UNIVERSIDADE FEDERAL DE LAVRAS

HENRIQUE JOSÉ GUIMARÃES MOREIRA MALUF

TECHNOLOGIES FOR THE EFFICIENT USE OF PHOSPHORUS IN THE PLANT-SOIL-FERTILIZER SYSTEM

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

Orientador
Dr. Carlos Alberto Silva

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RESUMO GERAL

Fósforo (P) é um nutriente que naturalmente limita o crescimento das plantas na maioria dos solos brasileiros. Essa condição exige uma aplicação contínua de fertilizante fosfatado, a fim de sustentar uma satisfatória produção das culturas e fornecer alimentos à uma população cada vez maior. Entretanto, a conversão do P aplicado ao solo em produtos de necessidade humana é muito baixa, o que exige estratégias mais efetivas de manejo e de desenvolvimento de fertilizantes para aumentar a eficiência de recuperação do P-fertilizante pelas plantas. Desse modo, foi estudado a aplicação de ácido húmico (AH) no solo e formulações de fertilizantes organominerais (FOMs) e de compostos de fosfato de magnésio (CFMs). Os objetivos desta tese foram: (i) avaliar a adsorção e a disponibilidade de P em solos com doses de AH combinadas com $CaCO_3$ ou $MgCO_3$; (ii) investigar a decomposição da matéria orgânica, perda de N e frações solúveis de P em misturas de esterco de galinha (EG) e casca de café (CC) com fosfato monoamônio (MAP) ou fosfatos naturais (FNs), submetidas à compostagem para produção de FOMs; (iii) sintetizar CFMs, caracterizar os teores de P e verificar o potencial agronômico dos novos fertilizantes fosfatados no milho. Inicialmente, amostras de Latossolo e de Gleissolo foram incubadas com doses de AH combinadas com $CaCO_3$ ou $MgCO_3$ e posterior avaliação da adsorção de P. Em sequência, essas amostras de solo foram novamente incubadas com fonte de P, a fim de verificar a disponibilidade desse nutriente. Após as incubações, verificou-se que o AH reduziu o fator capacidade de P e aumentou sua disponibilidade no Latossolo, ao passo que, a aplicação de AH no Gleissolo não influenciou essas variáveis respostas. Para a formulação de FOMs, as misturas com FNs, após 150 dias de compostagem, apresentaram maior decomposição dos resíduos orgânicos, EG e CC, em comparação aos compostos com MAP. O uso do MAP em compostagem resultou em maior rendimento em massa seca e retenção de N nos compostos finais, quando comparado às misturas com FNs. A compostagem de EG e CC com FNs não alterou as frações solúveis de P e não foi um processo eficiente para produzir FOMs. Em contrapartida, a compostagem entre EG, CC e MAP reduziu o P solúvel em água e aumentou o valor como fertilizante dos compostos produzidos. Por fim, seis diferentes relações entre P e Mg deram origem aos CFMs, que apresentaram P parcialmente solúvel em água e totalmente solúvel em citrato neutro de amônio mais água. O processo de síntese dos CFMs conferiu ao P uma liberação mais lenta do que o P liberado pelo superfosfato triplo (SFT). A adubação do milho com um dos CFMs formulados resultou em maior produção de massa seca em relação à aplicação do SFT e maior acúmulo de P na parte aérea do milho, comparado com os demais CFMs testados.

Palavras-chave: Ácido húmico. Fertilizante organomineral. Compostagem. Fosfato de magnésio. Fosfato de liberação lenta.

GENERAL ABSTRACT

Phosphorus (P) is a nutrient that naturally limits plant growth in most Brazilian soils. This condition requires a continuous application of phosphate fertilizer to sustain a satisfactory production of crops and to provide food to a growing population. However, conversion of P applied to soil in products of human needs is very low, which requires the adoption of strategies of management and development of fertilizers more effective in increasing the recovery efficiency of P-fertilizer by plants. Thus, application of humic acid (HA) in soil as well as formulations of organo-mineral fertilizers (OMFs) and, magnesium phosphate compounds (MPCs) were studied. The aims of this thesis were: (i) to evaluate adsorption and availability of P in soils limed with $CaCO_3$ or $MgCO_3$ combined with HA rates; (ii) to investigate organic matter decomposition, N loss and soluble P fractions in mixtures of chicken manure (CM) and coffee husk (CH) with monoammonium phosphate (MAP) or phosphate rocks (PRs) submitted to composting for OMFs production; (iii) to synthesize MPCs, to characterize P contents, and to verify agronomic performance of MPCs using maize as the test plant. Initially, Oxisol and Entisol samples were incubated with HA rates combined with $CaCO_3$ or $MgCO_3$, as liming materials, and subsequent evaluation of P adsorption. In sequence, these soil samples were again incubated with P source, to evaluate P availability. After incubations, it was verified that HA reduced buffering P capacity and increased P availability in Oxisol, whereas, application of HA in Entisol did not alter these response variables. For OMFs formulations, mixtures of PRs, after 150 days of composting, presented greater decomposition of organic wastes, CM and CH, in comparison to MAP-based composts. MAP use in composting resulted in greater dry mass yield and N retention in final composts when compared to PRs-mixtures. Composting of CM and CH with PRs did not alter the soluble P fractions and it was not an efficient process to produce OMFs. In contrast, composting of CM, CH and MAP reduced water-soluble P and increased the value as fertilizer of the produced composts. Finally, six different mixtures of P and Mg generated MPCs, which presented partially water-soluble P and totally soluble in neutral ammonium citrate plus water. Synthesis process of MPCs transferred to P a slower release than P from triple superphosphate (TSP). Maize fertilization with one of formulated MPCs resulted in a greater dry mass production in relation to application of TSP and higher P accumulation in maize shoot, compared to the others MPCs tested.

Keywords: Humic acid. Organo-mineral fertilizer. Composting. Magnesium phosphate. Slow-release phosphate.

SUMÁRIO

PRIMEIRA PARTE

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1 INTRODUÇÃO GERAL

Fósforo (P) é um elemento insubstituível, que participa de pelo menos um composto ou reação indispensável nos organismos vivos, o que caracteriza sua essencialidade a todas as formas de vida. Assim, como a água e a energia, o P é crucial para a produção de alimentos, fibra e combustível, com suprimento de P nos sistemas de produção agrícola, especialmente, pelo uso de fertilizante fosfatado (CORDELL; WHITE, 2015). Atualmente, quase todos os produtores agrícolas do mundo são dependentes de fertilizantes fosfatados, consequentemente, dependem da apatita, mineral abundante na rocha matriz utilizada para a produção desses fertilizantes (SCHOLZ; WELLMER, 2013). Com isso, a exploração dessa rocha tem se intensificado nas últimas décadas, impulsionada pelo aumento da demanda mundial por fertilizantes fosfatados, com risco de escassez das reservas de maior qualidade e de fácil extração, o que contribui para o aumento do preço desses fertilizantes (CORDELL; WHITE, 2015; WIEL; LINDEN; SCHOLTEN, 2016). Previsões mostram que as reservas de P podem ser esgotadas nos próximos 50 a 100 anos (CORDELL et al., 2011; CORDELL; WHITE, 2015).

Estimativas também indicam que, em 2050, se não houver mudanças nos padrões de emissão de CO_2 no ar, a concentração de CO_2 atmosférico aumentará de 400, condição atual, para 550 μmol mol^{-1} (IPCC, 2013; NOAA, 2015). Essa maior oferta de C-CO_2 na atmosfera potencializa o crescimento das culturas, o que aumenta a quantidade requerida de nutrientes pelas plantas, inclusive de P. Maluf et al. (2015) verificaram, em dois anos de avaliação, menor disponibilidade de P no solo cultivado com cafeeiro em atmosfera de 550 μmol mol^{-1} de CO_2, em comparação ao cultivo em condição atual de CO_2 atmosférico. Esse efeito sinaliza que, com o aumento da concentração de CO_2 no ar, haverá necessidade de repor maior quantidade de P-fertilizante no solo para sustentar o crescimento magnificado das culturas (MALUF et al., 2015; MANOJ-KUMAR et al., 2012).

Além disso, em razão do aumento da população mundial, nos próximos 40 anos, o planeta precisará produzir alimento equivalente à quantidade produzida nos últimos 8000 anos (PHILLIPS, 2013; PROCHNOW, 2017). Esse cenário desafiador de depleção das reservas fosfatadas não renováveis, aumento da exigência por P pelas culturas e da demanda por alimentos da população mundial indica que mudanças devem ocorrer, a fim de garantir a segurança alimentar global. Neste sentido, o Brasil se enquadra como País-chave para assegurar a maior oferta mundial de alimentos e a segurança alimentar para as próximas décadas (CLAY, 2009).

No entanto, para superar os desafios da produção de alimentos, o Brasil precisa prosperar em, pelo menos, três princípios: (i) conscientização da vocação agrícola do País no cenário político; (ii) efetivar os avanços no setor de logística; e (iii) alavancar o desenvolvimento tecnológico (PROCHNOW, 2017). Esse último princípio constitui-se no tema principal desta tese, com o foco em um dos nutrientes mais limitante em solos brasileiros para o adequado crescimento das culturas, o P. Nos solos brasileiros, especificamente naqueles em condições extremas de intemperismo, como os latossolos, o solo deixa de ser uma fonte preferencial de P e passa a ser dreno, competindo fortemente com a planta, sendo necessárias grandes quantidades de fertilizantes fosfatados para suprir a pequena exigência por P da planta (NOVAIS; SMYTH; NUNES, 2007). Esses solos podem reter cerca de 200 vezes mais P, formando espécies não lábeis do nutriente, do que plantas de cultivo anual, como a soja, que imobilizam em toda sua biomassa, aproximadamente, 20 kg ha^{-1} (NOVAIS; SMYTH; NUNES, 2007). Portanto, deve-se aliar tecnologias que minimizem, efetivamente, o caráter dreno dos solos, concentrando esforços para aumentar a eficiência de aproveitamento do P-fertilizante pelas plantas.

Para isso, manejos ou práticas agronômicas podem ser adotadas para minimizar as perdas e aumentar o aproveitamento dos nutrientes pelas plantas, como aqueles baseados no princípio dos 4 C, com aplicação da fonte Correta, na dose Correta, no local Correto e na época Correta (IPNI, 2017). Embora melhore a aquisição dos nutrientes pela planta, a adoção dessas boas práticas na adubação com P ainda não é suficiente para elevar a eficiência dos fertilizantes atuais, cujas perdas podem chegar a 80% do P aplicado no solo (BINDRABAN et al., 2015). A alta concentração de P solúvel em água, aliado ao caráter ácido dos fertilizantes fosfatados totalmente acidulados são algumas das propriedades que estão relacionadas com a perda de eficiência na recuperação do P-fertilizante pela planta (McLAUGHLIN et al., 2011).

Desse modo, estratégias podem ser melhor implementadas no sistema de produção, como o uso do calcário e da matéria orgânica (MO) no solo, que favorecem a redução das reações que causam a retenção de P desses fertilizantes solúveis (ROY et al., 2016). Entretanto, a escolha inadequada do tipo de calcário pode aumentar, de forma desbalanceada, o teor de Ca^{2+} no solo e inibir um maior aproveitamento de P pela planta. Por outro lado, a MO tem contribuído para o aumento da disponibilidade de P no solo, em que, atualmente, vem sendo aplicado o ácido húmico para a melhoria da eficiência de fertilizantes fosfatados. O ácido húmico no solo aumenta o P na solução do solo, em razão, principalmente, da complexação de Ca, Fe e Al, evitando a precipitação com P, e do bloqueio de sítios de adsorção de fosfato do solo (ERRO et al., 2012), mas, esse efeito ainda é pouco evidenciado em solos brasileiros.

Por outro lado, uma tecnologia que vem crescendo no Brasil são os fertilizantes organominerais, que têm sido produzidos tanto por produtores rurais quanto por industrias, por meio da compostagem de resíduos orgânicos com fertilizantes fosfatados. No entanto, pouco se sabe sobre a fonte ideal de P a ser utilizada, a proporção da mistura entre os materiais orgânicos e inorgânicos, e sobre a influência do processo de compostagem na solubilidade do P. Outra tecnologia que pode ser promissora é o uso do Mg na síntese de fertilizantes fosfatados, a fim de conferir ao fertilizante um pH mais próximo do neutro, uma liberação de P gradual, além da presença do Mg como elemento sinérgico à absorção de P pela planta.

Essas estratégias e tecnologias foram os principais objetos de estudo desta tese, que teve como objetivos: (i) avaliar em dois solos contrastantes, a combinação entre ácido húmico e carbonato de cálcio ou de magnésio na adsorção e na disponibilidade de P; (ii) investigar a influência da compostagem de misturas entre esterco de galinha e casca de café com fosfato solúvel, fosfato natural reativo ou fosfato natural sobre as características químicas e físico-químicas dos fertilizantes organominerais produzidos; (iii) desenvolver compostos à base de fosfato de magnésio, a fim de utilizá-los como fertilizantes fosfatados de liberação lenta, caracterizar as propriedades químicas e mineralógicas desses fertilizantes sintetizados, e verificar o potencial agronômico destas novas fontes de P no milho. Para alcançar cada um desses objetivos, a tese foi compartimentalizada em três artigos, ordenados na seguinte sequência:

a) Artigo 1 - Adsorption and availability of phosphorus in response to humic acid rates in soils limed with $CaCO_3$ or $MgCO_3$;
b) Artigo 2 - Is composting a route to solubilize low-grade phosphate rocks and improve MAP-based composts?;
c) Artigo 3 - Formulação, cinética de liberação de fósforo e potencial agronômico de fertilizantes à base de fosfato de magnésio.

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SEGUNDA PARTE

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ADSORPTION AND AVAILABILITY OF PHOSPHORUS IN RESPONSE TO HUMIC ACID RATES IN SOILS LIMED WITH $CaCO_3$ OR $MgCO_3$

ADSORÇÃO E DISPONIBILIDADE DE FÓSFORO EM RESPOSTA A DOSES DE ÁCIDO HÚMICO EM SOLOS CORRIGIDOS POR $CaCO_3$ OU $MgCO_3$

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ABSTRACT

Humic acid (HA) may reduce adsorption and increase soil P availability, however, the magnitude of this effect is different when Ca^{2+} prevails over Mg^{2+} in limed soils. The objective of this study was to evaluate the effects of HA rates and carbonate sources on the adsorption, phosphate maximum buffering capacity (PMBC), and P availability in two contrasting soils. Oxisol and Entisol samples were firstly incubated with the following HA rates: 0, 20, 50, 100, 200 and 400 mg kg^{-1}, combined with $CaCO_3$ or $MgCO_3$, to evaluate P adsorption. In sequence, soil samples were newly incubated with P (400 mg kg^{-1}) to evaluate P availability. The least P adsorption was found when 296 mg kg^{-1} of HA was added to Oxisol. Applying HA rates decreased maximum adsorption capacity, increased P binding energy to soil colloids and did not alter PMBC of Entisol. Available P contents in Oxisol increased with HA rates, but it did not change in Entisol. Choosing the right HA rate can decrease PMBC up to 40% and increase the Oxisol P availability by 17%. Application of $MgCO_3$ instead of $CaCO_3$ decreased P adsorption in both soils. Thus, a positive correlation between Ca^{2+} content and PMBC was verified. Optimum rate of HA and the preponderance of Mg^{2+} instead of Ca^{2+} in soil volume fertilized with P are effective practices to reduce adsorption and increase P availability, especially in clayey Oxisol.

Index terms: organic ligands, liming, humic acid-metal-P complexes, Langmuir isotherm, phosphate maximum buffering capacity.

RESUMO

O ácido húmico (AH) pode reduzir a adsorção e aumentar a disponibilidade de P nos solos, entretanto, a magnitude desse efeito é diferente quando o Ca^{2+} prevalece sobre Mg^{2+} em solos com acidez corrigida. Objetivou-se avaliar os efeitos de doses de AH e fontes de carbonato na adsorção, fator capacidade de P máximo (FCPm) e disponibilidade de P em solos contrastantes. Amostras de Latossolo e Gleissolo foram primeiramente incubadas com as seguintes doses de AH: 0, 20, 50, 100, 200 e 400 mg kg^{-1}, combinadas com $CaCO_3$ ou $MgCO_3$, para avaliar a adsorção de P. Em sequência, as amostras de solo foram novamente incubadas com P (400 mg kg^{-1}), para determinar a disponibilidade de P. A aplicação de doses de AH reduziu a capacidade máxima de adsorção, aumentou a energia de ligação do P e não alterou a FCPm do Gleissolo. O teor de P disponível aumentou com o acréscimo das doses de AH no Latossolo, contudo, não foram alterados no Gleissolo. A escolha correta da dose de AH reduziu a FCPm em até 40% e aumentou a disponibilidade de P no Latossolo em 17%. A aplicação de $MgCO_3$ em vez do $CaCO_3$ reduziu a adsorção de P em ambos os solos. Assim, houve correlação positiva entre o teor de Ca^{2+} e a FCPm. A dose ótima de AH e a predominância de Mg^{2+} sobre Ca^{2+} no volume de solo adubado com P são práticas efetivas para reduzir a adsorção e aumentar a disponibilidade de P, especialmente, no Latossolo argiloso.

Termos para indexação: ligantes orgânicos, calagem, complexos ácido húmico-metal-P, isoterma de Langmuir, fator capacidade de P máximo.

INTRODUCTION

Plants grown in tropical soils have low efficiency in uptake P, since the P-fertilizer recovery rates are in the range of 5 to 25% (Yang et al., 2013; Yu et al., 2013). Low P-fertilizer recovery is due to the specific phosphate adsorption, which rarely is returned to soil solution in highly weathered soils (Guedes et al., 2016), preventing P uptake by plants. Soil P maximum adsorption capacity (PMAC) is regulated mainly by soil pH, particle size distribution, clay mineralogy, Fe and Al oxide contents and types, and soil oxide crystallinity (Fink et al., 2014). Among other factors, increased P adsorption in tropical soil is due to lower pH and predominance of kaolinite and Fe and Al oxides in the clay fraction (Novais; Smyth, 1999). PMAC of Brazilian soils ranges from 297 to 4,561 mg kg^{-1} in the 0.0–0.1 m layer, and is highly correlated with Fe oxide content and soil mineral specific surface areas (Fink et al., 2014). Compared to temperate region soils, high amounts of P fixed in Brazilian soils explain the elevated P-fertilizer rates used to meet crop P requirement (Teles et al., 2017).

Besides liming in the soil, humic acid (HA) use is a strategy to reduce P adsorption in tropical soils (Fu et al., 2013; Wang et al., 2016). According to Guan, Shang and Chen (2006), among organic compounds studied, HA was the most effective in blocking the active sites for P adsorption in synthetic Al hydroxide. HA use also reduced P adsorption on synthetic goethite surface, mainly when HA was applied prior to P (Fu et al., 2013). For Brazilian soils, information about optimum HA rate to reduce adsorption and increase P availability along with its effect on plant nutrition and growth is not available. According to Atiyeh et al. (2002), plant growth is enhanced when HA is applied in the range of 50 to 500 mg kg^{-1}.

Liming is routinely used in tropical soils to raise pH, neutralize Al^{3+}, supply balanced amounts of Ca^{2+} and Mg^{2+}, and increase P availability (Sato; Comerford, 2005). Lime rates successively applied on soil surface of permanent crops or no-tillage areas may be high enough to cause overliming. Surface liming should be performed along with correct soil sampling to represent vertical stratification of soil acidity degree and to avoid wrong lime rate definition, otherwise surface soil layers can be alkalinized (Pádua; Silva; Melo, 2006). Low agronomic efficiency liming may also be related to limestone materials available in Minas Gerais, since most carbonates contains about 56% of CaO and less than 5% of MgO (Sampaio; Almeida, 2005). Even though liming is an effective practice to correct soil acidity, the use of limestones richer in Ca than in Mg can promote an imbalance of exchangeable Ca:Mg ratio in soil, resulting in an improper supply of Mg^{2+}, K^{+} and ammonium-N to plants (Pádua; Silva; Melo, 2006). Nature of phosphate-calcium carbonate interaction involves initially formation of precipitates of dicalcium phosphate, which alternatively may be converted into octacalcium phosphate and even in hydroxyapatite (Cole; Olsen; Scott, 1953; Perassi; Borgnino, 2014). HA added is likely to improve soil P availability (Perassi; Borgnino, 2014), increasing the recovery of applied P even in calcareous soils (Delgado et al., 2002).

Addition of Ca^{2+} to soils increases the density of positive charges on colloid surfaces, which may contribute to form new P adsorption sites, favoring P binds through metal bridges (Guppy et al., 2005; Weng; Riemsdijk; Hiemstra, 2012; Duputel et al., 2013). Influence of Ca^{2+} and Mg^{2+} on P adsorption and availability in tropical soils have not been documented so far. Thus, it is important to study if adsorbed and available P in Brazilian soils are regulated by HA rates and carbonate sources. We hypothesized that addition of HA in combination with $MgCO_3$ can increase P availability, mainly in clayey soils due to decreased P adsorption. This study was carried out to evaluate the effects of HA rates in combination with $CaCO_3$ or $MgCO_3$ as liming materials on P adsorption, phosphate maximum buffering capacity and P availability in two soils with contrasting particle size distribution, mineralogy and organic matter content.

