RESEARCH ARTICLE

Organic acid coated-slow-release phosphorus fertilizers improve P availability and maize growth in a tropical soil

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Abstract

In this paper, we report the results of studies on the solubility (water solubility trial) and the response by plants (greenhouse pot experiment using *Zea mays*) for four types of monoammonium phosphate fertilizers (Conventional MAP - MAP_1, MAP coated with a natural organic acid - MAP_2, MAP coated with a synthetic organic acid - MAP_3, and MAP coated with a peat humic organic acid - MAP_4) applied at five increasing doses (0, 100, 300, 600 and 1200 mg P dm^{-3}) and pre-incubated with the soil for five lengths of time before planting (0, 15, 30 and 60 d). The coating with organic acids reduced the water solubility of the P fertilizers - MAP_4 provided a more gradual release of P over time. In the soil pot experiment, it was found that MAP_1 required the highest dose to reach 90% of dry matter accumulation by the maize plant, followed by the Coated-Slow-Release Fertilizers (CSRF). The agronomic efficiency (AE) of P applied as the CSRF was 3 to 13% greater than that of MAP_1. In addition, MAP_4 led to higher values of AE (+11%) and apparent P recovery by maize (+41%) in comparison to MAP_1. The physicochemical properties imposed by the chemical composition of the organic acid coatings generated fertilizers with distinct release rates and improved agronomic efficiencies.

Keywords: P uptake, Agronomic efficiency, MAP.

1. Introduction

The need for more productive agricultural systems has required technological innovations that increase the efficiency of used inputs (Chien *et al.*, 2009). The management of phosphate fertilizers is a key factor in crop production, which is especially the case in highly weathered tropical soil. However, in more oxidic tropical soils, the acquisition of P by plants is usually limited due to soil sorption processes (Novais and Smyth, 1999; Novais *et al.*, 2007; Abdala *et al.*, 2015a), usually requiring P application rates that are as much as 10 times larger than the actual plant demands or more (Novais and Smyth, 1999).

Additionally, in recent years the application of P in medium to large-scale farms in Brazil has been used as a pre-planting operation (usually broadcast) in order to optimize the performance of the row crop planter (only seeds are actually planted). This strategy may reduce P availability if high solubility P fertilizers are used because of the increased contact time of fertilizer P to oxidic clay minerals. These soil minerals are known to form high stability, low reversibility bonds to P (Parfit, 1978), and more recent work using K-edge EXAFS with a synchrotron light source has shown that under low P concentrations, a stable monodentate surface complex is more likely to occur, although the formation of surface precipitates at higher concentrations of P in the goethite/water interface has also been demonstrated (Abdala *et al.*, 2015a).

Given the relevance in P sorption processes, research efforts have been dedicated to understanding the effect of the contact time of P with soil components. Earlier studies with highly weathered soils indicated that 75% of P adsorption occurred within 30 min of contact for those soils with higher P adsorption capacity (Gonçalves *et al.*, 1985). Santos *et al.* (2011) found that adsorption of 74% of the added P occurred within 5 min in soil with a high P sorption capacity (0.3473 mg g^{-1}). More recently, Guedes *et al.*, (2016) studying P adsorption and desorption kinetics using a stirred-flow system, observed that most of the P adsorption process occurs in the first minutes of contact with the solution. The reversibility of this process (P desorption) is rather limited in highly weathered tropical soils as result of the rapid formation of strong and stable bonds of phosphate ions with soil colloids, such as Fe-oxides (Abdala *et al.* 2015b).

Based on accumulating experimental evidence, it is not surprising that the longer the contact of fertilizer P to highly weathered soils, the greater the adsorption and the lower the availability of P to plants. Among the several strategies based on the soil-rhizosphere-plant continuum that could be used to improve P availability and P use efficiency (Shen *et al.*, 2011), the use of slow-release coated phosphate fertilizers has gained recognition (McLaughlin *et al.*, 2011). Research is increasingly being aimed at developing new technologies to supply plants with phosphorus in a slow manner. Among these slow-release fertilizers (SRF), the major categories are fertilizers coated with different materials. Recently, a number of materials have been tested: biodegradable polymers (Wu and Liu, 2008; Ao *et al.*, 2013; Jia *et al.*, 2013; Lubkowski *et al.*, 2015), superabsorbent polymers (Liang *et al.*, 2007; Teodorescu *et al.*, 2009), commercial polymers (Figueiredo *et al.*, 2012; Silva *et al.*, 2012; Ma *et al.*, 2013), oxides (Zhang *et al.*, 2014) and fly ash (Dong *et al.*, 2016). More specifically for MAP, a previous study has shown that when P is more slowly released from a thin polymer coated-MAP fertilizer granule, it increased P availability, P uptake and P use efficiency by barley plants (Pauly *et al.*, 2002). The polymer-coated fertilizers had a greater effect on late plant growth stages, whereas the commercial MAP fertilizer was more favorable for P uptake and plant growth at the beginning of the experiment. These results led us to surmise that coated slow-release fertilizers (CSRFs) may be more effective in applications before planting than uncoated conventional MAP if the soil has a large P adsorption capacity. However, to date, there is a scarcity of information to back up such a hypothesis.

