}$ cause higher shoot dry matter yield in the first crop cycle, in subsequent cultivations there was a marked reduction in the production. Positive impacts in the accumulated shoot dry matter were obtained for all BBFs, especially for the slow release P sources. Application of PLB-TSP promoted accumulation of both labile and moderately P pools in soil, despite the higher yield among the BBFs. Long-term studies are needed to verify if these changes in P fractions over time will promote higher plant P uptake and efficient P use.

REFERENCES

Abdala DB, Northrup PA, Arai Y, Sparks DL. Surface loading effects on orthophosphate surface complexation at the goethite/water interface as examined by extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. J Colloid Interface Sci. Elsevier Inc.; 2015;437:297–303.

Almeida DS, Penn CJ, Rosolem CA. Assessment of phosphorus availability in soil cultivated with ruzigrass. Geoderma. Elsevier; 2018;312:64–73.

Benício LPF, Constantino VRL, Pinto FG, Vergütz L, Tronto J, da Costa LM. Layered Double Hydroxides: New Technology in Phosphate Fertilizers Based on Nanostructured Materials. ACS Sustain Chem Eng. 2017;5:399–409.

Brookes PC, Powlson DS. Preventing Phosphorus Losses During Perchloric Acid Digestion of Sodium Bicarbonate Soil Extracts. J Sci Food Agric. 1981;32:671–674.

Caione G, Prado de M, Renato, Campos CNS, Rodrigues M, Pavinato PS, Agostinho FB. Phosphorus Fractionation in Soil Cultivated with Sugarcane Fertilized by Filter Cake and Phosphate Sources. Commun Soil Sci Plant Anal. 2015;46:2449–2459.

Condron LM, Goh KM, Newman RH. Nature and distribution of soil phosphorus as revealed by a sequential extraction method followed by 31P nuclear magnetic resonance analysis. 1985;36:199–207.

Cross AF, Schlesinger WH. A literature review and evaluation of the Hedley fractionation : Applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. Geoderma. 1995;64:197–214.

Dalólio FS, da Silva JN, Oliveira ACC de, Tinôco I de FF, Barbosa RC, Resende M de O, Albino LFT, Coelho ST. Poultry litter as biomass energy: A review and future perspectives. Renew Sustain Energy Rev. Elsevier Ltd; 2017;76:941–949.

Degryse F, Baird R, da Silva RC, McLaughlin MJ. Dissolution rate and agronomic effectiveness of struvite fertilizers – effect of soil pH, granulation and base excess. Plant Soil. Plant and Soil; 2017;410:139–152.

Everaert M, Warrinnier R, Baken S, Gustafsson JP, De Vos D, Smolders E. Phosphate-Exchanged Mg-Al Layered Double Hydroxides: A New Slow Release Phosphate Fertilizer. ACS Sustain Chem Eng. 2016;4:4280–4287.

Freese D, Zee SE van der, Riemsdijk W Van. Comparison of different models for phosphate sorption as a function of the iron and aluminium oxides of soils. J Soil Sci. 1992;43:729–738.

Gilbert N. The disappearing nutrient. Nature. 2009;461:716–718.

Guedes RS, Melo LCA, Vergütz L, Rodríguez-Vila A, Covelo EF, Fernandes AR. Adsorption and desorption kinetics and phosphorus hysteresis in highly weathered soil by stirred flow chamber experiments. Soil Tillage Res. Elsevier B.V.; 2016;162:46–54.

Hedley MJ, Stewart JWB, Chauhan BS. Changes in Inorganic and Organic Soil Phosphorus Fractions Induced by Cultivation Practices and by Laboratory Incubations1. Soil Sci Soc Am J. 1982;46:970.

Koch M, Kruse J, Eichler-Löbermann B, Zimmer D, Willbold S, Leinweber P, Siebers N. Phosphorus stocks and speciation in soil profiles of a long-term fertilizer experiment: Evidence from sequential fractionation, P K -edge

XANES, and 31 P NMR spectroscopy. Geoderma. Elsevier; 2018;316:115–126.

Li F, Cao X, Zhao L, Wang J, Ding Z. Effects of Mineral Additives on Biochar Formation: Carbon Retention, Stability, and Properties. Environ Sci Technol. 2014;48:11211–11217.

Lima RS, Atista MA, Inoue TT, Muniz AS, Pagliari PH. Organomineral Phosphate Fertilizers: Agronomic Efficiency and Residual Effect on Initial Corn Development. Agron J. 2016;108:2050.