MATERIAL AND METHODS

Soils

Samples from an Oxisol and Entisol were collected at the 0-20 cm depth under native vegetation in Lavras, MG, Brazil. Main chemical, physical, and mineralogical soil properties are shown in Table 1.

Table 1: Properties of the soil samples (0-0.2 m) investigated, under native vegetation.

Soil property	Oxisol[1]	Entisol[1]
pH in H_2O, 1:2.5 (v/v)	4.7	5.1
Total P of the clay fraction (mg kg^{-1})	165.8	87.3
Available P – M-1 (mg kg^{-1})	1.5	1.7
Ca^{2+} ($cmol_c$ kg^{-1})	0.1	0.5
Mg^{2+} ($cmol_c$ kg^{-1})	0.1	0.3
Al^{3+} ($cmol_c$ kg^{-1})	1.0	0.5
H+Al ($cmol_c$ kg^{-1})	7.1	4.1
CEC at pH 7 ($cmol_c$ kg^{-1})	7.7	5.9
Total C (g kg^{-1})	23.3	8.6
Rem-P (mg L^{-1})	19.2	31.5
PMAC (mg g^{-1})	0.8	0.5
Clay (g kg^{-1})	500.0	250.0
Silt (g kg^{-1})	130.0	160.0
Sand (g kg^{-1})	370.0	590.0
Total Fe_2O_3 (g kg^{-1})	49.7	10.1
Total Al_2O_3 (g kg^{-1})	214.7	59.0
Dithionite Fe_2O_3 (g kg^{-1})	49.6	7.3
Dithionite Al_2O_3 (g kg^{-1})	10.1	2.5
Oxalate Fe_2O_3 (g kg^{-1})	0.4	0.8
Oxalate Al_2O_3 (g kg^{-1})	1.2	1.2
Minerals of the clay fraction	Kt>Gb>Gt>Hm>Mh	Kt>Gb>Hm>Mh>Gt

[1]Soil Taxonomy; M-1 = available P extracted by Mehlich-1 solution; CEC = cation exchange capacity; Rem-P = Remaining P; PMAC = phosphate maximum adsorption capacity; Kt = kaolinite; Gb = gibbsite; Gt = goethite; Hm = hematite; Mh = maghemite.

Total P and Fe and Al oxides contents of the clay fraction were determined by sulfuric acid digestion (Vettori, 1969). Less crystalline Al and Fe oxides were determined using a single extraction with a 0.2 mol L^{-1} ammonium oxalate solution at pH 3 (McKeague, 1978), and the more crystalline Al and Fe oxides were determined by four successive extractions with sodium dithionite-citrate-bicarbonate (Mehra; Jackson, 1960). Al and Fe contents were quantified by inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro Analytical Instruments, Germany). Minerals in soil clay fraction were identified by X-ray diffractometry (Figure 1), using a Bruker Diffractometer, DZ phaser, with a vertical goniometer and an angular velocity of 0.5 º2θ min^{-1}, range from 10 to 50 º2θ, equipped with Cu tube and Ni filter, operating at 20 kV and 40 mA, employing the powder method with halite as an internal standard.

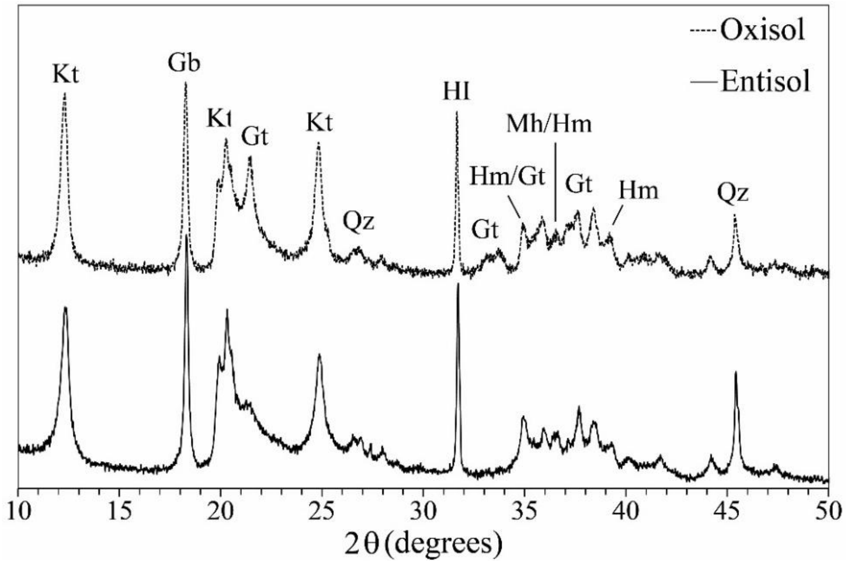

Figure 1: X-ray diffractogram of Na-saturated clay fraction of Oxisol and Entisol samples. Symbols above the peaks represent the minerals: Kt (kaolinite), Gb (gibbsite), Gt (goethite), Qz (quartz), HI (halite) (internal standard), Hm (hematite), Mh (maghemite).

Humic acid characterization

Humic acid (HA) was extracted from leonardite through the use of a 0.5 mol L^{-1} KOH solution, and, in sequence, purified, following the method recommended by the International Humic Substances Society (Swift, 1996). HA C content (372 g kg^{-1}) was measured in an elemental automated analyzer (Elementar, Vario Cube model, Germany). HA also contained 0.8 g kg^{-1} of Ca and 2.3 g kg^{-1} of Mg, both quantified by ICP-OES. Phosphorus was not present in the HA sample. Values of pH (9.7) and electrical conductivity (10.2 mS cm^{-1}) were both measured in a HA:water ratio of 1:5 (w/v). Humic acid E4/E6 ratio was 4.9, which was determined after dissolving HA in a 0.05 mol L^{-1} $NaHCO_3$; subsequently, the absorbance of C chemical groups in HA was measured, respectively, at 465 and 665 nm with a UV-Visible spectrophotometer, according to Reddy et al. (2014). E4/E6 ratio values inferior or equal to 5 are typically assigned to HA samples, while values greater than 5 are routinely related to fulvic acid samples (Reddy et al., 2014). Spectroscopic features from HA were recorded using the attenuated total reflection Fourier transform infrared (ATR-FTIR) technique, in a Bruker series vertex 70v machine. Spectrum bands were recorded in the range of 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1} (Figure 2). Assignments of chemical organic found in the HA were interpreted following library described by Stevenson (1994), as follows. Absorption ATR-FTIR bands in the range between 3400 and 3200 cm^{-1}, with a peak at 3332 cm^{-1}, are typical of OH groups. Bands at 2918 and 2850 cm^{-1} were assigned to aliphatic CH. The absorption band at 1574 cm^{-1} can be assigned to C=C aromatic structures, and at 1365 cm^{-1} to $C\text{-}CH_3$ groups bending.

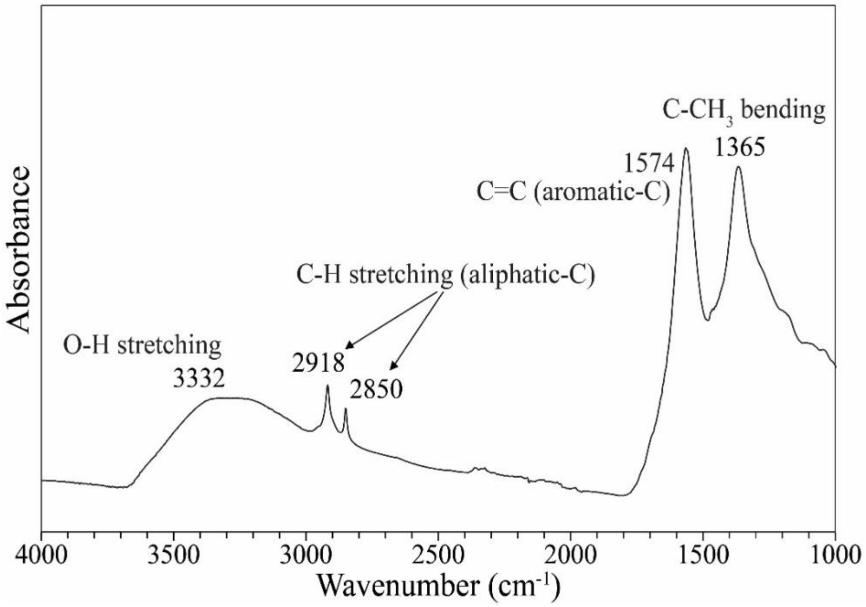

Figure 2: ATR-FTIR spectrum and the main organic chemical groups recorded for the humic acid sample extracted from leonardite.

Study description

Surface (0-0.2 m) samples of Oxisol and Entisol were incubated with different HA rates and carbonate sources. In both cases, a completely randomized design was adopted with four replicates. Two experiments, one with Oxisol and the other with Entisol samples, were carried out simultaneously. A 6 x 2 factorial scheme was adopted, since six HA rates (0; 20; 50; 100; 200 and 400 mg kg^{-1}) were combined with two carbonate sources ($CaCO_3$ and $MgCO_3$). Each experimental plot consisted of 150 g of sieved (< 2 mm) dry soil that were stored in a 200 mL polyethylene container. For each soil, two sequential incubations were carried out: firstly, $CaCO_3$ or $MgCO_3$ were mixed with each HA rate already described, which were incubated with soil samples during thirty days. During this first incubation, soil moisture was kept close to 60% of the soil field capacity. In the second incubation, 400 mg kg^{-1} of P (reagent grade KH_2PO_4) were added and mixed to dried and sieved (< 2 mm) soil samples, previously incubated with carbonate and HA rates, which were again incubated for another thirty days under the same incubation conditions already described for the first incubation.

Soil acidity was corrected aiming to reach a pH in water around 6 and to increase soil Ca^{2+} contents with $CaCO_3$, and Mg^{2+} contents with $MgCO_3$. Carbonate rates were estimated by soil acidity neutralization curves (soil pH as a function of increasing carbonate rates) described in Kaminski et al. (2002). Thus, concentration of carbonate applied in Oxisol was 1.26 g kg^{-1} of CO_3 (2.10 g kg^{-1} of $CaCO_3$ or 1.77 g kg^{-1} of $MgCO_3$); in Entisol samples was added 0.77 g kg^{-1} of CO_3 (1.28 g kg^{-1} of $CaCO_3$ or 1.08 g kg^{-1} of $MgCO_3$). Main soil chemical properties after incubations are shown in Table 2.

Table 2: Chemical properties of soil samples limed with $CaCO_3$ or $MgCO_3$ and treated with increasing humic acid (HA) rates, after incubations.

Soil property	Oxisol[1]					
	HA rate (mg kg^{-1})					
	0	20	50	100	200	400
	$CaCO_3$					
pH in H_2O, 1:2.5 (v/v)	6.4 ±0.05	6.4 ±0.02	6.3 ±0.03	6.4 ±0.02	6.4 ±0.02	6.5 ±0.02
Ca^{2+} ($cmol_c$ kg^{-1})	3.1 ±0.08	2.9 ±0.06	2.9 ±0.02	2.8 ±0.03	2.7 ±0.04	2.7 ±0.08
Mg^{2+} ($cmol_c$ kg^{-1})	0.1 ±0.01	0.1 ±0.01	0.1 ±0.01	0.1 ±0.01	0.1 ±0.01	0.1 ±0.01
CEC at pH 7 ($cmol_c$ kg^{-1})	7.2 ±0.19	6.8 ±0.06	6.6 ±0.12	6.6 ±0.12	6.8 ±0.10	6.9 ±0.15
Total C (g kg^{-1})	19.5 ±0.11	19.5 ±0.06	20.2 ±0.08	20.4 ±0.08	19.7 ±0.13	18.1 ±0.08
	$MgCO_3$					
pH in H_2O, 1:2.5 (v/v)	6.4 ±0.03	6.2 ±0.12	6.1 ±0.03	6.4 ±0.05	6.4 ±0.02	6.4 ±0.04
Ca^{2+} ($cmol_c$ kg^{-1})	0.1 ±0.01	0.1 ±0.01	0.1 ±0.01	0.1 ±0.01	0.1 ±0.01	0.1 ±0.01
Mg^{2+} ($cmol_c$ kg^{-1})	2.9 ±0.03	2.7 ±0.02	2.8 ±0.12	2.8 ±0.03	2.7 ±0.12	2.7 ±0.07
CEC at pH 7 ($cmol_c$ kg^{-1})	7.0 ±0.08	7.3 ±0.23	7.3 ±0.18	7.2 ±0.17	7.1 ±0.23	7.2 ±0.19
Total C (g kg^{-1})	17.4 ±0.08	17.9 ±0.10	16.3 ±0.06	18.3 ±0.11	17.6 ±0.06	17.9 ±0.09

Soil property	Entisol[1]					
	HA rate (mg kg^{-1})					
	0	20	50	100	200	400
	$CaCO_3$					
pH in H_2O, 1:2.5 (v/v)	6.2 ±0.05	6.3 ±0.05	6.3 ±0.02	6.3 ±0.04	6.3 ±0.04	6.3 ±0.05
Ca^{2+} ($cmol_c$ kg^{-1})	2.9 ±0.08	2.7 ±0.03	2.8 ±0.02	2.6 ±0.03	2.7 ±0.02	2.7 ±0.02
Mg^{2+} ($cmol_c$ kg^{-1})	0.2 ±0.03	0.2 ±0.03	0.2 ±0.03	0.1 ±0.02	0.1 ±0.02	0.1 ±0.02
CEC at pH 7 ($cmol_c$ kg^{-1})	6.4 ±0.12	6.5 ±0.07	6.6 ±0.07	6.6 ±0.15	6.6 ±0.11	6.5 ±0.04
Total C (g kg^{-1})	7.1 ±0.03	7.3 ±0.05	7.4 ±0.06	7.0 ±0.05	7.6 ±0.06	7.6 ±0.03
	$MgCO_3$					
pH in H_2O, 1:2.5 (v/v)	6.3 ±0.06	6.2 ±0.03	6.3 ±0.02	6.3 ±0.02	6.3 ±0.08	6.3 ±0.02
Ca^{2+} ($cmol_c$ kg^{-1})	0.3 ±0.02	0.2 ±0.02	0.2 ±0.03	0.3 ±0.01	0.3 ±0.01	0.3 ±0.02
Mg^{2+} ($cmol_c$ kg^{-1})	3.0 ±0.04	3.1 ±0.05	2.7 ±0.07	2.6 ±0.03	2.6 ±0.03	2.5 ±0.03
CEC at pH 7 ($cmol_c$ kg^{-1})	6.0 ±0.11	6.3 ±0.21	6.3 ±0.05	6.7 ±0.07	6.8 ±0.12	6.6 ±0.20
Total C (g kg^{-1})	7.3 ±0.03	7.3 ±0.03	7.0 ±0.05	7.4 ±0.09	7.0 ±0.05	6.9 ±0.10

[1]Soil Taxonomy.

Phosphorus adsorption and availability

After first incubation, 2.5 g of dried soil were stored in 50 ml tubes and mixed with 25 ml of 0.01 mol L^{-1} $CaCl_2$ solution to perform the P adsorption study. Oxisol samples were mixed with solutions containing eleven P concentrations (reagent grade KH_2PO_4), as follows: 0, 5, 11, 16, 27, 38, 49, 60, 77, 93 and 110 mg L^{-1}. Entisol samples were mixed with 0, 4, 8, 12, 20, 28, 36, 44, 56, 68 and 80 mg L^{-1} of P. P concentration in the mixing solutions were based on remaining P values of each soil, following methodology proposed by Alvarez V. et al. (2000). After mixing soil with P solutions and shaking them for 24 hours, tubes with soil were centrifuged for 5 minutes at 3,000 rpm and the supernatant was filtered. P content in the filtered solutions was determined in a UV-visible spectrophotometer, according to Murphy and Riley (1962).

The nonlinear model of the Langmuir isotherm (Equation 1) was fitted P adsorption data set to estimate P maximum adsorption capacity (PMAC) and P binding energy (BE), using the nonlinear regression model described below:

$$x/m = (PMAC \text{ x } BE \text{ x } C)/(1 + BE \text{ x } C) \qquad \text{Equation (1)}$$

Where, x/m is the adsorbed P (mg g^{-1}), $PMAC$ is the P maximum adsorption capacity (mg g^{-1}), BE is the binding energy (L mg^{-1}), as soil affinity parameter for P and C is the concentration of P in the equilibrium solution (mg L^{-1}). Based on the parameters generated by the Langmuir isotherm (PMAC and BE), soil P maximum buffering capacity (PMBC) (Equation 2) was calculated as the maximum slope of the Langmuir equation, evaluated at $C = 0$, according to Holford and Mattingly (1976), as follows:

$$PMBC = PMAC \text{ x } BE \qquad \text{Equation (2)}$$

Where, $PMBC$ is the soil P maximum buffering capacity (L g^{-1}), $PMAC$ is the P adsorption maximum capacity (mg g^{-1}) and BE is the binding energy (L mg^{-1}).

After the second incubation of soil with 400 mg kg^{-1} of P, soil samples of each treatment were air-dried and sieved (< 2 mm) to evaluate available P contents by ionic exchange resin (Raij; Quaggio, 2001) and Mehlich-1 soil tests. For both soil tests, the extracted P was determined in an UV-visible spectrophotometer (Murphy; Riley, 1962). Soil Ca^{2+} and Mg^{2+} were extracted by a 1 mol L^{-1} KCl solution and determined by atomic absorption spectrophotometry (Silva, 2009).

Statistical analysis

Data were submitted to analysis of variance and means were compared using the F test ($p<0.05$). Regression analyses were performed to evaluate PMAC, BE, PMBC and soil available P over HA rates. Exchangeable contents of Ca^{2+} and Mg^{2+} were correlated with PMBC. In all statistical steps, *R* program 3.0.3 version was employed and the ExpDes package was used (Ferreira; Cavalcanti; Nogueira, 2013). Choosing of the regression model that best fit to data set was based on the significance of the mathematical equation parameters ($p<0.05$) and in the equation with the highest adjusted coefficient of determination (R^2).

RESULTS AND DISCUSSION

Phosphate adsorption

Langmuir isotherm model was adjusted to soil P adsorption data set, and changes in adsorption patterns were observed for the humic acid (HA) rates combined with carbonate sources in both Oxisol and Entisol (Figure 3) samples. Differences in magnitude of P adsorption between the two studied soils are mainly related with particle size distribution (Table 1) and mineralogy of the clay fraction (Figure 1). Thus, greater clay, kaolinite (higher intensity in the X-ray diffractograms) and goethite (main diffraction peak at 4.15 Å - 21.38 °2θ) contents in Oxisol than in Entisol explain the differential P adsorption patterns between soils. For Brazilian soils, different studies have reported the role played by clay and its minerals in controlling P adsorption (Fink et al., 2014; Guedes et al. 2016; Teles et al. 2017). In addition, goethite tends to adsorb more P than hematite due to greater specific surface area and rugged surface of the first oxide (Wang et al. 2016).

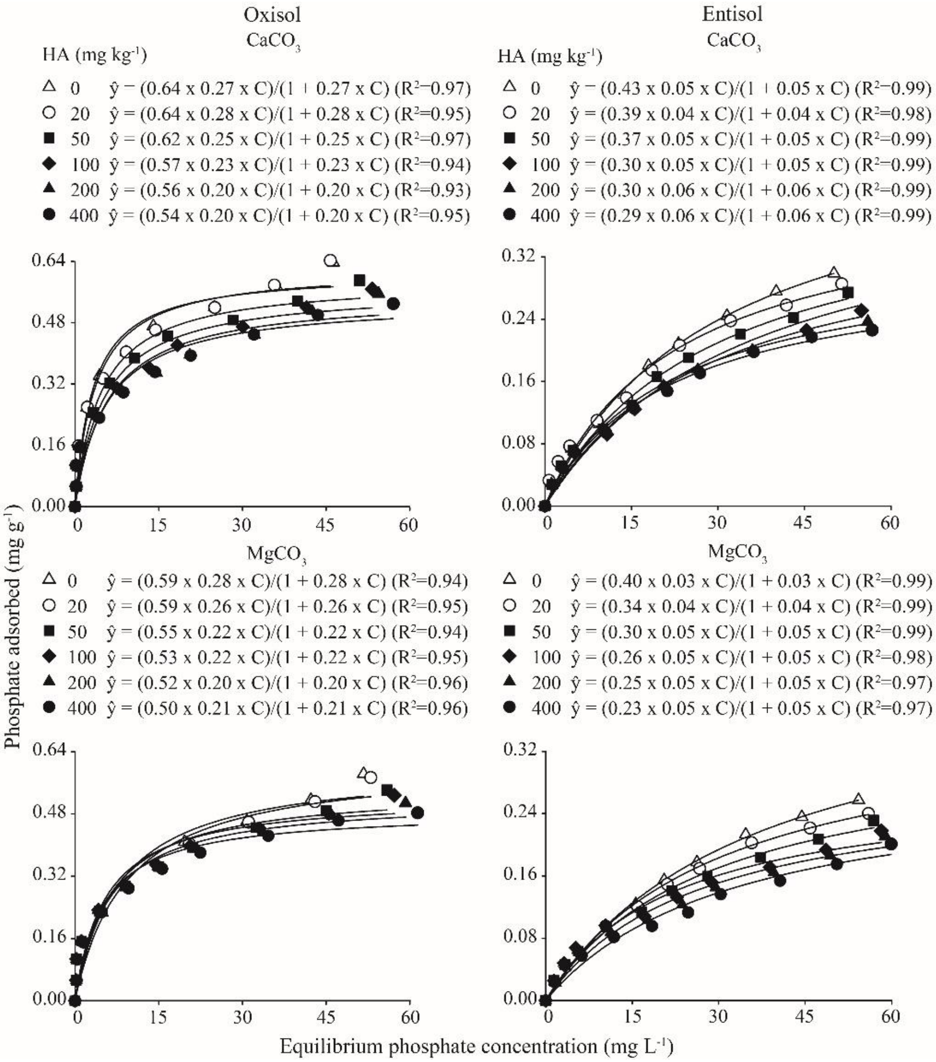

Figure 3: Phosphate adsorption isotherms adjusted to the Langmuir model for different humic acid (HA) rates added to the Oxisol and Entisol samples limed with $CaCO_3$ or $MgCO_3$.