The ideal CSRF should control the release rate of nutrients according to different environmental conditions, prevent the accumulation of undesirable synthetic residues in the soil and minimize the frequency and dose of fertilizer applications. However, it is difficult to find a coating material that enables these features. Many researchers report that the molecular composition of coating materials used in CSRFs have influence over P release (Wu and Liu, 2008; Tyliszczak *et al.*, 2009; Jia *et al.*, 2013; Ahmad *et al.*, 2015).

In this context, organic polymers are a promising coating material because they are easily degradable and non-toxic to the environment. Although there are many studies that demonstrate the CSRF water dissolution rate (Bortolin *et al.*, 2012; Lubkowski, 2014; Lubkowski *et al.*, 2015; Ahmad *et al.*, 2015) and agronomic efficiency (Pauly *et al.*, 2002; Figueiredo *et al.*, 2012; Silva *et al.*, 2012; Chagas *et al.*, 2015), little is known about the characteristics of organic polymers that could reduce the negative effects of previous fertilizer P contact time with soil on P availability and the consequent growth response by the plant.

Thus, the purpose of this study was to investigate two commercial CSRFs coated with organic polymers (organic acids) and a CSRF coated with a peat humic organic acid in the laboratory. The kinetic parameters of P release were determined, and the responses of maize plants to different doses and pre-application times (previous fertilizer P contact with soil) were evaluated.

2. Materials and Methods

2.1. Monoammonium phosphate (MAP) coating

An uncoated commercial monoammonium phosphate fertilizer (MAP_1, 52% P_2O_5) and three coated monoamonium phosphate formulations were tested. The size range of MAP granules was standardized to 2 to 3 mm diameter each. The slow release MAP fertilizers were obtained by coating with a distinct organic acid, i.e., MAP_2 (50% P_2O_5 was coated with a natural organic acid), MAP_3 (48% P_2O_5 was coated with a synthetic organic acid, which is commercially available as Kimcoat P™ from Kimberlit Agrociências, Olimpia, SP, Brazil) and MAP_4 (43% P_2O_5 was coated with a humic acid extracted from peat). Coated MAP_2 and MAP_3 were obtained from Kimberlit, and the MAP_4 coating was prepared in our laboratory.

The humic organic acid was extracted from peat (Arraial do Cabo, RJ-Brazil) using an alkaline procedure with further purification as in Swift (1996). The coating of MAP_4 with a peat humic organic acid was initially carried out by stirring 2% (w/w) soybean cooking oil with MAP_1 (10 g) for 5 min. Then, lyophilized peat humic acid (1.5 g) was added and stirred in a rotary shaker for 15 min. The MAP fertilizer was weighted before and after coating with humic acid. A mass of 0.61 g (41% of added peat humic organic acid) was adsorbed onto the conventional MAP_1.

Spectral characterizations of organic acids samples used for coating of the MAP fertilizer were performed in the 500-4000 cm^{-1} region using a VARIAN 660 infrared spectrophotometer fitted with a total attenuated reflectance (PIKE GladiATR) accessory (Figure 1).
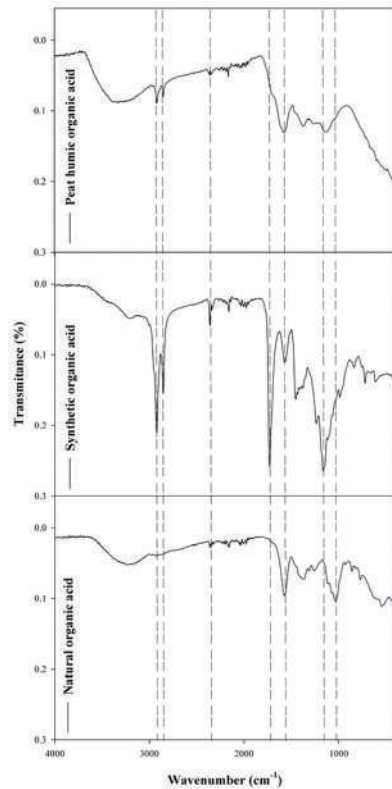

Figure 1. FTIR spectra of natural organic acid, synthetic organic acid and peat humic organic acid utilized in the coating of fertilizers

2.2. Kinetics of P release in water

A leaching column test was carried out to estimate P release from coated MAPs over 22 hours. Five grams of fertilizer were put into leaching columns, and a controlled flow of water at 2 mL min^{-1} was applied at the top. Leachate samples were collected from 0 up to 22 h, their volumes were measured, and t and P concentrations were determined colorimetrically based on the ascorbic acid method (Braga and Defelipo, 1974). The values of P released over time were fitted with a pseudo-first order model according to the Lagergren equation (Equation 1).

$$Q_t = Qe \ (1-e^{\ kt})\ \ \ \ \ \ \ \ \ \ \text{Equation 1}$$

where Q_t is released fertilizer P and Q_e is the fast release P pool at equilibrium time and at time t, respectively, and k_1 is the rate constant of the pseudo-first order release.