Lustosa Filho JF, Penido ES, Castro PP, Silva CA, Melo LCA. Co-Pyrolysis of Poultry Litter and Phosphate and Magnesium Generates Alternative Slow-Release Fertilizer Suitable for Tropical Soils. ACS Sustain Chem Eng. 2017;5:9043–9052.

Montalvo D, Degryse F, McLaughlin MJ. Fluid Fertilizers Improve Phosphorus Diffusion but not Lability in Andisols and Oxisols. Soil Sci Soc Am J. 2014;78:214–224.

Murphy J, Riley JP. A modified single solution method for the determination of phosphate in natural waters. Anal Chim Acta. 1962;27:31–36.

Novais RF, Smyth TJ. Fósforo em solo e planta em condições tropicais. Viçosa: Universidade Federal de Viçosa; 1999. p. 399.

Olibone D, Rosolem CA. Phosphate fertilization and phosphorus forms in an Oxisol under no-till sob sistema de semeadura direta. 2010;465–471.

Pavinato PS, Merlin A, Rosolem CA. Phosphorus fractions in Brazilian Cerrado soils as affected by tillage. Soil Tillage Res. 2009;105:149–155.

R core Team. R: A language and environment for statistical computing. Vienna: R Foundation for Statistical Computing.; 2016.

Ramos SJ, Faquin V, Rodrigues CR, Silva CA, Boldrin PF. Biomass production and phosphorus use of forage grasses fertilized with two phosphorus sources. Rev Bras Ciência do Solo. 2009;33:335–343.

Rivaie AA, Loganathan P, Graham JD, Tillman RW, Payn TW. Effect of phosphate rock and triple superphosphate on soil phosphorus fractions and their plant-availability and downward movement in two volcanic ash soils under Pinus radiata plantations in New Zealand. Nutr Cycl Agroecosystems. 2008;82:75–88.

Rivaie AA, Tillman RW. Phosphorus fractions of fertiliser-derived P in an allophanic soil under Pinus radiata seedlings grown with broom and ryegrass. J For Res. 2009;20:229–236.

Rodrigues M, Pavinato PS, Withers PJA, Teles APB, Herrera WFB. Legacy phosphorus and no tillage agriculture in tropical oxisols of the Brazilian savanna. Sci Total Environ. 2016;542:1050–1061.

Roy ED, Richards PD, Martinelli LA, Coletta L Della, Lins SRM, Vazquez FF, Willig E, Spera SA, VanWey LK, Porder S. The phosphorus cost of agricultural intensification in the tropics. Nat Plants. 2016;2:16043.

Sá JM e, Jantalia CP, Teixeira PC, Polidoro JC, Benites V de M, Araújo AP. Agronomic and P recovery efficiency of organomineral phosphate fertilizer from poultry litter in sandy and clayey soils. Pesqui Agropecuária Bras. 2017;52:786–793.

Sakadevan K, Bavor HJ. Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems. Water Res. 1998;32:393–399.

Schneider F, Haderlein SB. Potential effects of biochar on the availability of phosphorus — mechanistic insights. Geoderma. 2016;277:83–90.

Schwertmann U. Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung. Zeitschrift für Pflanzenernährung, Düngung, Bodenkd. 1964;105:194–202.

Soltangheisi A, Rodrigues M, Coelho MJA, Gasperini AM, Sartor LR, Pavinato PS. Changes in soil phosphorus lability promoted by phosphate sources and cover crops. Soil Tillage Res. Elsevier; 2018;179:20–28.

Tahir S, Alam SM, Ahmad Z. Wheat yield and phosphorus fertilizer efficiency as influenced by pre-incubated use of single superphosphate and poultry litter and its time of application. J Plant Nutr. 2011;34:1034–1040.

Teles APB, Rodrigues M, Bejarano Herrera WF, Soltangheisi A, Sartor LR, Withers PJA, Pavinato PS. Do cover crops change the lability of phosphorus in a clayey subtropical soil under different phosphate fertilizers? Soil Use Manag. 2017;33:34–44.

USEPA - United States Environmental Protection Agency. Methods for chemical analysis of water and wastes. Environmental Protection Agency, Cincinnati, US; 1971.

Waldrip HM, Pagliari PH, He Z, Harmel RD, Cole NA, Zhang M. Legacy Phosphorus in Calcareous Soils: Effects of Long-Term Poultry Litter Application. Soil Sci Soc Am J. 2015;79:1601.

Walkley A, Black IA. An examination of the degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. Soil Sci. 1934;37:29–38.

Wang T, Camps-Arbestain M, Hedley M. The fate of phosphorus of ash-rich biochars in a soil-plant system. Plant Soil. 2014;375:61–74.