Phosphorus maximum adsorption capacity (PMAC) values showed in Table 1 are greater than values verified in the not-HA-treated Oxisol (Figure 4) and Entisol (Figure 5) samples. Decrease in PMAC values is explained by liming

(Table 2), since minerals with variable charges dominate both soils. As soil pH increased, higher negative charges density is found on soil colloids along with decreased P adsorption (Sato; Comerford, 2005; Benício et al. 2017). PMAC reduction was more pronounced in Oxisol than in Entisol due to greater difference between initial pH and pH reached after liming along with the different clay contents of the two soils.

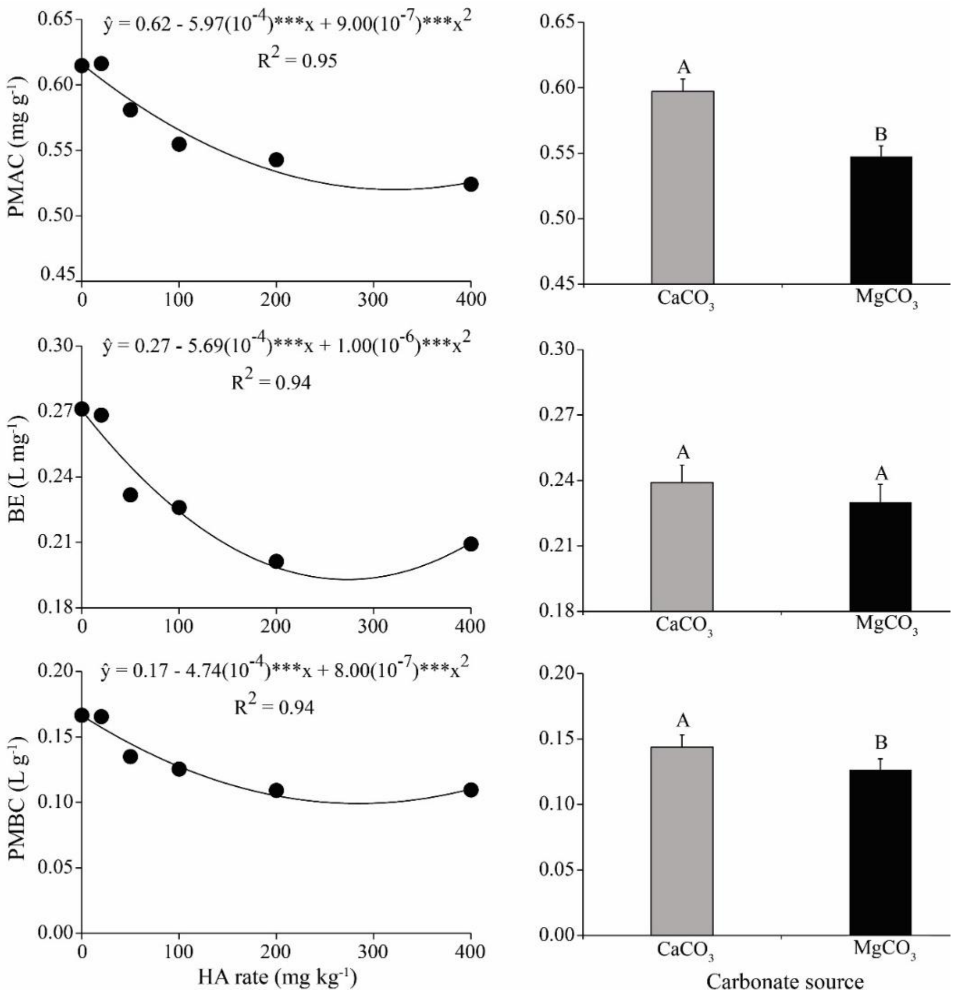

Figure 4: Phosphate maximum adsorption capacity (PMAC), binding energy (BE) and phosphate maximum buffering capacity (PMBC) of Oxisol samples

affected by humic acid (HA) rates and carbonate sources. * $p<0.05$; ** $p<0.01$; *** $p<0.001$. Means followed by the same letter are not statistically different by the F test ($p<0.05$). Bars represent the standard error of the mean.

PMAC, binding energy (BE) and P maximum buffering capacity (PMBC) of both soils were not significantly affected by the HA rate-carbonate source interaction ($p>0.05$). Thus, the factors studied were isolated to evaluate the separate influence of the HA rates on PMAC, BE and PMBC, both in Oxisol (Figure 4) and in Entisol (Figure 5) samples. In Oxisol, PMAC and P-BE were reduced over HA rates, and a quadratic model was the best equation fitted to the data set. When HA was applied at the rate of 332 mg kg^{-1}, PMAC was reduced by 16%. PMAC reduction verified in HA-treated soils prevented 198 kg ha^{-1} of P to be adsorbed onto soil colloids, considering the soil depth of 0 to 20 cm. In Oxisol samples, P affinity on colloid surfaces was reduced due to BE decrease.

Evaluating the interaction of P with goethite and hematite in a broad pH range (4.5 to 8), Wang et al. (2016) verified that HA reduced PMAC and P-BE. Polycarboxylic groups found in HA can inhibit P adsorption in tropical soil colloids by at least four different mechanisms: (i) blocking P binding sites; (ii) increasing the negative electric potential in the plane of adsorption; (iii) causing steric hindrance on the mineral surfaces (Fu et al., 2013; Wang et al., 2016); and (iv) decreasing goethite and hemathite specific surface area (Wang et al., 2016). These mechanisms reduce P affinity with the mineral surface of highly weathered soils, and may decrease soil P buffering capacity.

PMBC is an index from which it is possible to infer soil resistance and rate to transfer P from solid to liquid phase, thus, it may be an indirect index of soil P availability (Novais; Smyth, 1999). PMBC was reduced over HA rates, with lesser values in Oxisol limed with $MgCO_3$ than in sample treated with $CaCO_3$, as it was verified for PMAC (Figure 4). In relation to the HA untreated soil samples, application of 296 mg kg^{-1} of HA reduced PMBC in 40%. Therefore, not only the P adsorption in the Oxisol decreased, but also increased the ability of clayey soil to release P from mineral surfaces to soil solution, which reduces hysteresis or adsorption irreversibility.

Decrease in PMBC was also verified by Mejías, Alfaro and Harsh (2013), as the increase in P rate reduced the adsorption energy and enhanced P mobilization in a volcanic soil from Chile. Yu et al. (2013) also observed a reduction of P adsorption and PMBC by applying poultry manure in soil derived from basalt and incubated for up to 60 days. Organic matter can act preventing P hysteresis and optimizing P fertilization in Brazilian soils (Guedes et al., 2016). Thus, results of this study have confirmed that soil P buffering capacity is a dynamic soil property, which is controlled by management and C fractions added to soil.

Analysis of Oxisol PMBC showed that, after the minimum value, PMBC tended to increase or even stabilize depending on the HA rate applied (Figure 4). Thus, increase of HA rates added to soil may also favor P sorption through the formation of HA-cation-P complexes (Guppy et al., 2005), preventing a linear decrease of Oxisol PMBC. Adsorption of organic anions on soil colloid surfaces can increase P adsorption through interactions of phosphate with Ca^{2+}, reducing P mobility and availability (Weng; Riemsdijk; Hiemstra, 2012; Duputel et al. 2013). Thus, adding HA to Oxisol can either decrease or increase P adsorption, depending mainly on the HA rate added, exchangeable cation contents and organic-cation-P complexes formed in soil.

Organic-metallic-P complexes can be formed by different cations (Gerke, 2010), such as Fe, Al, Ca, and Mg with distinct chemical stability (Guppy et al., 2005; Urrutia et al., 2014). Jiang et al. (2015) verified that Ca^{2+} and Mg^{2+} from biochars increased the apparent adsorption of P in an Oxisol and an Ultisol. Association of cations with phosphate can occur on the mineral surface or in soil solution, through the formation of $MgPO_4^+$ or $CaPO_4^+$ ion pairs; these salts can be adsorbed in the negative charges of soil minerals or organic compounds; besides, the binding strength of P associated to Ca^{2+} is greater compared to P bonded to Mg^{2+} (Millero et al., 2001; Xu et al., 2014). In accordance with Li et al. (2016), association of Ca^{2+} to bentonite increased PMAC and P-BE in relation to Mg^{2+}. Nevertheless, the formation of HA-cation-P complexes may be a strategy to assure better conditions for plant P uptake in soil. HA-metal-P complexes prevent phosphate to be specifically adsorbed onto mineral surfaces, since P tends to be slowly released into soil solution (Gerke, 2010).

In Entisol, PMAC decreased as HA rates increased, and the quadratic model was the equation that best fitted to data set (Figure 5). The lowest PMAC value was found when 275 mg kg^{-1} of HA was added to Entisol samples, which increased P in the equilibrium solution. However, BE increased up to 230 mg kg^{-1} of HA, which P maximum binding energy to soil colloids was 26% greater than the soil non-treated with HA. Consequently, PMBC was not significantly affected by HA rates (p=0.08), but, $CaCO_3$ addition increased PMBC in relation to $MgCO_3$, as was observed for the Oxisol samples. Yu et al. (2013) verified a similar result as PMAC decreased over poultry manure in soil derived from alluvium, and BE increased significantly after 30 days of incubation.

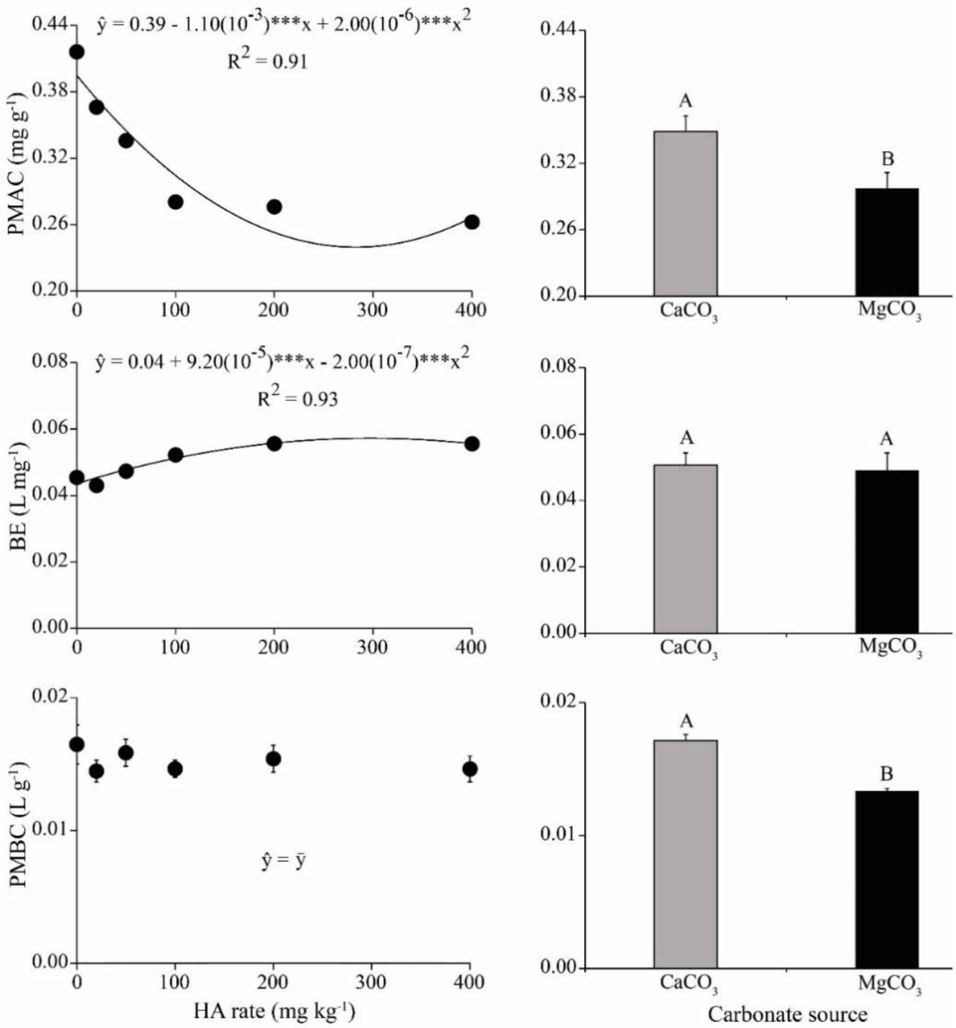

Figure 5: Phosphate maximum adsorption capacity (PMAC), binding energy (BE) and phosphate maximum buffering capacity (PMBC) of Entisol samples as related to humic acid (HA) rates and carbonate sources. * $p<0.05$; ** $p<0.01$; *** $p<0.001$. Means followed by the same letter are not statistically different by the F test ($p<0.05$). Bars represent the standard error of the mean.

Absence of PMBC response over HA rates in Entisol is related to increase of BE (Figure 5) and it is linked to soil properties. The Entisol had half the clay content of the Oxisol (Table 1) and, therefore, the application of HA and P promoted increased competition between both anionic species for positively charged colloids. Theoretically, it is plausible to anticipate, without a prove of concept, that a possible interaction between HA and phosphate might have occurred. Initially, HA applied is preferentially adsorbed in soil colloids. However, with the addition of P (P adsorption study), competition for adsorption sites between HA and phosphate increases, probably causing displacement of the HA previously adsorbed.

Thereby, as P adsorbed on soil colloids and HA molecules around adsorption sites, colloids affinity for P is increased due to closeness of this anion with the adsorption plane, increasing BE to the extent that HA rates increased. Results found in this study are in accordance with Afif, Barrón and Torrent (1995), who verified that, in the presence of organic matter, colloid affinity for P in Brazilian soils is increased, with slow replacement of organic anions at the sorption sites. Therefore, it may be inferred that HA strongly competes for the same P binding site, and that the role played by HA in blocking P sorption is transient in the Entisol.

It should also be taken into account that interaction of HA to soil mineral constituents is weak through *van der Waals forces*, and it cannot effectively compete with P for soil colloids binding sites (Sibanda; Young, 1986). Furthermore, Lindegren and Persson (2009) reported that binding of carboxylic acids onto goethite does not occur through inner-sphere complexes. Guan, Shang and Chen (2006) examined the competitive adsorption between HA and P on the surface of synthetic aluminum hydroxide and found that HA added was completely adsorbed to the mineral, however, in the presence of P, HA adsorption was reduced in up to 66%.

Phosphorus availability

Available P contents in soils recovered by resin and Mehlich-1 soil tests were not altered by the HA rate-carbonate source interaction ($p > 0.05$), both in Oxisol (Figure 6) and in Entisol (Figure 7) samples. For Oxisol samples, soil P availability was influenced by HA rates. Resin-P contents reached the maximum value (204 mg kg^{-1}) in Oxisol samples treated with 294 mg kg^{-1} of HA, which represents an increase of 17% in soil resin-P content. Increase in P availability is associated to a decrease of P adsorption parameters (Figure 4). Mehlich-1 P (M1-P) contents were linearly increased over HA rates. Thus, maximum M1-P content (99 mg dm^3) was verified at the rate of 400 mg kg^{-1} of HA in Oxisol samples. Differences between resin and M1-P contents are related to the reduced capacity of Mehlich-1 solution in recovering P, mainly in high-clay-content soils (Novais; Smyth, 1999).

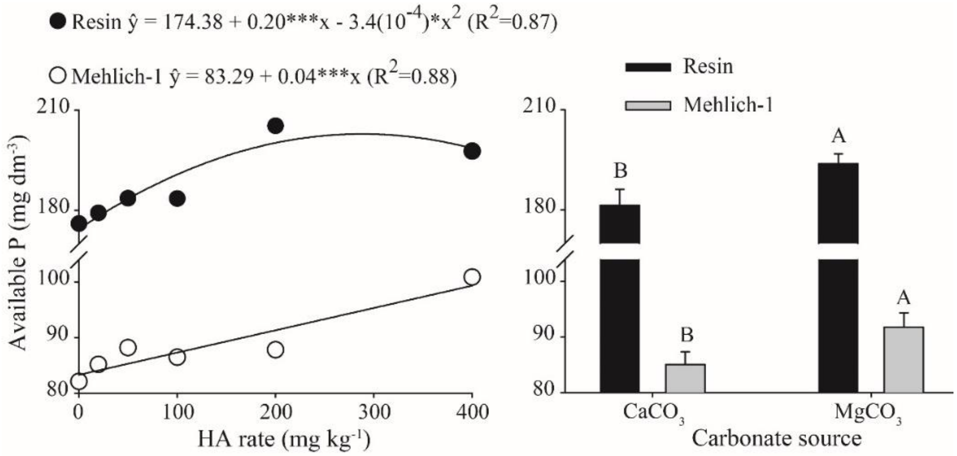

Figure 6: Resin-P and Mehlich-1 P contents in Oxisol samples treated with humic acid (HA) rates and carbonate sources. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$. Means followed by the same letter are not statistically different by the F test ($p < 0.05$). Bars represents the standard error of the mean.

In an acid and weathered soil, Yang et al. (2013) observed that the combination of fulvic acid and KH_2PO_4 increased soil labile P extracted by 0.5 mol L^{-1} $NaHCO_3$. Increase of P availability after use of humic substances was verified by Hua et al. (2008) in Chinese soils. Even increasing soil P availability, optimum rate of humic substances to P availability in soils are not mentioned in the studies performed by Yang et al. (2013) and Hua et al. (2008). Optimum HA rate found in the present work for maximum P availability (Figure 6) may be prohibitive for some crop fields mainly where P-fertilizer is broadcasting applied. However, it may be feasible for some agricultural systems where HA is applied only in the soil volume under the influence of roots or in strip band or in row where P fertilizer is placed. Use of HA as an accompanying ligand to phosphate fertilizers may also be another strategy to prevent P fixation in highly weathered soils, which may optimize P-fertilizer use efficiency (Urrutia et al., 2014). Formulation of P-fertilizer with HA is a technology already used by the Brazilian fertilizer industry and incorporated in some crop fertilization programs (Herrera et al., 2016).

Greater resin- and M1-P contents were determined for Oxisol samples limed with $MgCO_3$ than in those treated with $CaCO_3$ (Figure 6). Hence, choosing the right source of lime materials ($CaCO_3$ or $MgCO_3$) may alter both P adsorption and availability in soil, probably affecting P uptake by plants. In Entisol, neither effect of HA rates nor carbonate sources were observed for resin- or M1-P contents ($p>0.05$) (Figure 7), which is partially related to the absence of PMBC response to HA rates in this soil (Figure 5). Thus, effects of HA rates on P adsorption and availability is soil-dependent, mainly relying on clay content and mineralogy. Herrera et al. (2016) verified that the application of single superphosphate complexed to HA did not alter resin-P contents in comparison to single superphosphate applied in non-HA treated soil with 22 g kg^{-1} of clay, under the effect of a rotation cropping system.

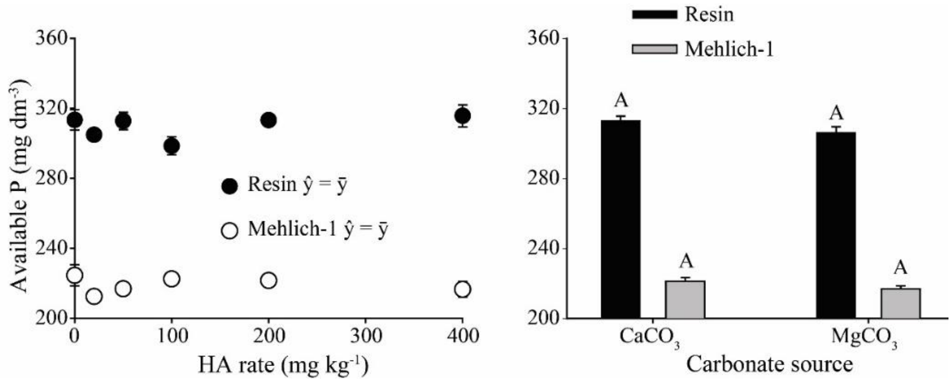

Figure 7: Resin-P and Mehlich-1 P contents in Entisol samples as related to humic acid (HA) rates and carbonate sources. Means followed by the same letter are not statistically different by the F test (p<0.05). Bars represent the standard error of the mean.

Significant and positive correlations were found between exchangeable Ca contents and PMBC for both Oxisol and Entisol samples limed with CaCO$_3$ (Figure 8). This indicates that the higher Ca^{2+} content, the greater the soil resistance to release P from solid phase to soil solution. However, there was not a significant correlation between exchangeable Mg^{2+} contents and PMBC in both soils limed with MgCO$_3$. Thus, P-complexes are less stable with Mg than with Ca (Millero et al., 2001; Li et al., 2016), mainly, due to the largest ionic size of Mg in its hydrated form, which contributes to reduce P sorption (Xu et al., 2014).

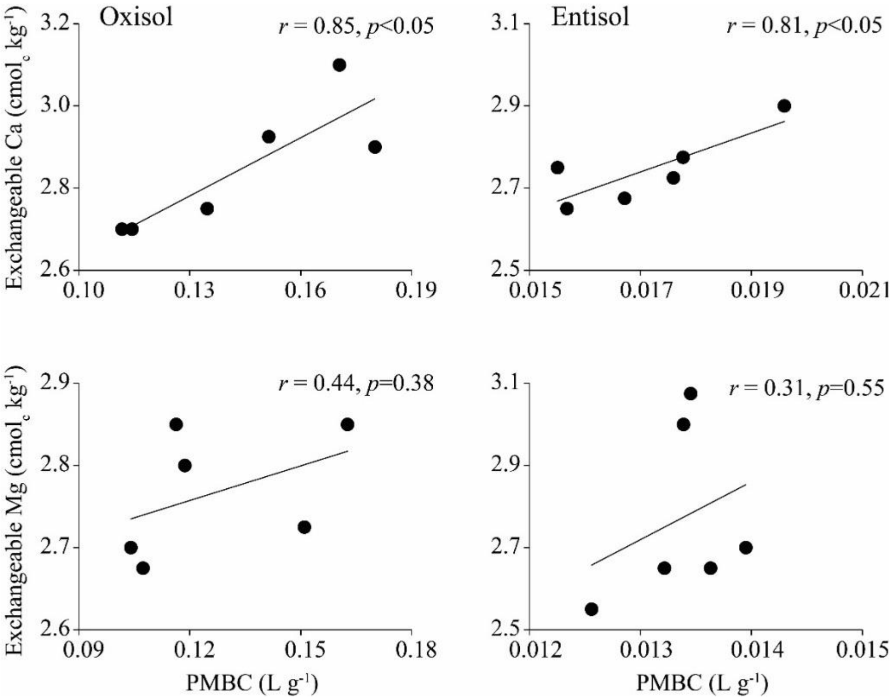

Figure 8: Linear correlations between exchangeable contents of Ca or Mg and phosphate maximum buffering capacity (PMBC) for Oxisol and Entisol samples.

Very few studies have reported the influence of HA rates on the adsorption and availability of P in weathered soils. Effect of carbonate accompanying cations (Ca or Mg) on P adsorption is also lacking for highly weathered Brazilian soils. Greater contents of Ca^{2+} in soils increase the density of positive charges on the colloid surfaces, which result in increased P adsorption and a decrease in available P contents in comparison to Mg^{2+}. Thus, the presence of Mg^{2+} in tropical soil play an important role to improve the efficiency use of P-fertilizers. Agronomically, $CaCO_3$ can not replace $MgCO_3$ in liming practices and, Ca and Mg must be added in adequate and balanced rates in soils. However, in crop fields where $CaCO_3$ is successively applied over $MgCO_3$, some effort should be made to apply Mg together with P source in order to meet crop Mg^{2+}

requirement and to optimize agronomic performance of soluble P-fertilizers used in most Brazilian crop fields.

In future studies, adequate soil Ca:Mg ratio which catalyzes the HA rates effect on decreasing P adsorption and increasing availability should be investigated. An ample variability of soil types, mineralogy, particle size distribution, and organic matter contents should be included in these experiments in order to understand the factors affecting P sorption, availability, forms and dynamics in tropical conditions, along with the role played by HA in optimizing P supplying to crops.

CONCLUSIONS

Humic acid rates and carbonate sources affected phosphate adsorption in Brazilian Oxisol and Entisol samples, and P availability only for the Oxisol samples. Choosing the adequate humic acid rate reduces P maximum adsorption capacity and binding energy on the colloid surfaces as well as decreases P maximum buffering capacity in the clayey Oxisol. Inhibition on P adsorption caused by the use of humic acid in the Oxisol increases P availability, with greater P recovery by resin than by the Mehlich-1 soil test. Adding humic acid extracted from leonardite to Brazilian Oxisols is an effective strategy to decrease P adsorption and increase soil P availability. Regardless of the humic acid rate added to soil, the preponderance of Mg^{2+} instead of Ca^{2+}, only in soil volume fertilized with P, is an option to decrease phosphate adsorption and buffering P capacity in both Oxisol and Entisol samples.

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IS COMPOSTING A ROUTE TO SOLUBILIZE LOW-GRADE PHOSPHATE ROCKS AND IMPROVE MAP-BASED COMPOSTS?

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Running title: Does composting improve phosphate rocks and MAP?

RESUMO: Em compostos alcalinos e ricos em Ca, a solubilização da apatita de fosfatos naturais (FNs) não é garantida. Entretanto, agentes quelantes e substâncias humificadas produzidas durante a compostagem podem alterar os teores solúveis e as formas de P dos compostos com MAP. Esses efeitos podem ser dependentes das proporções de resíduos orgânicos e da fonte de P utilizada no composto. O objetivo deste estudo foi avaliar o efeito da compostagem de esterco de galinha, casca de café e FN de Araxá, FN de Bayóvar ou MAP em diferentes proporções sobre a decomposição da matéria orgânica, teores totais de N, de Ca e frações solúveis de P nos compostos. Os tratamentos consistiram da combinação de três fontes de P (FN Araxá, FN Bayóvar e MAP), com quatro misturas em diferentes proporções, 25; 40; 50 e 75 % de fonte de P com esterco de galinha (37,5; 40; 25 e 12,5 %) e casca de café (37,5; 20; 25; 12,5 %) submetidos ou não a 150 dias de compostagem. Os compostos com FNs apresentaram as maiores reduções no C total, C solúvel em água e menor rendimento em massa seca que as misturas compostadas com MAP. O uso do MAP nas misturas resultou em menores perdas de N comparado aos compostos formulados com FNs. Independentemente da mistura entre esterco de galinha, casca de café e FNs, a compostagem aumentou o pH e os teores de Ca, e não alterou as frações de P solúvel em água, ácido cítrico e citrato neutro de amônio mais água no composto final. A compostagem dessas misturas não foi uma rota eficiente para solubilizar P do FN de Araxá e de Bayóvar. Os valores de pH acima de 8 e alto teor de Ca foram os principais fatores que explicam a estabilidade e a não solubilização da apatita de FNs nos compostos. A compostagem com MAP, misturado a diferentes proporções de esterco de galinha e casca de café, reduziu o P solúvel em água, manteve o pH das misturas na faixa de 5 a 7 e enriqueceu o composto com N e P.

Palavras-chave: apatita, esterco de galinha, casca de café, ácidos orgânicos, equivalente NPK.

ABSTRACT: In alkalinized and rich-Ca composts, solubilization of apatite from phosphate rocks (PRs) is not guaranteed, however, chelating agents and humified substances produced during composting may alter soluble contents and P forms of MAP-based composts. These effects may rely on the proportions of organic wastes and P source used in the compost piles. The aim of this study was to evaluate the effect of composting among chicken manure, coffee husk and Araxá PR, Bayóvar PR or MAP in different proportions on the organic matter decomposition, total N, Ca contents and soluble P fractions in the composts. The treatments consisted of a combination of three P sources (Araxá PR, Bayóvar PR and MAP), with four mixtures in different proportions, 25, 40, 50 and 75 % of P source with chicken manure (37.5, 40, 25 and 12.5 %) and coffee husk (37.5, 20, 25 and 12.5 %) submitted or not to 150 days of composting. The composts with PRs showed the greatest reductions in total C, water-soluble C and lower dry mass yields than MAP-based composts. The use of MAP in mixtures assured lower N losses compared to composts formulated with PRs. Regardless of the mixture between chicken manure, coffee husk and PRs, composting increased the pH and total Ca contents, and did not alter the fractions of soluble P in water, citric acid and neutral ammonium citrate plus water in the final PRs-based composts. Composting of these mixtures was not an efficient route to solubilize P from Araxá and Bayóvar PRs. Values of pH above 8 and high Ca contents were the main factors explaining the stability and non solubilization of the apatite of PRs in the composts. Composting with MAP, mixed in different proportions with chicken manure and coffee husk, reduced water-soluble P, maintained the pH of the mixtures in the range of 5 to 7, and enriched the composts with N and P.

Keywords: apatite, chicken manure, coffee husk, organic acids, NPK fertilizer equivalent.

INTRODUCTION

Phosphorus (P) global demand increases and phosphate rock reserves reduction have raised the costs of P-fertilizer (Cordell et al., 2009), which reinforces the importance of P efficient use in the Brazilian agriculture. Brazil imports more than 50 % of P used in crop fields (ANDA, 2011). Most of P added into soil as fertilizer are used with low efficiency by plants, which is specially related to the intense P retention process in soil (Roy et al., 2016). In this scenario, there is a search for more efficient alternative P sources (Christel et al., 2014). Formulation process of organo-mineral fertilizers (OMFs) in composting mixtures of wastes with soluble fertilizers or low-grade phosphate rocks can be one of the alternatives to reduce P sink in Brazilian soils, and to promote a nutrient release more compatible with the crop demand phases, which may optimizes its capacity of P acquisition.

Application of phosphate rocks (PRs) *in natura* is not appropriate to supply the requirement of P from crops due to their low P solubility/release in soil, which does not meet P demand from plant in a timely manner (Novais et al., 2007). Thus, Brazilian coffee farmers have been mixing PR in composting piles with coffee husk (CH) and chicken manure (CM) as a route to produce OMFs, though they do not know the efficiency of this process for P-PRs solubilization. During composting, not only humic substances are produced, but also low molecular weight organic acids found in CM (Pinheiro et al., 2013) and synthesized by microorganisms in composting piles can complex Ca, Fe, and Al of the PR, destabilizing the apatite from PR and increasing P solubility (Welch et al., 2002; Vassilev et al, 2013).

The ratio between PR and waste in composting is another factor that influences the decomposition and P solubility. Bangar et al. (1985), studying P solubilization with different proportion of PR in composting, verified, with addition of 25 % PR in the composting pile, an increase in citric acid-soluble P content after 90 days of composting low-grade P source with cattle manure and vegetable waste. The ratio among wastes is also important, since the combination of CM, an alkaline waste rich in Ca and N, and CH, an acid byproduct with greater K content among crop residues (Higashikawa et al., 2010) may provide suitable conditions for P-PR solubilization in composting.

However, composting process may increase the final compost pH (Fernández et al., 2016), which implies in a higher apatite stability (Mendes et al., 2013). Whereas, if there is a predominance of fungi, pH may decrease and favor P solubilization during this process (Zayed and Abdel-Motaal, 2005). Therefore, there is a need for further research to define suitable conditions for P-PR solubilization during composting, mainly regarding the function of organic ligands, pH changes, and Ca concentration (Chien et al., 2011). Such studies have become relevant in Brazil. Since PRs used have different chemical and mineralogical composition, such as Araxá PR, which is a Brazilian rock consisting of fluorapatite of igneous origin with low reactivity (Novais et al., 2007), and Bayóvar PR, which is a sedimentary francolite (Bech et al., 2010) with higher P reactivity/solubility than Araxá PR.

In addition to the use of PRs, another route to produce OMF is the application of soluble phosphate fertilizers, such as single superphosphate (SSP), triple superphosphate (TSP) and monoammonium phosphate (MAP) in the composting pile. These soluble phosphate fertilizers and their phosphate accompanying cation do not differ in the P solubility, since water-soluble P fraction taking place in 85-90 % of the total P, and the remaining fraction of P is soluble in citrate (Chien et al., 2011). Soluble P form found in MAP is majorly $NH_4H_2PO_4$, and this fertilizer shows the highest P content, about 22% (IPNI, 2017), which implicate in lower cost per kilogram of P in relation to SSP and TSP. For these reasons, MAP is the most P source used in OMFs production in Brazil, besides enriching the compost with N. However, little is known about the N-MAP losses during the composting process and changes in P forms and solubility of MAP-based final composts.

Both high water-soluble P content and the acidity of soluble phosphate fertilizers promote a rapid P release to soil solution, which favors precipitation of P with Fe and Al, and adsorption of phosphate to soil colloids (McLaughlin et al., 2011), contributing to the reduction of P-fertilizer use efficiency by crops in Brazilian soils (Prochnow et al., 2006). Composting can reduce water-soluble P content through P complexation by organic acids, forming organo-metallic complexes (Gerke, 2010; Urrutia et al., 2014), and maintaining compost pH close to neutrality. Yang et al. (2015) verified that the use of SSP in composting promoted a slow decomposition of organic matter, reduced the volatilization of N-NH_3 and maintained pH values close to 7 in the final compost. Therefore, the magnitude of solubilization, precipitation, and organic complexation reactions that can alter P solubility in the final compost is probably conditioned by changes in pH and Ca concentration, which are controlled by the ratio among P source, CM, and CH.

Taking into account several production routes for OMF and compost formulations used in Brazil, the main hypothesis of this study are: (i) increased CM proportions in PR composts piles increase Ca concentration and pH in the final compost, which prevents the solubilization of apatite, even in humified composts rich in organic ligands; (ii) in composts formulated with MAP, increased proportion of CM decreases water-soluble P without altering citrate-soluble P, besides giving the final compost an acidic character, which reduces N losses during composting. The aims of this study were to evaluate: i) C forms, dry mass and N losses, pH and total Ca content in mixtures of P source, CM and CH submitted to 150 days of composting; ii) the effect of composting on soluble P forms in the PRs mixtures; iii) the changes of P solubility in water, citric acid and citrate of the composted mixtures with MAP; and iv) determine N, P_2O_5, and K_2O (NPK fertilizer equivalent) contents of the formulated composts.

MATERIALS AND METHODS

Organic wastes, phosphorus sources and composting process

Chicken manure (CM) was collected in poultry facilities located at the Department of Animal Science, and coffee husk (CH), in postharvest facility found at the Department of Agriculture both located at the Federal University of Lavras (UFLA). These wastes were dried in a forced air oven for 72 h at 60 °C, then milled in a Willey mill and passed through a 1 mm mesh sieve. Mineral P sources, Araxá phosphate rock (Araxá PR), Bayóvar phosphate rock (Bayóvar PR) and monoammonium phosphate (MAP) were purchased from commercial establishments and from fertilizer companies. Araxá and Bayóvar PRs were used in composting with particle size <0.25 mm, while MAP was used in the granulated form. The organic wastes and mineral P sources were characterized in relation to the main chemical (Table 1), and physicochemical properties (Figure 1). The main chemical groups present in organic wastes and in P sources were identified by the attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (Figure 1), which were interpreted according to Silverstein et al. (2006) and Berzina-Cimdina and Borodajenko (2012).

Table 1. Chemical properties of phosphate rocks, monoammonium phosphate and organic wastes samples used in composting.

Material	pH in $CaCl_2$	EC(1)	P content soluble in			Total content			
			Water	CA(2)	NAC(3)	P	N	K	Ca
		dS m^{-1}		g kg^{-1}			g kg^{-1}		
Araxá(4)	6.9	0.1	0.1	26.6	5.7	126	nd(9)	nd	329
Bayóvar(5)	6.5	2.2	0.2	41.1	9.7	134	nd	nd	361
MAP(6)	4.1	71.5	219	225	235	237	110	nd	nd
CM(7)	7.1	11.6	5.4	23.9	17.9	34.2	30.2	28.4	134
CH(8)	4.6	8.1	1.0	1.1	1.2	1.2	17.3	42.4	3.4

(1)EC: Electrical conductivity; (2)CA: Citric acid; (3)NAC: Neutral ammonium citrate plus water; (4)Araxá: Araxá phosphate rock; (5)Bayóvar: Bayóvar phosphate rock; (6)MAP:

Monoammonium phosphate; (7)CM: Chicken manure; (8)CH: coffee husk; (9)nd: non-determined.

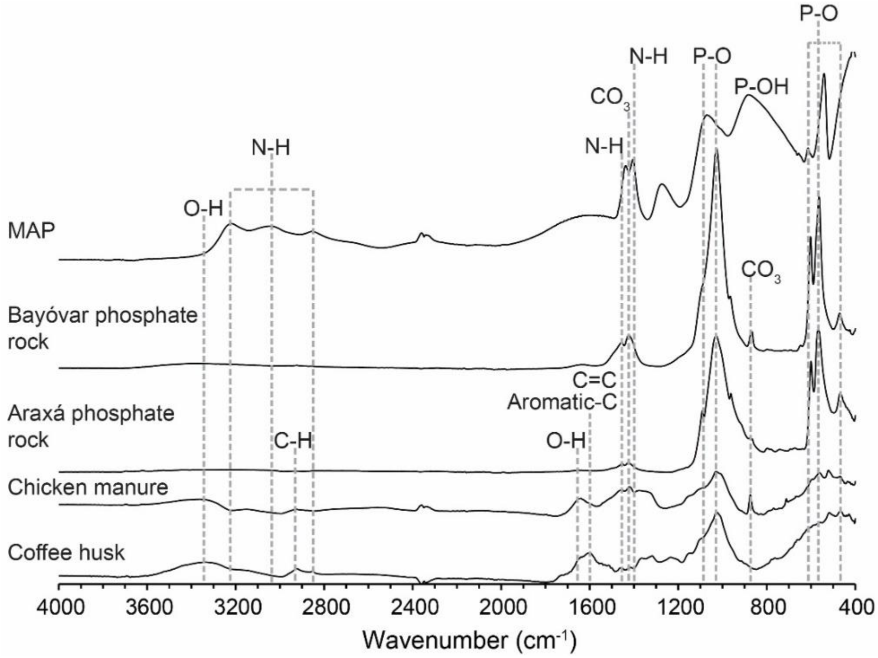

Figure 1. ATR-FTIR spectra and the main chemical groups recorder for the coffee husk, chicken manure, Araxá phosphate rock, Bayóvar phosphate rock, and monoammonium phosphate (MAP) samples.

Mixture of 500 g of organic wastes and mineral P source were stored and incubated in polyethylene bags, which constituted the experimental unit. Deionized water was added to mixtures of organic wastes and P sources to maintain moisture close to 70 % of the maximum water retention capacity of each mixture during the 150 days of incubation. The plastic bags containing wastes-P sources mixtures were composted in greenhouse conditions and inserted in hard polyethylene pots with capacity of 3 L coated with aluminum foil. Bags containing mixtures were daily opened during 15 minutes to allow gas exchanges, and all plots were sequentially revolved to optimize composting until the end of the incubation.

Experimental design

A 3 x 4 x 2 factorial scheme was chosen, in which three P sources (Araxá PR, Bayóvar PR and MAP) were combined with four mixtures, in different proportions, of CH and CM with P sources (Table 2), in two incubation conditions: without and after 150 days of composting. A completely randomized design with 3 replicates was used.

Table 2. Treatment description and their acronyms to each mixture among P source (Araxá phosphate rock, Bayóvar phosphate rock or monoammonium phosphate), chicken manure, and coffee husk, dry mass-based.