Warren GP. Influence of soil properties on the response to phosphorus in some tropical soils: I. Initial response to fertilizer. Eur J Soil Sci. 1994;45:337–344.

Withers PJA, Rodrigues M, Soltangheisi A, De Carvalho TS, Guilherme LRG, Benites VDM, Gatiboni LC, De Sousa DMG, Nunes RDS, Rosolem CA, Andreote FD, Oliveira A De, Coutinho ELM, Pavinato PS. Transitions to sustainable management of phosphorus in Brazilian agriculture. Sci Rep. Springer US; 2018;8:1–13.

Zhao L, Cao X, Zheng W, Kan Y. Phosphorus-Assisted Biomass Thermal Conversion: Reducing Carbon Loss and Improving Biochar Stability. Zhou Z, organizador. PLoS One. 2014;9:e115373.

Zhao L, Cao X, Zheng W, Scott JW, Sharma BK, Chen X. Copyrolysis of Biomass with Phosphate Fertilizers To Improve Biochar Carbon Retention, Slow Nutrient Release, and Stabilize Heavy Metals in Soil. ACS Sustain Chem Eng. 2016;4:1630–1636.

CONCLUDING REMARKS

The BBFs produced from poultry litter impregnation with phosphate sources showed desirable characteristics to be applied as slow release phosphate fertilizers, especially those also impregnated with MgO. Interesting aspects were observed regarding the characterization of BBFs as an effect of the mineral additives added to the biomass for its production. Firstly, addition of MgO to poultry litter corrected the pH of the BBFs and reduced drastically the initial P release kinetics in water due to formation low-solubility phosphate compounds, such as pyrophosphates ($Ca_2P_2O_7$ and $Mg_2P_2O_7$). In addition, there was an increase in CEC and Mg content of these BBFs. Despite the low solubility in water, MgO-impregnated BBFs were able to meet the demand of maize at levels close to those observed by the conventional soluble phosphate source. The correction of the pH of the BBFs by MgO promoted a slight soil pH increase after cultivation, as well as increasing the residual level of exchangeable Mg^{2+} in soil. This increase in soil pH eliminated exchangeable Al^{3+} in the soil solution that could precipitate soluble P forms released by BBFs.

Despite the low solubility in water, the BBFs PLB-H_3PO_4-MgO and PLB-TSP-MgO have solubility in citric acid and neutral ammonium citrate (NAC+H_2O) equivalent to phosphate soluble source. To the best of our knowledge, these data are unprecedented and reinforce the notion that BBFs have slow release, however with high availability to the NAC+H_2O extractor, which best correlates with plant uptake for acidulated P sources. Additionally, the results observed in P diffusion in soil using a visualization technique helped to confirm some of the findings from the BBFs characterization, mainly regarding its slow and steady release in the soil. The analysis of the region around the granule showed that after 42 days of incubation in the soil, there was an increase in soil phosphorus content of about 200 and 400% for PLB-H_3PO_4-MgO and PLB-TSP-

MgO, respectively, as compared to the TSP, showing the rapid sorption of P in the soil when using a soluble source. The physical form as the BBF is applied to the soil (granular or powder) interferes directly in its performance. For PLB-TSP-MgO, the powder application appears to be the most suitable for rapid cycle culture cultivation. In contrast, for PLB-H_3PO_4-MgO the granular application showed a TSP equivalent performance in maize cultivation. Additionally, the BBFs maintain a high amount of P in the granule, protecting it from interaction with the soil.

Even incubated for more than 100 days, BBFs were able to promote higher accumulated yield of the three harvests of Marandu grass as compared to the soluble source applied just before planting. Additionally, from the second cropping cycle that all the BBFs have obtained production superior to the soluble source. The application of the BBFs significantly altered P in soil pools, with emphasis to PLB-TSP that increased the labile and moderately labile P fractions in soil after cultivation. The results above, opens encouraging perspectives for use BBFS aiming to enhance P use efficiency in tropical soils and add value to residues produced in large quantities in Brazil, such as the PL.

Further investigations on application of BBFs should be carried out under field studies, which can reveal more accurate estimation of the benefits of the gradual release of P from the BBFs and the assessment of the actual duration of these impacts. This is fundamental to assess the real capacity of these sources as an alternative of use in tropical weathered soils aiming to establish new management practices in these soils. Additionally, the use of BBFs has to be explored regarding the synergism of P with Mg, combinations with P soluble sources in annual crops, in order to expand our knowledge on this research in Brazil and worldwide.