Treatment/acronyms	P source - P	Chicken manure - CM	Coffee husk - CH
		%	
P25:CM37.5:CH37.5	25	37.5	37.5
P40:CM40:CH20	40	40	20
P50:CM25:CH25	50	25	25
P75:CM12.5:CH12.5	75	12.5	12.5

Chemical and physicochemical analyses

At the end of the 150 days of composting, the composted mixtures were dried in a forced air circulation oven for 72 h at 60 ºC and weighed to determine dry mass. In sequence, the mixtures were milled in a Willey mill and sieved (<1 mm) to evaluate pH in a solution of 0.01 mol L^{-1} of $CaCl_2$ and the electrical conductivity (EC) in a compost:water ratio of 1:5 (w/v). Water-soluble P contents were determined in the composts after successive washings with deionized water in 1 g of compost until a final volume of 250 mL; citric acid (CA)-soluble P was extracted stirring the mixtures with a 2 % citric acid (CA) solution for 30 minutes, in a compost:solution ratio of 1:100 (w/v). In addition to these fractions, neutral ammonium citrate plus water-soluble P (NAC+H_2O-soluble P) was extracted by boiling the sample with neutral ammonium citrate solution (pH 7) in a compost:solution ratio of 1:50 (w/v). Total P determination was performed after digestion of mixtures with concentrated nitric acid and, in sequence, with concentrated perchloric acid. These analytical procedures were performed according to official methods described in Brasil (2013). Quantification of P fractions in composts was done by inductively coupled plasma optical emission spectrometry (ICP-OES, Spectro Blue, Spectro Analytical Instruments, Germany). Each of the contents related to the soluble P fractions were relativized individually, in relation to the total P, according to the Equation 1, in which the soluble P index calculation was based.

$$\text{Soluble P index (\%)} = (\text{soluble P content} / \text{total P content}) \times 100 \qquad \text{Equation (1)}$$

Soluble P index was calculated for soluble P fractions in water, CA and NAC+H_2O in order to equalize the concentration effect promoted by mass loss at the end of the composting and to determine the relative proportion of soluble P in relation to total P content, which allowed to compare P contents of a composted mixture with another.

Composts were also submitted to the nitric-perchloric digestion in 4:1 ratio (nitric acid: perchloric acid) for determining total K contents in flame emission photometer and Ca by atomic absorption spectrophotometry. Total N content was determined by the Kjeldahl method after the compost sample digestion with sulfuric acid, based on the methodology proposed by Tedesco et al. (1995), which allowed estimating N loss at the end of composting, according to the Equation 2.

$$\text{N loss (\%)} = 100 - 100 \times [(DM_2 \times N_2) / (DM_1 \times N_1)] \qquad \text{Equation (2)}$$

Where DM_1 and DM_2 are the respective dry masses (g) of the compost at the beginning and at the end of composting, and N_1 and N_2 are the initial and final N contents (g kg^{-1}), respectively.

Contents of total P, CA-soluble P, and NAC+H_2O-soluble P of each composted mixture were also converted to P_2O_5, and the total K to K_2O, using multiplicative factors of 2.29 and 1.20 respectively. These conversions were carried out to characterize the composts and to calculate its NPK fertilizer equivalent, through of the sum of the concentrations of N, CA-soluble P_2O_5 for mixtures with PRs, or NAC+H_2O-soluble P_2O_5 for mixtures with MAP, and K_2O.

Water-soluble C (WSC) in composts was extracted using the same analytical procedure chosen for water-soluble P determination, and total C and WSC were determined using a dry combustion analyzer (Elementar, Vario Cube model, Germany). The compost spectroscopic main features were also identified by ATR-FTIR in a spectrometer of the Bruker series vertex 70v machine. The spectra of each mixture refers to the mid-infrared region, from 4000 to 400 cm^{-1}, with a resolution of 2 cm^{-1}.

Statistical analysis

Data were submitted to analysis of variance, and means were compared by the Tukey test ($p<0.05$). Statistical analyses were performed through the computer program R 3.0.3 (R Core Team, 2014), using the ExpDes package (Ferreira et al., 2013). Principal component analysis (PCA) was also performed by grouping the infrared spectral information of each compost, specifically in the region of higher absorption frequency of phosphate and nitrogen groups (1500 to 800 cm^{-1}), to verify compost clustering regarding their physico-chemical properties. Another PCA was performed to verify the existence of multiple and linear relationships among the studied factors (compost, incubation, and P sources) and compost properties, such as pH, EC, total N contents, Ca, and C, water-soluble C, and soluble P fractions. In both PCAs, vegan package (Oksanen et al., 2015) installed in the program R 3.0.3 was used (R Core Team, 2014). Besides, linear regression analyses were carried out to predict soluble P contents from EC values only for composts formulated with MAP.

RESULTS AND DISCUSSION

C and N changes and compost properties

Total C contents of composts reduced significantly ($p<0.05$) after 150 days of incubation (Figure 2). The total remaining C varied among the different composted mixtures, in the range of 57 to 70 % with phosphate rocks (PRs) and from 78 and 90 % in composts produced with monoammonium phosphate (MAP). Carbon losses in mixtures with PRs were similar to those verified by Dias et al. (2010), where 54 % of total C remained in compost piles of poultry manure and coffee husk (CH), mixed in a proportion of 1:1, after 210 days of incubation. Water-soluble C (WSC) contents presented smaller variations in relation to total C, but with similar patterns, except in composted mixtures with MAP, in which only the compost with 25 % of MAP showed a significant reduction ($p<0,05$) of WSC. In general, composts with CH tend to maintain greater contents of WSC as compared to other organic matrices in decomposition, due to a higher presence of phenols and soluble carbohydrates in CH (Dias et al., 2010).

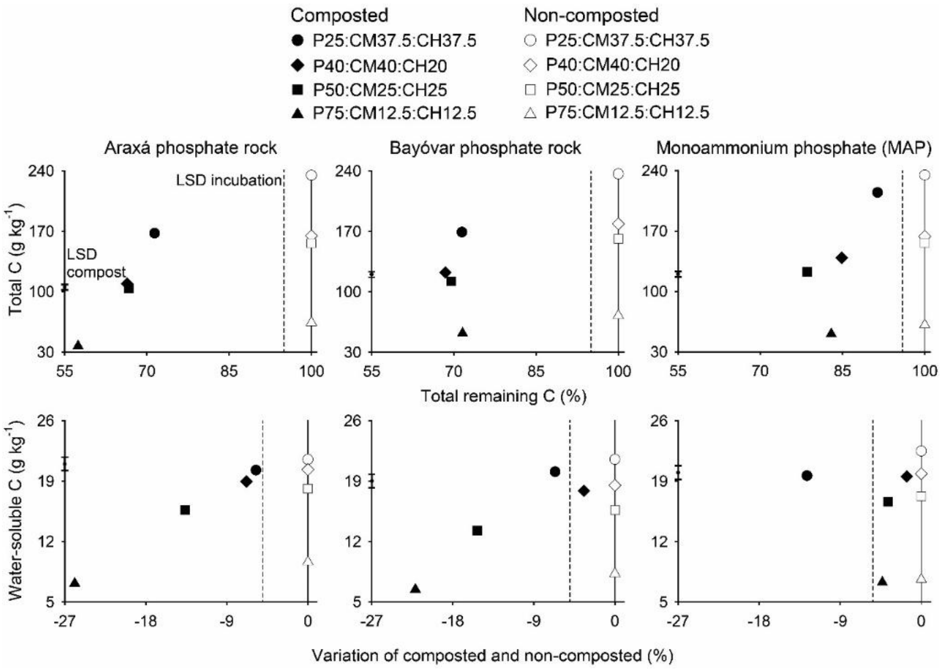

Figure 2. Total C and water-soluble C contents in composted mixtures (150 days of incubation) and non-composted (without incubation) for different proportions of chicken manure (CM), coffee husk (CH), and Araxá phosphate rock, Bayóvar phosphate rock or MAP. LSD, Least Significant Difference by Tukey test (*p*<0.05) for compost and incubation.

Reductions in total C and WSC contents of composted matrices are associated to microbial oxidation of the organic substances to CO_2, indicating increased decomposition of organic matter (OM) (Gómez-Brandón et al., 2008; Wichuk and McCartney, 2010) and, consequently, dry mass loss of composted mixtures (Table 3). Decrease in WSC contents has also been associated with the compost maturation degree, considering that, during composting, the C processed by decomposers are converted to C-humic substances with higher condensation degree, therefore, with more chemically stabilized and less soluble C in water (Dias et al., 2010; Wichuk and McCartney, 2010). Thus, the reduction in WSC contents and the increase of C-humified are important attributes to evaluate the progress and intensity of the composting process (Dias et al., 2010).

Table 3. Dry mass and N losses in mixtures with chicken manure, coffee husk, and Araxá phosphate rock (PR), Bayóvar PR or monoammonium phosphate (MAP), after 150 days of composting.

Compost	Dry mass loss			N loss		
	Araxá PR	Bayóvar PR	MAP	Araxá PR	Bayóvar PR	MAP
	%			%		
P25:CM37.5CH37.5	12.2 aA	12.0 aA	5.8 aB	11.0 cA	10.1 dA	0.7 aB
P40:CM40:CH20	10.5 abA	8.4 bB	4.9 aC	28.3 bA	26.3 cA	0.4 aB
P50:CM25:CH25	9.6 bA	8.6 bA	5.1 aB	32.0 bA	31.1 bA	0.1 aB
P75:CM12.5:CH12.5	5.2 cA	5.0 cA	2.1 bB	44.8 aA	42.5 aA	1.1 aB

Means followed by the same letter, lowercase for compost (column) and uppercase for P source (row), are not statistically different by Tukey test (*p*<0.05).

Dry mass losses of the composts are related to mineral P source proportion used in the mixture (Table 3). The magnitude of reductions in dry mass, and total C and WSC contents of the composts were greater with PRs than in composted materials formulated with MAP (Figure 2). This indicates that the presence of MAP, a readily available P source, decreased OM decomposition rate and, consequently, the C-CO_2 flow to the air during composting. According to the study carried out by Yang et al. (2015), low decomposition of kitchen waste was verified with the addition of 10 % of single superphosphate in the composting pile, since 78 % of total C remained in the final compost. It is known that single superphosphate improves N retention in compost (Prochnow et al., 2001). Therefore, the use of soluble P sources may promote retention of C, which increases dry mass yield in the final compost in relation PRs-based composts. Lee et al. (2009) observed also a slow swine manure decomposition after mixing

KH_2PO_4 in different proportions in the composting pile, which was attributed to the inhibition of the decomposers activity due to increased addition of soluble salts into the compost piles.

At the end of composting, pH of mixtures containing PRs increased, considering that at the beginning of the incubation the pH values were in the range of 6.5 to 8 and, when composted, the mixtures presented pH close to 10 (Figure 3). In MAP-based composts only mixtures with 25 and 40 % of P-fertilizer increased the pH at the end of the incubation, to 6.7 and 6.1 values, respectively, therefore, lower than pH values of the PRs-based composts. OM decomposition rate is regulated by pH, as well as it controls microbial activity, since fungi act more effectively in the decomposition processes in acidic conditions and, bacteria in a neutral to alkaline environment (Gómez-Brandón et al., 2008; Vassilev et al., 2013). N loss is also regulated by pH, since ammonia ($N\text{-}NH_3$) volatilization is increased when pH values reach the alkaline range (Wichuk and McCartney, 2010). This is the reason why composts with PRs have lost more N than MAP-based composts (Table 3). It may be inferred that MAP addition in compost piles is a suitable strategy to retain $N\text{-}NH_4^+$ in the final compost, probably related to the lower NH_3 volatilization, due to the lower pH of these mixtures. Trends verified in this study for N losses during composting are in agreement with those results obtained by Yang et al. (2015), when superphosphate was added in compost piles.

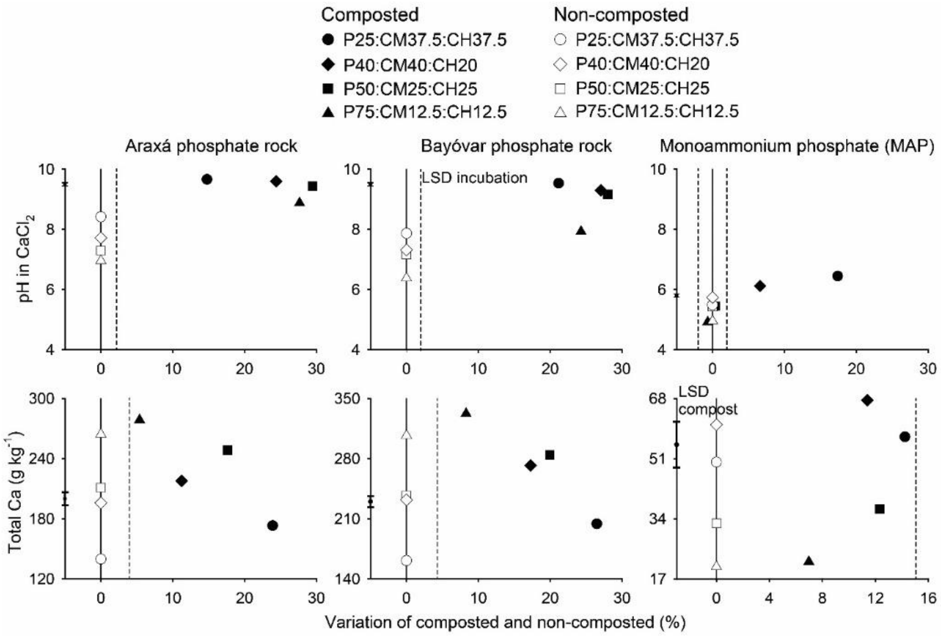

Figure 3. pH in $CaCl_2$ and total Ca content in composted mixtures (150 days of incubation) and non-composted (without incubation) for different proportions of chicken manure (CM), coffee husk (CH), and Araxá phosphate rock, Bayóvar phosphate rock or MAP. LSD, Least Significant Difference by Tukey test ($p<0.05$) for compost and incubation.

Total Ca contents increased also in mixtures treated with PRs after incubation, mainly in composts with higher proportion of organic wastes, which may be related to the effect of concentration caused by the mass loss of the produced compost (Figure 3). In mixtures with MAP, the total Ca contents were not influenced by incubation ($p>0.05$), probably, due to the lower mass loss than those verified for PRs-based composts (Table 3). Absence of Ca in MAP explains the low concentration of Ca in composts produced with MAP as compared to composts formulated with PRs.

Compost P fractions

Indices of water-soluble P (H_2O-P), citric acid (CA-P), and neutral ammonium citrate plus water (NAC+H_2O-P) did not increase in mixtures with Araxá and Bayóvar PRs after 150 days of composting (Figure 4). Thus, there was no solubilization of P-PRs at the end of composting; on the contrary, there was a reduction of CA-P when Bayóvar PR was added to mixtures at the rate of 40 and 50 %. This effect is mainly related to high pH values found for composts with PRs, which reached values close to 10, and high Ca concentrations (Figure 3). These chemical changes in the composted mixtures with PRs characterize an unsuitable environment for P-apatite solubilization, taking into account that these condition favor the formation of stable precipitates between P and Ca, increasing the chemical stability of tricalcium phosphate (apatite) (Mendes et al., 2013). Thus, even in an environment rich in organic matter, the effect of organic compounds in solubilizing P-apatite is overcome by other chemical factors, such as the high pH values and Ca contents in the compost pile. Although chicken manure (CM) has greater content of low molecular weight organic acids than other wastes (Pinheiro et al., 2013), the alkaline characteristic and the high Ca concentration especially in the form of $CaCO_3$ of this waste (Higashikawa et al., 2010) may also explain the low P-PRs solubilization after 150 days of composting.

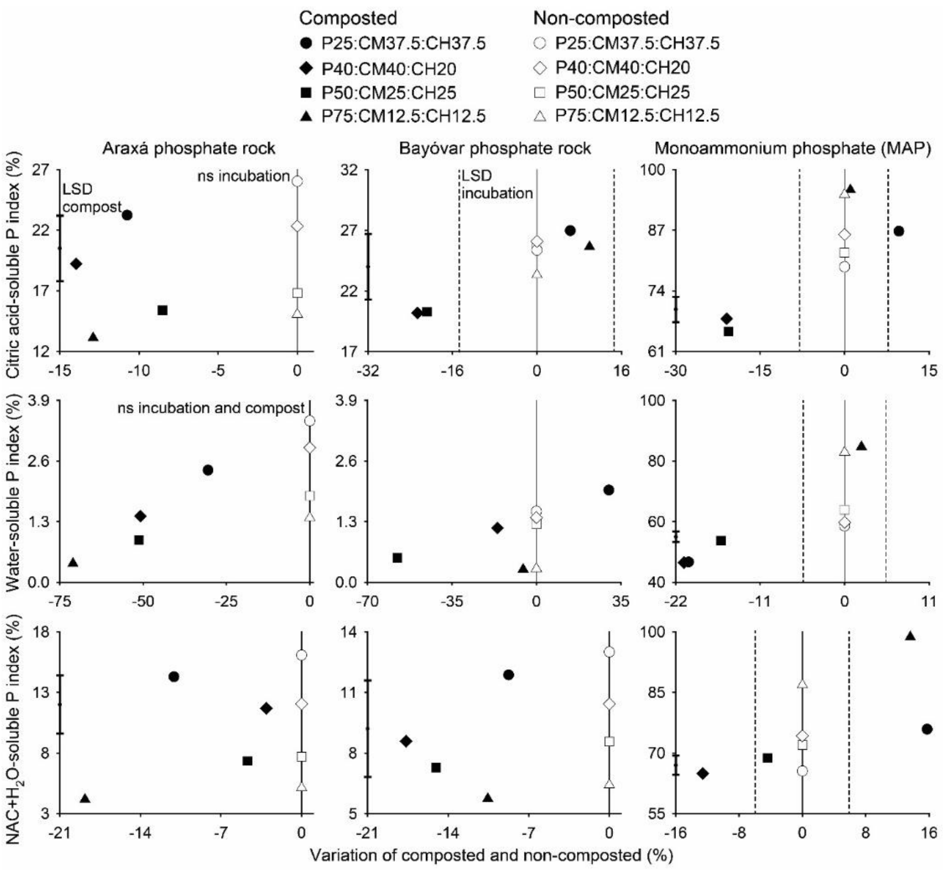

Figure 4. Indices of soluble P in citric acid, water, and neutral ammonium citrate plus water (NAC+H_2O) of each composted mixture (150 days of incubation) and non-composted (without incubation) for different proportions of chicken manure (CM), coffee husk (CH), and Araxá phosphate rock, Bayóvar phosphate rock or MAP. LSD, Least Significant Difference by Tukey test (*p*<0.05) for compost and incubation. ns, not significant.

In alkaline medium, organic acids have their capacity to complex metals neutralized and their production is reduced due to a low activity of fungi, reducing potential of P-PRs solubilization (Chatli et al., 2008, Wei et al., 2011). In acidic conditions, fungi activity is optimized, as well as the production of organic acids, which favors complexation of cations associated with PRs, reducing the activity of these ions and altering solution saturation point, therefore, increasing PR dissolution (Welch et al., 2002; Mendes et al., 2013). Thus, fungi are superior to bacteria in solubilizing P due to the greater production of organic acids and, consequently, higher acidification in the surrounding medium (Chatli et al., 2008). Acidification is the main factor regulating PRs dissolution rate; besides the complexation of cations, organic acids may contribute to the effective pH reduction. According to Kpomblekou-a and Tabatabai (1994), organic acids, such as citric and oxalic acids, are as efficient in PRs solubilization as sulfuric acid.

Zayed and Abdel-Motaal (2005) inoculated *A. niger* and *T. viride* in sugarcane bagasse and PR composting and found that the action of these fungi reduced pH from 8 to 4.8, and increased water-soluble P content. However, Biswas and Narayanasamy (2006) verified a reduction of water-soluble P and a small increase, less than 1 %, in citrate-soluble P in composts inoculated with *A. awamori*, which may be related to the species of fungus used in the inoculation. Vassilev et al. (1996), using a solid-state fermentation system with beet waste, PR and *A. niger*, verified pH values from 3 to 3.5 with solubilization of 76 % of P-PR. In addition, the release of other chemical elements present in PRs can also influence this process, such as fluorine, which inhibits microbial activity and can reduce P solubilization by 50 % (Mendes et al., 2013). Mixing of elemental S with PR and inoculation with *A. thiooxidans* can also be used to acidify the medium and solubilize P (Stamford et al., 2016), which may be an alternative to increase P-PRs solubility during composting.

The greatest effects on P solubility indices were observed for MAP composts (Figure 4). Reductions of CA-P and H_2O-P were verified in composted mixtures with MAP, mainly when this P source was added at rates of 40 and 50 %. Such reduction in water-soluble P may be related to the formation of more stable phosphate compounds, or even due to complexes formed between organic ligands and P. Organic-P complexes can be formed through of cationic metal bridges, such as Ca^{2+}, which reduces water solubility of the soluble P-fertilizer, but it does not prevent plants from acquiring this form of P (Gerke, 2010; Urrutia et al., 2014). NAC+H_2O-P also reduced in the composted mixture where MAP was added at 40 % rate, however this soluble P form did not change when the rate was at 50 %, and it increased in the mixtures where MAP were added at rates of 25 and 75 %. Reduction of H_2O-P and maintenance or increase of NAC+H_2O-P, as observed in composted mixture with 25 and 50 % of MAP, may represent an improvement of the chemical properties of organo-mineral fertilizers (OMF).

Low solubility of P-fertilizer in water and high in citrate is an effective strategy in protecting P against reactions that may cause soil P retention (Urrutia et al., 2014). This effect may be particularly beneficial for Brazilian tropical soils, which have low pH and predominance of kaolinite and Fe and Al oxides in the clay fraction. In these highly weathered soils is not uncommon P be adsorbed in more than 2000 mg kg^{-1}, considering a 0 to 20 cm soil depth (Novais et al., 2007). Thus, fertilizers with lower water-soluble P contents can be more efficient in supplying P to plants in soils with high P adsorption capacity (Prochnow et al., 2006) due to the gradual release of P, which is more synchronized with the phases of higher P requirement by crops (Urrutia et al., 2014), especially in long-cycle crops or perennials. Other improvement of MAP in composting is the greater pH value in compost (Figure 2), compared to the pH of conventional MAP fertilizer (Table 1). This effect in pH of compost also minimizes the precipitation of P-Fe and P-Al and P adsorption in soil minerals, which occur in the granule surroundings of soluble fertilizers applied to soil, as reported by McLaughlin et al. (2011). Moreover, the application of P in soil along with OM can increase the P-fertilizer use efficiency by plants (Roy et al., 2016) taking into account that organic compounds act blocking P adsorption sites on the colloid surface (Wang et al., 2016).

Compost infrared spectroscopic features

The principal component analysis divided the composts into two groups, distinguishing the clusters of composts with PRs from those produced with MAP, due to the contrast in ATR-FTIR spectral signatures. In each group of composts, little variation was identified between the composted and non-composted mixtures (Figure 5). Thus, each group was represented by the average spectrum of the mixtures related to P source, with identification of absorption bands according to the assignments features found in Silverstein et al. (2006) and Berzina-Cimdina and Borodajenko (2012). Spectral bands between 3400 and 3200 cm^{-1}, and 1640 cm^{-1} represent O-H bonds. Weak peaks at 2918 and 2850 cm^{-1} were observed in composed mixtures with PRs which, according to Stevenson (1994), are associated with aliphatic C-H groups of humic substances. Absorption bands at 1460 and 870 cm^{-1} found in mixtures with PRs are represented by CO_3^{2-} groups; whereas at 1100, 1000, 600, 560 and 470 cm^{-1} are associated with PO_4^{3-} groups through P-O bond. Changes were not observed in the PO_4^{3-} groups between composted and non-composted mixtures with PR, which reinforces non-alteration of the soluble P fractions indices (Figure 4), demonstrating absence of P solubilization from PR at the end of composting.

In the spectra generated for MAP composts, bands of P=O and P-OH bonds were identified at 1270 and 890 cm^{-1}, respectively (Figure 5). Changes in the composted mixtures were only found in composts with 40 and 50 % of MAP, in relation to non-composted mixtures. These composts had spectral bands poorly defined at 1010 and 968 cm^{-1}, which are related to symmetrical vibrations of P-O bonds; for that reason, the average spectrum of mixtures with 40 and 50 % MAP is presented separately. These bands may be associated with the formation of phosphate compounds with greater stability or complexes among composting organic anions and PO_4^{3-} groups, since these composted mixtures were the only ones that reduced H_2O-P, CA-P, as well as presented the lowest NAC+H_2O-P compared to other MAP composted mixtures (Figure 4). Increase in the absorption bands between 3200 and 2800 cm^{-1} and between 1440 and 1400 cm^{-1} were verified in composted mixtures with 40 and 50 % of MAP, which are associated to N-H bonds.

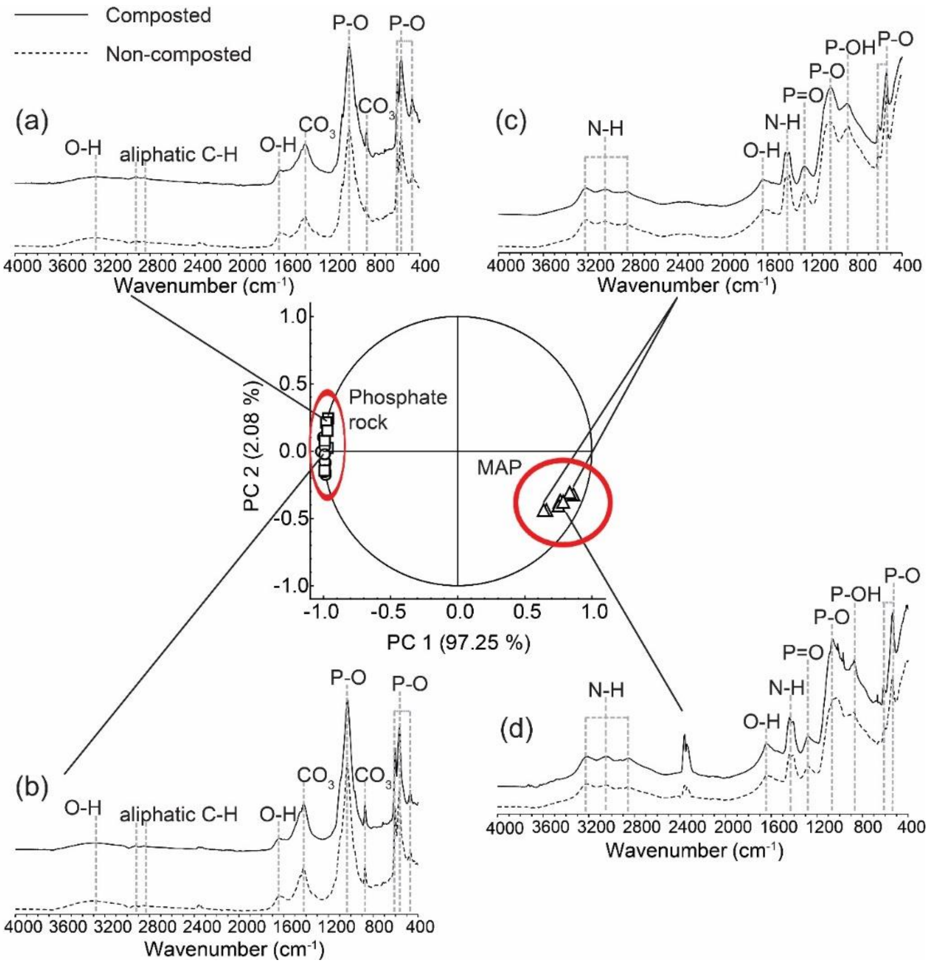

Figure 5. Principal component analysis (PCA) of absorption bands and mean spectra of ATR-FTIR and main chemical groups recorded for the mixtures with Araxá phosphate rock (a), Bayóvar phosphate rock (b), 25 and 75 % of MAP (c),

and 40 and 50 % of MAP (d) composted (150 days of incubation) and non-composted (without incubation).

Organo-mineral fertilizers

Composts presented different chemical characteristics, mainly due to the P source used in the mixture (Figure 6). Contents of soluble P fractions, total N, and values of electrical conductivity (EC) were positively related to MAP-based composts (Figure 6). Composts formulated with Araxá and Bayóvar PRs presented similar chemical properties and positively related to pH values and total Ca contents. However, soluble P fractions indices were inversely related to Ca contents and pH. Therefore, using acidic agro-industrial waste with low Ca content may be a reliable strategy to improve solubilization of low-grade phosphate rocks. Along with that, the use of inputs that favor the maintenance of the composting final pH below 5 (Welch et al., 2002; Vassilev et al, 2013; Stamford et al., 2016) is also a practice that may be used to increase P-apatite solubilization. It is also necessary to investigate whether composted mixtures increase the solubility of chemical elements potentially inhibitory to fungal activity, such as fluorine found in PRs (Mendes et al., 2013). The study of the liquid phase of materials under decomposition is another action that deserves attention to investigate changes in pH values, and Ca^{2+} and P contents during composting.

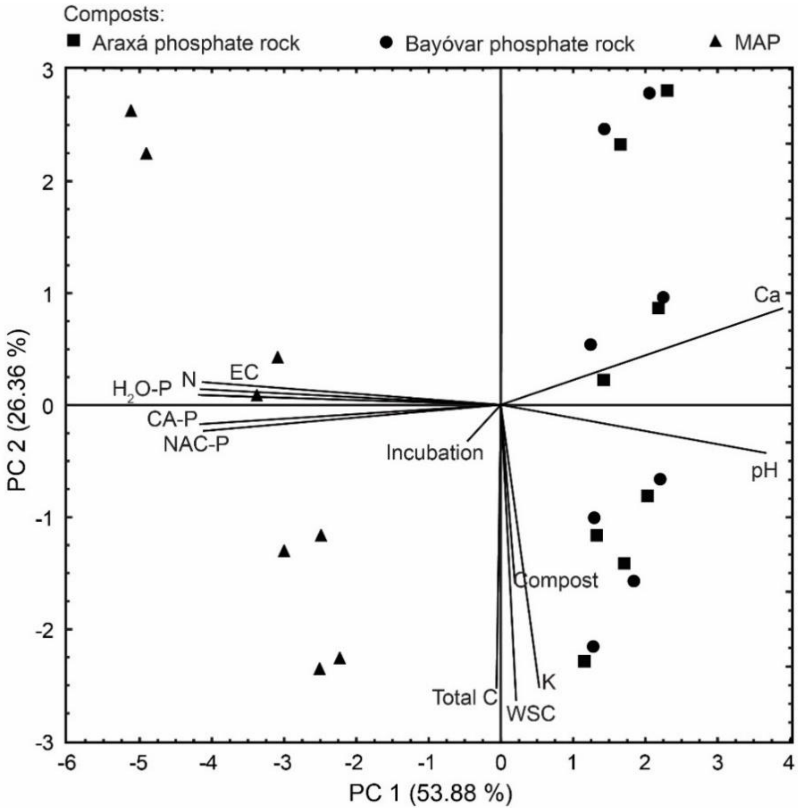

Figure 6. Principal component analysis (PCA) among study factors: P source (clustering), type of compost and incubation; and evaluated variables: pH, total contents of Ca (Ca), K, N, C and water-soluble C (WSC), indices of soluble P in water (H_2O-P), citric acid (CA-P) and neutral ammonium citrate plus water (NAC-P), and electrical conductivity (EC).

The principal components analysis indicated a high correlation between EC and indices of soluble P fractions in MAP-based composts (Figure 6). The association degree of these variables shows that the EC can be used to predict the contents of H_2O-P, CA-P, and NAC+H_2O-P of MAP composts (Figure 7). The relevance of the use of EC to estimate each soluble P fraction of MAP-based composts is due to analytical procedures used to measure soluble P contents, which are costly and laborious to be accomplished than EC determination.

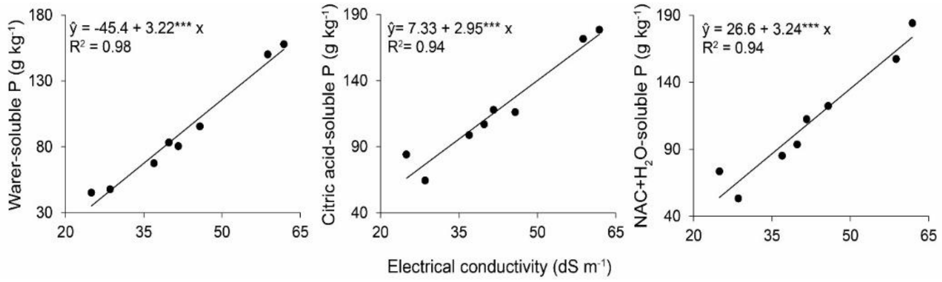

Figure 7. Contents of soluble P in water, citric acid and neutral ammonium citrate plus water (NAC+H_2O) as related to electrical conductivity of different mixtures, composted or not, of chicken manure, coffee husk, and monoammonium phosphate (MAP). *** *p*<0.01.

Among the different composts studied, mixtures with MAP produced OMFs with the highest values as fertilizer. It can be highlighted the composted mixture with 50 % of MAP, 25 % of CM and 25 % of CH. After 150 days of composting, this compost showed pH equal to 5.5, 18 % of reduction in H_2O-P and keep the same NAC+H_2O-P determined for this initial compost, without incubation. Such profile of P fractions in the compost already mentioned may indicate a more gradual release of P in relation to P from the conventional MAP fertilizer. Moreover, this composted mixture presented 18 % of total P or 41 % of P_2O_5 and 28 % of NAC+H_2O-soluble P_2O_5; besides P, this and other composts also have N and K (Table 4).

Table 4. Total N, P_2O_5, and K_2O contents, contents of citric acid-soluble P_2O_5 for mixtures with phosphate rocks, and neutral ammonium citrate plus water-soluble ($NAC+H_2O$) P_2O_5 for mixtures with monoammonium phosphate, and NPK fertilizer equivalent, followed by standard error, after 150 days of composting.

Compost	N	Total P_2O_5	Citric acid-P_2O_5	K_2O	NPK f. e.(1)
Araxá phosphate rock					
			%		
P25:CM37.5CH37.5	1.6 ±0.03	15.8 ±0.10	3.7 ±0.04	3.2 ±0.07	8.5 ±0.10
P40:CM40:CH20	1.2 ±0.01	20.6 ±0.27	3.9 ±0.04	2.9 ±0.11	8.0 ±0.12
P50:CM25:CH25	0.9 ±0.03	24.1 ±0.07	3.7 ±0.08	2.3 ±0.15	6.9 ±0.20
P75:CM12.5:CH12.5	0.5 ±0.02	30.8 ±0.38	4.0 ±0.03	1.2 ±0.03	5.7 ±0.05
Bayóvar phosphate rock					
P25:CM37.5CH37.5	1.6 ±0.01	17.3 ±0.10	4.6 ±0.23	3.5 ±0.07	9.7 ±0.17
P40:CM40:CH20	1.2 ±0.07	24.0 ±0.59	4.8 ±0.07	2.9 ±0.14	8.9 ±0.12
P50:CM25:CH25	0.9 ±0.01	26.5 ±0.63	5.4 ±0.17	2.6 ±0.05	8.9 ±0.21
P75:CM12.5:CH12.5	0.5 ±0.01	33.8 ±0.37	8.7 ±0.15	1.3 ±0.03	10.5 ±0.12
Monoammonium phosphate (MAP)					
Compost	N	Total P_2O_5	$NAC+H_2O$-P_2O_5	K_2O	NPK f. e.(1)
			%		
P25:CM37.5CH37.5	5.1 ±0.02	22.2 ±0.12	16.9 ±0.36	3.9 ±0.19	25.9 ±0.58
P40:CM40:CH20	6.2 ±0.05	39.7 ±0.18	25.8 ±0.20	2.9 ±0.03	34.9 ±0.24
P50:CM25:CH25	7.2 ±0.06	40.8 ±0.41	28.1 ±0.27	2.4 ±0.09	37.7 ±0.23
P75:CM12.5:CH12.5	9.4 ±0.17	42.7 ±0.09	42.2 ±0.37	0.9 ±0.01	52.5 ±0.52

(1)NPK fertilizer equivalent (%): Sum of N, citric acid-soluble P_2O_5 for composts with phosphate rocks or $NAC+H_2O$-soluble P_2O_5 for composts with MAP, and K_2O contents.

In order to improve the capacity of act as nutrient sources to crops, there should be an increase in its NPK fertilizer equivalent, since this index quantitatively indicates the available content of N, P_2O_5, and K_2O in the composted mixtures (Table 4). In composts formulated with Araxá PR, the increase in proportion of P source in the mixture and decrease of organic wastes reduced the NPK fertilizer equivalent of composts, which indicates that the value as fertilizer of composts is more related to CM and CH than to proportions of low-grade rocks in the compost. In MAP composted mixtures, the enrichment in the compost of NPK levels is more dependent of the P source than of the organic wastes. Increasing of MAP in the composted matrices assures higher capacity of the produced OMFs in supplying N, P, and K to plants, and possibly a more gradual release of P than the use of conventional MAP fertilizer as an exclusive source of N and P.

CONCLUSIONS

Regardless of the proportions of chicken manure, coffee husk and Araxá or Bayóvar phosphate rocks, composting is not a suitable route to solubilize P-apatite. Increased Ca contents and pH values in composted mixtures favor stabilization of phosphate rock, instead of solubilizing apatite, besides contributing to higher N losses during composting.

Use of MAP instead of low-grade phosphate rocks in composting increases dry mass yield, decreases N losses, maintains composts pH in the range of 5 to 7, and raises the compost NPK fertilizer equivalent. The composted mixture with 50 % of MAP, 25 % of chicken manure and 25 % of coffee husk stands out to contain 7 % of N, 28 % of P_2O_5 and 2 % of K_2O, low content of water-soluble P and maintenance of neutral ammonium citrate plus water-soluble P.

Electrical conductivity can be used as a predictor of water, citric acid and neutral ammonium citrate plus water-soluble P contents of the composted mixtures formulated with MAP.

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FORMULAÇÃO, CINÉTICA DE LIBERAÇÃO DE FÓSFORO E POTENCIAL AGRONÔMICO DE FERTILIZANTES À BASE DE FOSFATO DE MAGNÉSIO

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Resumo

Fosfato de magnésio com baixa acidez e fósforo (P) parcialmente solúvel em água são características promissoras para aumentar a eficiência de uso do P-fertilizante pelas plantas. O objetivo do estudo foi sintetizar compostos de fosfato de magnésio (CFMs) com seis diferentes relações entre P e Mg (FM1, FM2, FM3, FM4, FM5 e FM6), caracterizar os CFMs quanto às propriedades químicas e mineralógicas, avaliar a cinética de liberação de P-fertilizantes e o potencial agronômico dos novos fertilizantes, tendo o milho como planta-teste. Os CFMs apresentaram teores de P na faixa de 21 a 47% de P solúvel em água em relação ao P total (P-H_2O). A variação do P-H_2O foi dependente da relação estequiométrica dos CFMs e do processo de síntese. A liberação de P pelos CFMs foi cerca de 4 a 8 vezes menor do que a liberação de P pelo superfosfato triplo (SFT). A aplicação do FM2 e do FM3 aumentou cerca de 20% a massa seca do milho em comparação à biomassa produzida com o uso do SFT. A adubação com FM3 resultou em maior acúmulo de P na parte aérea do milho entre os demais CFMs testados. Após o cultivo do milho, houve mais P residual disponível nos solos adubados com CFMs do que naqueles em que o nutriente foi adicionado com SFT.

Palavras-chave: Fertilizante fosfatado de liberação lenta, fósforo solúvel em água, fósforo, sinergia P-Mg, *Zea mays* L.

INTRODUÇÃO

Em solos tropicais intemperizados, o P é o nutriente que mais limita a produção agrícola (Kochian, 2012). Nesses solos, doses mais elevadas de P-fertilizante são necessárias para saturar a elevada quantidade de sítios de adsorção de fosfato e, com o excedente de P na solução do solo, suprir a exigência da planta (Novais et al., 2007; Rodrigues et al., 2016). Com isso, menos de 25% do P aplicado é absorvido pela planta, particularmente, nas lavouras em que são utilizados fertilizantes fosfatados totalmente acidulados, como os superfosfatos (Novais et al., 2007; Syers et al., 2008). Essa baixa taxa de recuperação do P-fertilizante está relacionada à alta acidez e solubilidade do P em água dessas fontes, que confere uma rápida liberação de P e contribui para as reações de adsorção na caulinita e em óxidos de Fe e de Al, e de precipitação do P com Fe e Al no solo, especificamente no entorno dos grânulos do fertilizante (McLaughlin et al., 2011). Além disso, a baixa eficiência de uso do P na agricultura acelera o processo de depleção das rochas fosfatadas, o que torna menos sustentável a produção agrícola, com aumento subsequente dos preços dos fertilizantes (Cordell et al., 2009; Cordell e White, 2015). Diante desse cenário, há necessidade de desenvolver novas tecnologias em fertilizantes, que sejam mais eficientes em fornecer P às plantas.

Uma das formas de reduzir o dreno P do solo é tornar a liberação de P-fertilizante mais lenta (Everaert et al., 2016). Estudos recentes têm demonstrado que a propriedade de liberação lenta ou controlada do P-fertilizante pode ser adquirida por duas tecnologias, compostos fosfatados pobremente solúveis em água e fertilizantes solúveis revestidos com polímeros (Everaert et al., 2016; Teixeira et al., 2016). Benício et al. (2017) sintetizaram nanoestruturas de hidróxido duplo lamelar com P intercalado, o que conferiu uma baixa solubilidade do P em água e uma lenta liberação, cerca de 75% menor do que o P-superfosfato triplo. Teixeira et al. (2016) verificaram que o revestimento do fosfato monoamônio (MAP) com ácidos orgânicos alterou os padrões de liberação de P-MAP, diminuindo de 3 a 16 vezes a velocidade de liberação do P. Entretanto, muitas dessas tecnologias com liberação gradual do P-fertilizante, não são compatíveis com às fases de maior exigência do nutriente pelas diferentes culturas (Erro et al., 2007). Assim, novas tecnologias também devem assegurar que a liberação do P-fertilizante seja, em parte, controlada pelas raízes das plantas, por meio da acidificação da rizosfera e, ou exsudação de ânions orgânicos (Erro et al., 2007; Everaert et al., 2016).

Fertilizantes constituídos por espécies de P pouco solúveis em água, mas com alta solubilidade em citrato neutro de amônio, podem apresentar, além de uma liberação lenta de P, um maior controle da planta na dissolução do fertilizante, por meio da exsudação de substâncias orgânicas, assegurando maior aproveitamento do P pelas culturas (Erro et al., 2007). Maior eficiência agronômica pode ser alcançada se o fertilizante apresentar também baixa capacidade em acidificar o solo no entorno do grânulo (Benício et al., 2017). Essas propriedades têm sido verificadas em fertilizantes à base de fosfato de magnésio (FM), como na estruvita ($MgNH_4PO_4.6H_2O$), com N em sua constituição (Antonini et al. 2012; Talboys et al., 2016), ou no multifosfato magnesiano, com parte do P associado ao Ca (Prochnow et al., 2006; Lana et al., 2007). Entretanto, a estruvita possui baixa proporção de P solúvel em água, de 1 a 5% em relação ao P total, o que diminui o crescimento inicial da planta (Talboys et al., 2016). Enquanto que o Ca em teores desbalanceados pode inibir a absorção de Mg e K pela planta (Gransee e Führs, 2013). Assim, o FM sem N nem Ca, além de otimizar a produção desses fertilizantes, magnifica o efeito do Mg sobre a aquisição de P pelas culturas.

Esse efeito sinérgico pode estar relacionado com a participação do Mg nas reações de transferência de P na planta, especialmente, como substrato da H^+-ATPase na membrana plasmática, fator essencial à absorção de nutrientes

(Malavolta, 2006; White, 2012). Lasa et al. (2000) verificaram que a aplicação de concentrações de Mg aumentou linearmente a absorção de P pela planta. Assim, como esses nutrientes agem de forma conjunta, é possível que a interação entre Mg e P durante a síntese dos fertilizantes seja benéfica, podendo assegurar maior aquisição de P pelas plantas e maior efeito residual da adubação fosfatada, pela diminuição do contato P-fertilizante com o solo.

Diante da busca por fontes alternativas de P mais eficientes para agricultura, as principais hipóteses desse estudo são: (i) a síntese de compostos fosfatados com Mg promove uma liberação de P mais lenta do que o P-superfosfato triplo; (ii) a quantidade de P liberada do fertilizante pode ser alterada pela estequiometria de produção dos FMs; (iii) há uma relação estequiométrica ótima para a síntese do fertilizante que promove uma maior produção de massa seca e absorção de P pelo milho em comparação a outras fontes de P. Para testar essas hipóteses, objetivou-se: (i) sintetizar FMs, determinar os teores de P e sua solubilidade relativa em água, ácido cítrico e citrato neutro de amônio mais água, bem como caracterizá-los quanto à composição mineralógica; ii) avaliar a cinética de liberação de P; e (iii) o potencial agronômico dos novos fertilizantes no crescimento inicial do milho.

MATERIAL E MÉTODOS

Síntese dos compostos de fosfato de magnésio

Os compostos de fosfato de magnésio (CFMs) foram sintetizados a partir da mistura em solução de fonte de magnésio e de fósforo, com o uso de seis diferentes formulações, baseados nas relações entre os nutrientes, aqui denominados como FM1, FM2, FM3, FM4, FM5 e FM6. Cada mistura entre os reagentes gerou um precipitado, em que o sólido foi secado em estufa de circulação forçada de ar, a 65 ^{o}C por 80 h. Todas as etapas de síntese foram realizadas sob condições naturais de pressão atmosférica e de temperatura.

Caracterização dos fertilizantes sintetizados

Nas amostras dos CFMs foram determinados o pH em solução de 0,01 mol L^{-1} de $CaCl_2$, os teores totais de P e as frações de P solúvel em água, em solução de ácido cítrico a 2% e em citrato neutro de amônio mais água (P-CNA+H_2O). Para essas avaliações, foram adotadas as metodologias oficiais descritas em MAPA (2013) e o superfosfato triplo (SFT) como amostra controle. A caracterização mineralógica da estrutura cristalina também foi realizada nas amostras dos CFMs por difratometria de raios-X (DRX), com o uso da radiação síncrotron do Laboratório Nacional de Luz Síncrotron (LNLS), na faixa angular de 5 a 50 º2θ, com resolução de 0,004 º2θ.

Cinética de liberação de fósforo

Este estudo foi conduzido em mini-lisímetros, por meio da incubação dos fertilizantes em areia, em temperatura de 25,9 ±0,6 ºC, e submetidas à lixiviação periódica com água deionizada. Cada mini-lisímetro, unidade experimental, foi preparado da seguinte forma: no compartimento superior, o fundo foi coberto com lã de vidro com 1 cm de espessura para evitar a passagem de sólido para o coletor do lixiviado (compartimento inferior); em sequência, foi adicionado 10 g de areia; 200 mg de P-fertilizante; 20 g de areia e; por fim, coberto com mais uma camada de 2 cm de lã de vidro, a fim de evitar o impacto direto da água na areia e a formação de fluxo preferencial. A areia possuía partículas < 2 mm e foi previamente lavada com solução de 1 mol L^{-1} de HCl e posteriormente com água deionizada até pH próximo a 6.

Os fertilizantes sintetizados foram preparados, fisicamente, na forma de tabletes com 5 mm de diâmetro e 3 mm de espessura. Em cada mini-lisímetro, foram aplicadas porções de água deionizada com pH corrigido para 6 ±0,2, com coleta das soluções em tempos determinados até 624 h (26 dias). A quantidade de água inicial foi de 50 mL e logo após a passagem desse volume pelo sólido, a solução lixiviada foi coletada, marcando o tempo zero. A partir disso, a quantidade de água foi aplicada de forma acumulada para cada intervalo de tempo, na proporção de 7 mL h^{-1}, e coletada após o período, antes da próxima aplicação.

O experimento de cinética de liberação de P foi constituído por 6 tratamentos, representados pelos CFMs mais concentrados em P, FM1, FM2, FM3 e FM4, além de dois controles, um controle absoluto, apenas com lã de vidro e areia, e outro com aplicação de SFT granulado, com parcela subdividida no tempo de coleta em: 0, 2, 4, 6, 8, 10, 12, 24, 36, 48, 72, 96, 120, 144, 168, 192, 216, 240, 288, 336, 384, 432, 480, 528, 576 e 624 h após a aplicação da quantidade de água inicial. Utilizou-se delineamento inteiramente casualizado, com três repetições. Após cada coleta, a solução foi filtrada, condicionada em tubo hermeticamente fechado e armazenada em câmara fria até determinação dos teores de P em ICP-OES. A quantidade liberada de P foi expressa em valores líquidos, ou seja, pela diferença entre o P liberado do fertilizante e o liberado no controle absoluto, acumulado no tempo de avaliação.

Os dados foram submetidos à análise de variância e as médias foram comparadas pelo teste Tukey ($p<0,05$), utilizando o programa SISVAR 5.3 (Ferreira, 2014). Análises de regressão foram realizadas, a fim de determinar os modelos matemáticos que melhor se ajustaram às quantidades liberadas e acumuladas de P de cada fertilizante em função do tempo de avaliação. Quando modelos exponenciais foram ajustados, o parâmetro exponencial (k) foi utilizado para estimar a meia-vida ($t_{1/2}$) do P-fertilizante, ou seja, o tempo estimado para liberação de 50% de P, baseado na equação matemática proposta por Paul e Clark (1996) (Equação 1).

$$t_{1/2} = - \ln(0,5) / k = 0,693 / k \qquad \text{Equação (1)}$$

Milho como planta-teste para os fosfatos de magnésio

O milho foi cultivado sob casa de vegetação, em vasos preenchidos com amostras de Latossolo Vermelho húmico, coletado na camada de 1,5 a 2,0 m. Esse solo contém 700 g kg^{-1} de argila e tem a caulinita como mineral predominante na fração argila, seguido pela gibbsita, identificados por difratometria de raios-X (Figura 1) em um difratômetro Bruker, DZ phaser, equipado com tubo de Cu e filtro de Ni, em que foi misturado halita na amostra, como um padrão interno. Sob condições naturais, esse solo apresentou pH em água de 4,7; P disponível extraído por resina de trona iônica mista de 2,3 mg dm^{-3} e, P extraído pela solução de Mehlich-1 de 0,4 mg dm^{-3}; capacidade máxima de adsorção de P de 1,7 mg g^{-1}; K disponível de 73 mg dm^{-3}; Ca^{2+} e Mg^{2+} trocáveis de 0,1 e 0,1 $cmol_c$ dm^{-3}, respectivamente; capacidade de troca de cátions a pH 7 de 3,28 $cmol_c$ dm^{-3} e C total de 8,3 g kg^{-1}.

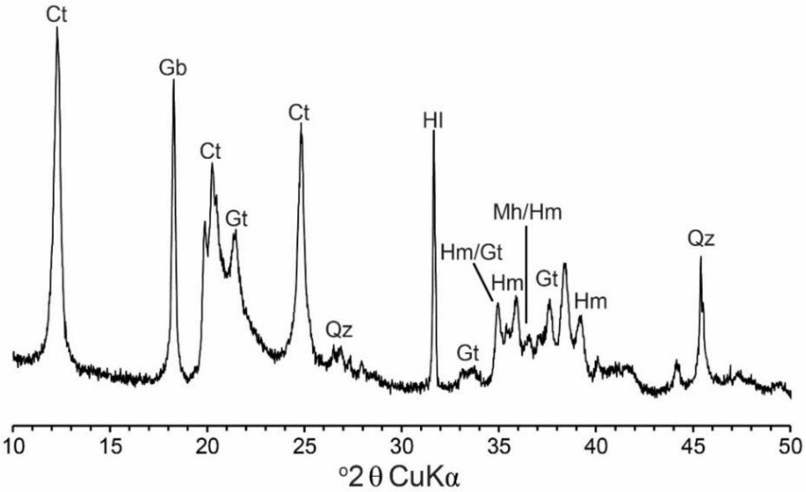

Figura 1. Difratograma de raios-X da fração argila saturada com Na da amostra de Latossolo Vermelho húmico. Símbolos sobre os picos representam os minerais: Ct (Caulinita); Gb (Gibbsita); Gt (Goethita); Qz (Quartzo); HI (Halita, utilizado como padrão interno); Hm (Hematita); Mh (Maghemita).

Para correção da acidez e elevação dos teores de Ca^{2+} e de Mg^{2+} no solo foi aplicado $CaCO_3$ e $MgCO_3$, na relação 4:1. A concentração de carbonato aplicado ao solo foi estimada pela curva de neutralização da acidez, como descrito em Kaminski et al. (2002), previamente realizada para corrigir o pH em água do solo para 6. Após 30 dias de incubação do solo com os carbonatos e água, na quantidade equivalente a 60% da capacidade de campo, o solo foi secado ao ar e peneirado em malha de 4 mm, em que foi utilizado para preencher os vasos para o cultivo do milho.

Cada vaso foi preenchido com 1,3 kg de solo seco, e adicionado 400 mg kg^{-1} de P-fertilizante, referente a fração solúvel em CNA+H_2O, misturado em todo volume de solo. Os demais nutrientes foram aplicados na forma de solução nas concentrações de: 100 mg kg^{-1} de N e de K; 40 mg kg^{-1} de S; 0,8 mg kg^{-1} de B; 1,3 mg kg^{-1} de Cu; 1,5 mg kg^{-1} de Fe; 3,7 mg kg^{-1} de Mn; 4,0 mg kg^{-1} de Zn e 0,15 mg kg^{-1} de Mo, a fim de atender a demanda nutricional de plantas cultivadas em vaso, como recomendado por Novais et al. (1991). Na sequência, a umidade do solo foi corrigida para 60% da capacidade de campo e realizado a semeadura com 5 sementes de milho (híbrido simples, Pionner 30F53 YH) por vaso. Após 5 dias da emergência das plântulas, realizou-se o desbaste, mantendo apenas uma planta por vaso. Durante o cultivo, foi realizado uma cobertura após 15 dias da semeadura, com 100 mg kg^{-1} de N e de K, utilizando as fontes nitrato de potássio e nitrato de amônio.

O experimento foi constituído por 6 tratamentos, representados pelos CFMs tabletados, FM1, FM2, FM3 e FM4, e dois tratamentos controle, SFT granulado e SFT tabletado. Utilizou-se o delineamento inteiramente casualizado, com quatro repetições. O milho foi cultivado por 26 dias. Após o cultivo, foi separada a parte aérea da planta, que foi secada em estufa de circulação forçada de ar, a 60 ºC por 72 h, e pesada, para avaliar a massa seca. Na sequência, o material vegetal foi moído e passado em malha de 1 mm, para digestão das amostras com ácido nítrico e ácido perclórico, misturados na proporção 4:1, a fim de determinar os teores totais de P por espectrofotometria UV-visível. Os teores de P (mg kg^{-1}) foram relacionados com a massa seca, a fim de verificar o conteúdo ou quantidade acumulada do nutriente na parte aérea do milho (mg $planta^{-1}$). Ao final do cultivo do milho, o solo foi secado ao ar e peneirado (2 mm), para avaliar o pH em água, na relação solo:água de 1:2,5 (v/v) e o P disponível extraído por resina de troca iônica mista (Raij e Quaggio, 2001), determinado em espectrofotômetro UV-visível (Murphy e Riley, 1962).

As variáveis avaliadas na planta e no solo foram submetidas à análise de variância e as médias referentes aos tratamentos foram comparadas pelo teste Scott-Knott ($p<0,05$), por meio do programa SISVAR 5.3 (Ferreira, 2014).

RESULTADOS E DISCUSSÃO

Composição química e mineralógica dos fertilizantes sintetizados

Os compostos sintetizados à base de fosfato de magnésio (CFMs) apresentaram valores de pH em $CaCl_2$ próximos uns dos outros, entre 6,8 e 7,0, e diferentes teores de P total (Tabela 1), em razão, principalmente, das relações estequiométricas entre os reagentes utilizadas na síntese. A proporção do P total solúvel em água (P-H_2O) aumentou, de 21% no FM1 para 47% no FM6, o que representa um incremento de 2,2 vezes. Essa variação no P-H_2O pode indicar que diferentes espécies de P foram formados durante a síntese dos CFMs, o que alterou a estabilidade química dos compostos e a solubilidade do P.

Tabela 1. Valores de pH, teor total e frações solúveis de P dos fertilizantes (Fert) à base de fosfato de magnésio (FM) e do superfosfato triplo (SFT)

Fert	pH em $CaCl_2$	P total	Solubilidade de P			P solúvel / total		
			Água	AC[a]	CNA[b]	Água	AC[a]	CNA[b]
		---------------------- g kg^{-1}			----------------------	------------- %		-----------
FM1	7,0 ±0,01	142 ±2,5	30,3 ±0,2	133 ±0,7	140 ±0,1	21,3	93,7	98,6
FM2	6,9 ±0,01	144 ±7,5	33,7 ±0,1	134 ±0,1	144 ±3,8	23,4	93,1	100
FM3	6,8 ±0,01	137 ±6,4	34,5 ±0,2	129 ±1,8	135 ±0,8	25,2	94,2	98,5
FM4	6,8 ±0,02	136 ±9,5	35,4 ±0,3	121 ±0,1	134 ±1,6	26,0	89,0	98,5
FM5	6,8 ±0,01	110 ±8,7	35,8 ±1,5	98,1 ±1,0	108 ±2,2	32,5	89,2	98,2
FM6	6,8 ±0,04	77,1 ±3,8	36,6 ±0,2	65,9 ±0,2	77,0 ±0,1	47,5	85,5	100
SFT	2,8 ±0,01	197 ±5,3	170 ±2,2	177 ±4,9	196 ±0,2	86,3	89,8	99,5

[a] AC, ácido cítrico. [b] CNA, citrato neutro de amônio mais água. ±, erro padrão da média.

Nos CFMs foi verificado também que grande parte do P total é solúvel em ácido cítrico e, quase 100% é solúvel em citrato neutro de amônio mais água (CNA+H_2O) (Tabela 1). A alta proporção de P solúvel em ácido e complexante orgânicos, aliado a baixa solubilidade em água confere aos compostos fosfatados uma maior solubilidade em rizosfera, ou seja, a liberação do P seria mais controlada pela atividade radicular da planta, por meio da exsudação de substâncias orgânicas do que pelo ambiente, como a umidade do solo (Erro et al., 2007). Com isso, os CFMs apresentaram propriedades diferenciais em relação ao superfosfato triplo (SFT), especialmente, pelo pH próximo ao neutro e maior participação de P insolúvel em água. Ainda, a manutenção de certa proporção de P-H_2O nos CFMs é importante para uso como fertilizante, pois segundo Chien et al. (2011) e Talboys et al. (2016), essa fração de P é essencial no estádio inicial de crescimento das plantas, por propiciar um efeito de arranque para as culturas.

Assim como verificado nas propriedades químicas (Tabela1), a composição mineralógica dos CFMs apresentou mudanças, especialmente relacionada à proporção dos minerais cristalinos (Figura 2). Nos difratogramas do

FM1 até FM6 foi observado uma redução da maioria dos picos que representam os minerais característicos. Por outro lado, seis picos aumentaram a medida em que modificou a relação estequiométrica entre os reagentes até FM6. Assim, cada CFM apresenta uma assinatura cristalográfica específica, intrínseca ao processo de síntese. Essas características diferenciais na estrutura cristalina dos CFMs confirmam que houve alterações nos minerais que constituem as amostras, o que pode estar relacionada às mudanças observadas no P-H_2O, apresentando um gradiente de solubilidade/reatividade dessas fontes de P.

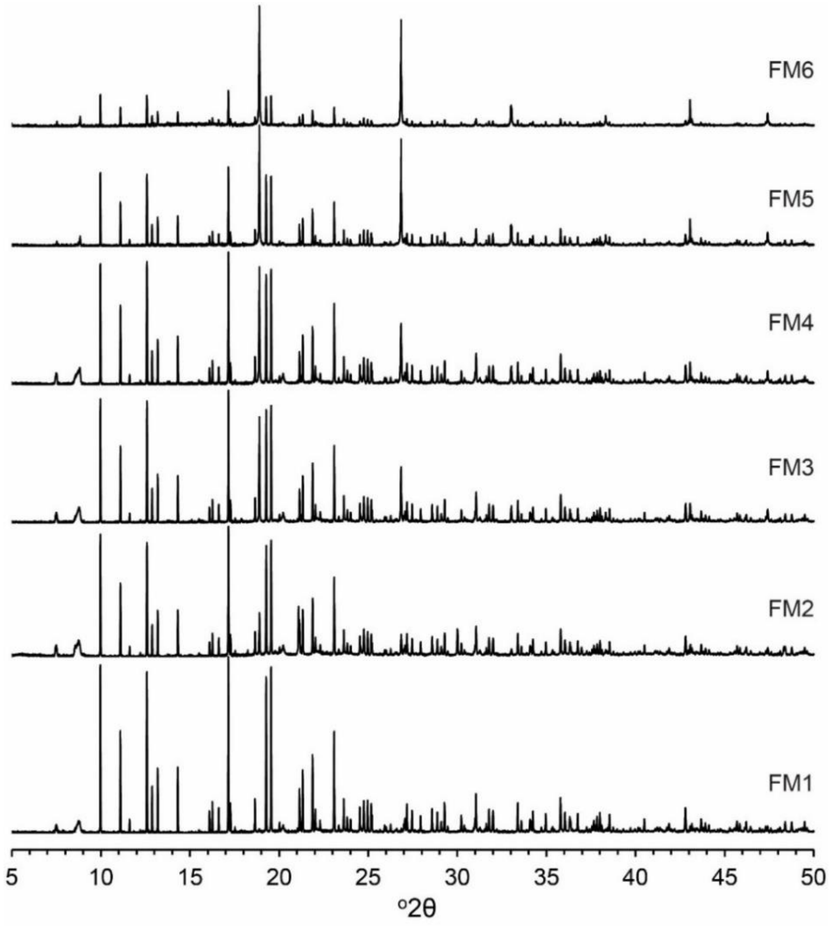

Figura 2. Difratogramas de raios-X dos seis fertilizantes sintetizados à base de fosfato de magnésio (FM).

Cinética de liberação de fósforo

As fontes de P testadas e o tempo de avaliação alteraram a quantidade e o padrão de liberação de P ($p<0,05$) (Figura 3). Os CFMs apresentaram aumento linear na liberação de P até 624 h (26 dias) de avaliação, com padrão de liberação diferente e mais lento do que o P liberado pelo SFT. O SFT liberou 92% do P em apenas 4 horas, com liberação de 50% da quantidade de P aplicada ($t_{1/2}$) em 2,39 h. Essa rápida liberação de P dos fertilizantes com alta solubilidade em água, como o SFT, MAP e superfosfato simples, é comumente relatada em outros estudos (Erro et al., 2007; Everaert et al. 2016; Teixeira et al., 2016; Benício et al., 2017). Entre os CFMs, foi verificado diferentes quantidades de P liberada ao longo do tempo, na seguinte ordem decrescente: FM4, com 25% de liberação do P aplicado > FM3 = FM2 > FM1, esse último com liberação de apenas 12% de P. Constata-se, portanto, que os CFMs apresentam uma liberação lenta do P, com taxas de 0,04, 0,03, 0,03 e 0,02% de P liberado por hora para FM4, FM3, FM2 e FM1, respectivamente.

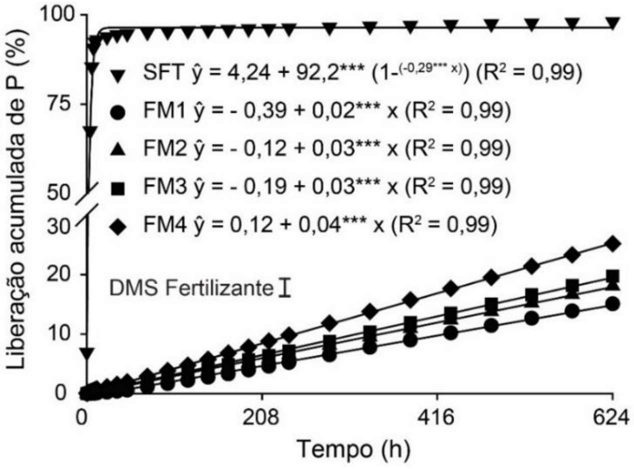

Figura 3. Quantidade relativa de P liberado de cada fosfato de magnésio (FM) sintetizado e do superfosfato triplo (SFT) em função do tempo de avaliação. DMS, Diferença Mínima Significativa pelo teste Tukey ($p<0,05$).

A cinética de liberação de P confirma a estabilidade em água dos constituintes fosfatados dos CFMs, cuja magnitude dessa liberação mais lenta do P é controlada pelas características de síntese (Figura 3). Assim, a taxa de liberação do P-CFMs é regulada pela química dos fosfatos de magnésio, com a dissolução influenciada pelo pH e pela concentração de Mg^{2+} do meio (Babic-Ivancic et al., 2006; Bhuiyan et al., 2008), e pode ser aumentada pela presença de ácidos e, ou ânions orgânicos (Talboys et al., 2016).

Esse mecanismo de liberação de P dos fosfatos de magnésio difere dos fertilizantes revestidos, cuja a liberação é controlada por barreira física e, ou química, que normalmente ocorre em três estágios: primeiro, a água penetra lentamente nos poros do revestimento do fertilizante; em sequência, os nutrientes são gradualmente dissolvidos; e, por fim, ocorre a difusão dos íons do fertilizante para a solução do solo (Wu e Liu, 2008). O coeficiente de difusão do fosfato do fertilizante revestido para a solução do solo, muitas vezes é variável e dependente do tipo de polímero e espessura do revestimento (Wu e Liu, 2008; Ahmad et al., 2015; Lubkowski et al., 2015; Teixeira et al., 2016). Essas características dos fertilizantes revestidos combinada com as diferentes fases de requerimento de P pelas plantas tem dificultado o desenvolvimento de uma tecnologia em fertilizante, cujo padrão de liberação de P seja sincronizada com a exigência por P das culturas (Erro et al., 2007).

Assim, fertilizantes parcialmente solúveis em água, de liberação lenta de P, mas com alta solubilidade do P em ácido cítrico e citrato neutro de amônio, como verificado nos CFMs, conferem características potenciais para uso como fertilizantes fosfatados, especialmente, para fornecer P às plantas cultivadas em solos altamente intemperizados, com forte caráter dreno de P.

Crescimento e nutrição fosfatada do milho

O crescimento da parte aérea e a nutrição com P do milho foram influenciados pela aplicação dos diferentes fertilizantes ($p<0,05$) (Figura 4). Maior produção em massa seca da parte aérea (MSPA) do milho foi verificado quando se utilizou o FM2 e o FM3 em relação aos demais fertilizantes, com cerca de 20% de acréscimo no crescimento em relação ao superfosfato triplo granulado (SFTgr). A adição de FM3 e de SFTgr no solo promoveram os maiores conteúdos de P na parte aérea do milho cultivado até 26 dias, comparado às outras fontes de P. Assim, o FM3 foi tão eficiente no fornecimento de P para planta quanto à fonte comercial. Menor crescimento e conteúdo de P na planta foi verificado quando se utilizou o SFT na forma de tablete (SFTtb), a mesma forma de acabamento dos CFMs, em comparação ao SFTgr. Esse efeito sinaliza que os CFMs na forma de grânulos poderiam apresentar melhores respostas em termos de suprimento de P ao milho, contudo, outros estudos devem ser conduzidos para verificar o melhor acabamento físico dos CFMs.

O acúmulo de P na parte aérea do milho demonstra que não há necessidade de uma intensa liberação de P-fertilizante para suprir o requerimento inicial de P da planta (Figura 4). Benício et al. (2017) verificaram maior produção de massa seca e conteúdo de P na parte aérea do milho cultivado por 25 dias com fertilizante fosfatado de liberação lenta, comparado ao milho adubado com SFT. A estruvita ($MgNH_4PO_4.6H_2O$) também é considerada um fertilizante de liberação lenta, com baixa solubilidade em água (Tallboys et al., 2016). No estudo realizado por Cabeza et al. (2011), foi observado que mesmo liberando menores quantidades de P na solução do solo, a estruvita foi tão eficiente quanto o SFT na nutrição fosfatada do milho em solo ácido e neutro.

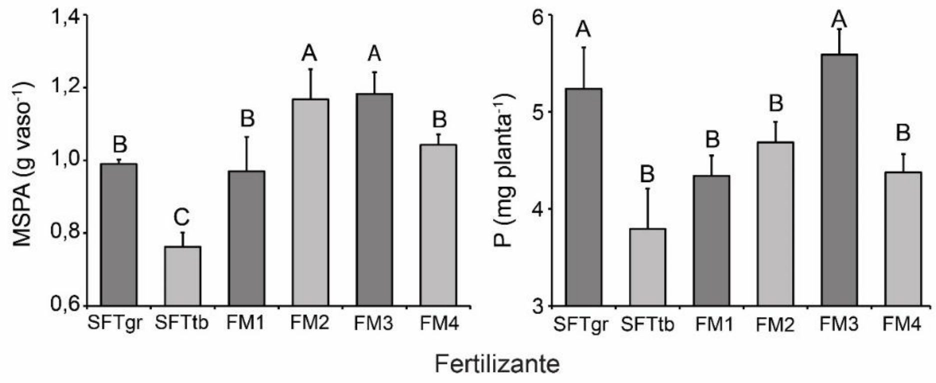

Figura 4. Massa seca (MSPA) e conteúdo de P da parte aérea do milho adubado com superfosfato triplo granulado (SFTgr) ou tabletado (SFTtb) e com cada fosfato de magnésio (FM) sintetizado. Médias seguidas por mesma letra não diferem estatisticamente pelo teste Scott-Knott ($p<0,05$). Barra representa o erro padrão da média.

A aplicação de Mg ligado ao P dos CFMs também pode ter favorecido a absorção de P pelo milho (Figura 4). O Mg atua nos processos de transferência de P na planta, como cofator e modulador alostérico das fosfatases, quinases, ATPases, entre outras enzimas, regulando a absorção e a velocidade de utilização de P na planta (Malavolta, 2006; Dechen et al., 2015). Antonini et al. (2012) verificaram maior crescimento e absorção de P pelo milho e pelo azevém quando utilizou estruvita em comparação a duas fontes comercias de P, o que também pode estar relacionado ao Mg dessa fonte. Os efeitos benéficos do Mg sobre a absorção de P, também pode estar relacionado a exsudação de ácido cítrico e citrato pelas plantas. A exsudação radicular dessas substâncias é induzida por fatores externos, como presença de Al^{3+} e deficiência de P, e aumentada quando a planta absorve Mg^{2+} (Silva et al., 2001; Erro et al., 2009; Chen et al., 2015).

A absorção de Mg^{2+} pela planta aumenta a atividade da H^{+}-ATPase da membrana plasmática, por meio do complexo Mg-ATP, a força próton motora, a exsudação de citrato, e ativa os transportadores secundários (Chen et al., 2015), relacionados à absorção de fosfato (Taiz e Zeiger, 2009; White, 2012). Além de citrato, raízes de milho podem exsudar outros ânions orgânicos, como oxalato, malato e malonato, bem como ácido cítrico sob deficiência de P (Erro et al. 2009; Neumann e Römheld, 2012). A presença dessas substâncias orgânicas na interface raiz-fertilizante pode aumentar a taxa de dissolução dos CFMs, o que modifica o padrão de liberação de P e magnifica a absorção desse nutriente pela planta. Assim, os CFMs podem apresentar não apenas uma liberação lenta ou gradual do P, mas uma propriedade de liberação controlada pela a atividade radicular das plantas, influenciada pela concentração de Mg do fertilizante e pela taxa de liberação desse nutriente no solo.

No solo após cultivo, os diferentes fertilizantes também modificaram os atributos químicos ($p<0,05$) (Figura 5). Com o uso dos CFMs foi verificado valores de pH do solo maiores do que com a aplicação dos SFTs. A elevação do pH de solos bem intemperizados aumenta a proporção de cargas negativas dos minerais constituintes, o que favorece o fluxo difusivo de fosfato na solução do solo e a absorção pelas plantas (Benício et al., 2017). Além disso, a manutenção do pH do solo próximo a 6,5, contribui para a disponibilidade da maioria dos nutrientes e, consequentemente, maior aproveitamento e eficiência da adubação pelas plantas (Fageria e Baligar, 2008).

O solo utilizado para este estudo possui propriedades que potencializam ou favorecem as perdas de P por adsorção específica, em razão, principalmente, da alta capacidade máxima de adsorção de P (1,7 mg g^{-1}). Além disso, os fertilizantes foram misturados em todo volume de solo, o que aumenta o contato da superfície do fertilizante com as partículas de solo, favorecendo a reação de adsorção. Mesmo assim, maiores teores de P disponível extraídos pela resina (P-resina) foram observados com a aplicação dos CFMs no solo, próximos dos 400 mg kg^{-1} de P aplicados inicialmente, comparado aos SFTs (Figura 5).

Provavelmente, grande parte desses teores de P foram extraídos do próprio CFM aplicado ao solo, que ainda poderão ser liberados e utilizados pela planta ao longo do cultivo. Em contrapartida, no solo com SFTgr ou SFTtb, apenas metade da quantidade aplicada de P foi recuperada pelo extrator resina, o que evidencia que grande parte do P-fertilizante foi transformado em formas não lábeis.

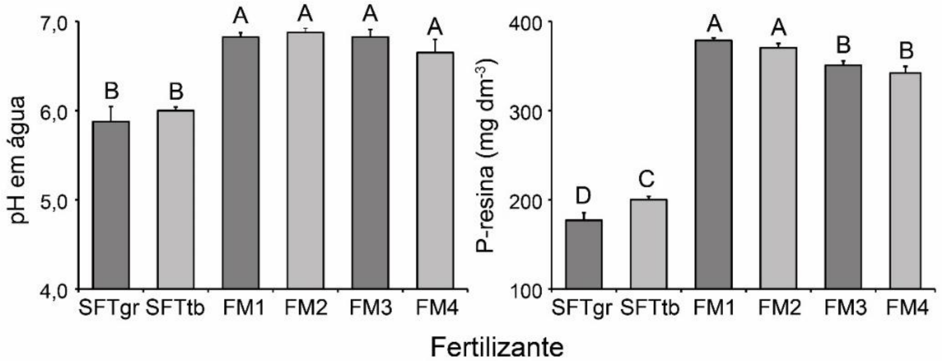

Figura 5. pH em água e P disponível extraído por resina (P-resina) em amostras de Latossolo Vermelho húmico tratados com superfosfato triplo granulado (SFTgr) ou tabletado (SFTtb) e com cada fosfato de magnésio (FM) produzido, após o cultivo do milho. Médias seguidas por mesma letra não diferem estatisticamente pelo teste Scott-Knott ($p<0,05$). Barra representa o erro padrão da média.

A rápida formação de espécies de P não lábeis no solo impedem a absorção desse nutriente ao longo do cultivo das plantas. Bender et al. (2013), estudando a absorção de nutrientes em híbridos de milho, verificaram que o acúmulo de P aumenta a partir do desenvolvimento inicial da planta e apresenta a maior exigência por esse nutriente durante o enchimento dos grãos. O trabalho realizado por Bender et al. (2013), exemplifica a necessidade do fertilizante apresentar uma liberação de P gradual e compatível com as fases de maior demanda da cultura. Desse modo, a falta de sincronia entre a liberação de P dos fertilizantes solúveis e as fases de maior requerimento do nutriente pela cultura, possivelmente, é um dos principais fatores responsáveis pela baixa taxa de recuperação de P-fertilizante pela planta.

Essa taxa de recuperação pela planta varia de 5 a 25% do P-fertilizante aplicado, especialmente em solos tropicais (Syers et al., 2008). Nesses solos, a rápida liberação de P pelos fertilizantes solúveis favorece a nutrição inicial da cultura. Entretanto, a maior parte do P aplicado é rapidamente adsorvida no solo, com baixa reversibilidade, devido ao aumento da energia dessa ligação com o tempo (Novais et al., 2007; Santos et al., 2011; Guedes et al., 2016). Essas reações impedem com que a cultura absorva o P, particularmente, durante os estádios reprodutivos.

Potencial agronômico

O uso de Mg no desenvolvimento de fertilizante fosfatado é uma alternativa vantajosa para conferir uma liberação gradual de P, possivelmente mais sincronizada com as fases de maior demanda da planta pelo nutriente, com menor contato do P-fertilizante com o solo e maior eficiência na aquisição desse nutriente pelas plantas. O FM3 foi a formulação que apresentou o maior potencial de uso como fertilizante, em razão da contribuição mais efetiva para o crescimento inicial e nutrição do milho com P. A relação entre os nutrientes, bem como o processo de síntese também são características regulatórias da solubilidade do P em água e da magnitude da liberação de P-fertilizante. Ainda, a aplicação dos CFMs reduz a retenção de P no solo, mantendo mais P residual após o cultivo. A importância agronômica dos CFMs também está relacionada ao Mg. O Mg é um nutriente que tem sido esquecido ou relegado a segundo plano na agricultura, o que está em desacordo com suas funções essenciais desempenhadas na planta, como no processo de fotossíntese, síntese de clorofila e no crescimento de raízes (Cakmak e Yazici, 2010).

Atualmente, no manejo da correção da acidez do solo e implantação das culturas é aplicado o calcário, muitas vezes com elevado teor de CaO, e o gesso agrícola, visando maior crescimento radicular das culturas em camadas mais profundas do solo. Além disso, majoritariamente, são utilizadas fontes de P ligado ao Ca, como os superfosfatos. Esse manejo pode aumentar de forma desbalanceada o teor de Ca^{2+} no solo e inibir a absorção de Mg^{2+} pela cultura (Gransee e Führs, 2013), o que compromete, entre outras funções, a partição de carboidratos na planta, reduzindo o crescimento de raízes (Cakmak e Kirkby, 2008; Cakmak e Yazici, 2010). Ainda, o predomínio desequilibrado de Ca^{2+} em relação ao Mg^{2+} no volume de solo adubado com P também pode reduzir a aquisição de P pela planta, pela inibição do sinergismo entre Mg e P (Malavolta, 2006; Dechen et al., 2015) e pela alta afinidade entre P e Ca, formando compostos estáveis e pontes metálicas entre o coloide do solo e o fosfato (Duputel et al., 2013; Xu et al., 2014). Desse modo, futuras pesquisas devem ser conduzidas para melhor elucidar os efeitos do Mg na eficiência de uso de P-fertilizante pelas culturas.

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CONSIDERAÇÕES FINAIS

Inúmeros estudos já foram realizados com P, inclusive com desenvolvimento de novos fertilizantes fosfatados. Mesmo assim, desde 1840, nos primórdios da reação do superfosfato simples, até os tempos atuais, os fertilizantes fosfatados totalmente acidulados, tais como os superfosfatos e o MAP, são majoritariamente aplicados na agricultura mundial. Isso implica que, talvez, essas tecnologias não tenham tido incentivo, de alguma maneira, para serem utilizados no lugar dos fertilizantes atuais.

Esse cenário reflete a dificuldade em tornar um manejo, atualmente sabido e dito como de baixa eficiência do ponto de vista de aproveitamento de P pelas plantas, em uma prática agrícola de elevada eficácia no uso de fertilizantes fosfatados. Dificilmente, os estudos realizados nesta tese reverterão as perdas de 80% do P aplicado para 80% de P-fertilizante absorvido pelas culturas. Mas, os resultados e processos apresentados neste documento poderão lançar luz sobre estratégias de manejo e tecnologias que aperfeiçoem a forma de uso do P na agricultura, como a aplicação de ácido húmico no solo, que pode aumentar a disponibilidade de P às plantas, dependendo das propriedades do solo. A tese também incentiva o aproveitamento de resíduos orgânicos agroindustriais como forma de reciclagem do P e como fonte de outros nutrientes, bem como estabelece bases para processos mais eficientes de produção de fertilizantes organominerais, por meio da compostagem. Além disso, são descritos novos fosfatos de magnésio sintetizados, que apresentaram características químicas vantajosas para uso como fertilizante fosfatado.

Essas tecnologias estudadas são distintas entre si, mas apresentam, pelo menos, uma estratégia em comum para aumentar a aquisição de P pelas culturas, como: bloqueio de sítios de adsorção de fosfato no solo; predomínio de Mg no volume de solo adubado com P; e fertilizante com pH mais próximo do neutro; P de liberação gradual; menor proporção de P solúvel em água e maior solubilidade em ácido orgânico ou complexante. Esses fatores, em conjunto, podem ser determinantes e efetivos para inibir o dreno P do solo e dar condições para um maior aproveitamento de P-fertilizante pela planta, como demonstra a Figura 1.

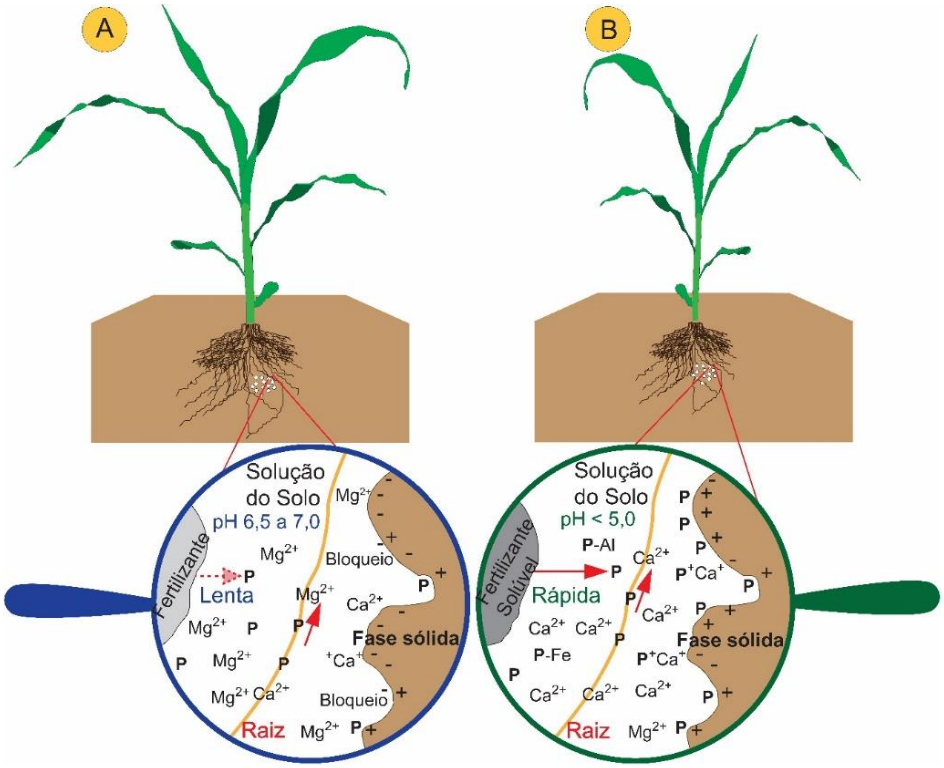

Figura 1 Esquema ilustrativo das estratégias para a melhoria do uso de P pelas plantas (A) e do manejo convencional (B) na interface fertilizante, solo e planta (raiz)

Estudos conduzidos em laboratório e em casa de vegetação muitas vezes antecipam os efeitos ou transmitem, de forma mais rápida, a potencialidade de fontes de nutriente para as plantas. Os estudos desenvolvidos nesta tese representam de certa forma, essa visão, como um passo de grande importância na seleção de materiais para estudos mais comprobatórios e em condições reais, como o uso no cultivo de plantas a campo, a fim de investigar a eficiência agronômica da tecnologia estudada ou desenvolvida.