Then, using the estimated values of P release rates (k), it was possible to calculate the time required for 50% of the fertilizer P to be released ($t_{1/2P}$), based on Paul and Clark (1996) (Equation 2).

$$t_{1/2\,P} = ln\ (2)/k_1\ \ \ \ \ \ \ \ \ \ \text{Equation 2.}$$

2.3. Greenhouse pot experiment

Phosphate fertilizers were evaluated in a greenhouse pot experiment with maize plants. The soil was a clayey Oxisol (Typic Hapludox) collected from the 0-20 cm layer: pH (water): 5.00; Ca^{2+}: 0.27 cmol$_c$ dm^{-3}; Mg^{2+}: 0.06 cmol$_c$ dm^{-3}; P: 2.30 mg dm^{-3}; CEC: 3.78 cmol$_c$ dm^{-3}; Equilibrium phosphorus (Alvarez *et al.*, 2000): 8.10 mg L^{-1}; Organic matter: 1.14 %; Clay: 80 %; Silt: 10 % and Sand: 10%. The soil was air-dried and passed through a 2-mm sieve, and then 2.5 dm^3 of homogenous soil was placed into plastic bags.

Lime (CaCO$_3$ and MgCO$_3$ *p.a.* (3:1 molar ratio)) and a basal nutrient solution (Novais *et al.*, 1991) were applied and mixed, and the soil was wetted to 80% of field capacity. Next, the soil was accommodated in 3 dm^3 plastic pots.

A specific stainless apparatus was built to study phosphorus diffusion from the fertilizer dissolution zone into the soil without allowing direct contact of the roots with the fertilizer granules (Figure 2). The apparatus had two concentric cylindrical compartments (inner and outer) built with 0.25 and 1.0 mm mesh size stainless steel sieves, respectively. A defined amount of the four MAP fertilizers previously described were applied into the inner cylinder, and then the soil was accommodated inside the outer cylinder. The apparatus was then inserted into the pot soil. In a preliminary study, we observed that maize plant roots could access the outer cylinder soil (data not shown) and P, but they could not access fertilizer P inside the inner cylinder where the MAP granules were located (Figure 2).
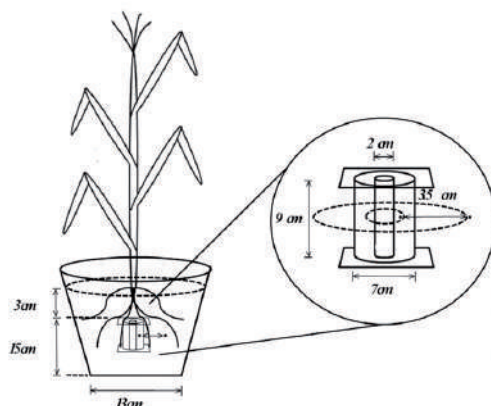

Figure 2. Scheme of experimental unit (pot with plants) and apparatus used to study phosphorus diffusion. By applying granular phosphate fertilizers into the inner cylinder and placing soil into the outer cylinder, roots can not access P directly from fertilizer granules.

The fertilizers were applied at rates equivalent to 0, 100, 300, 600 and 1200 mg of P dm^{-3} of soil in the whole pot. To simulate an early field pre-planting application (with the consequent increase in P contact time with the surface of soil particles), the four MAP fertilizers were applied into the inner cylinder and incubated under moist soil conditions for 0, 15, 30, 60 and 120 d before planting. Four seeds of *Zea mays* (DKB 390 hybrid) were planted in pots with 2.5 dm^3 of soil, and after germination and thinning, a single plant per pot was grown for 35 d.

Treatments were arranged in a 4 x 5 x 5 factorial scheme composed of the four MAP fertilizers (MAP$_1$, MAP$_2$, MAP$_3$ and MAP$_4$), applied at four rates (0, 100, 300, 600 and 1200 mg of P dm^{-3} of soil) and five incubation times before planting (0, 15, 30, 60 and 120 d). The experiment was carried out in a completely randomized block design with three replications.

2.4. Chemical analysis

At 35 d after planting, the maize plants were harvested. The roots were washed to remove soil particles prior to separation into roots and shoots. Then, they were dried in an oven at 65 °C for 72 h, weighed and milled. Dried ground samples were digested with a nitric-perchloric solution (Johnson and Ulrich, 1959), and the P in the extract was determined by the colorimetric ascorbic acid method (Braga and Defelipo, 1974). The soil that was inside the outer cylinder and that outside the apparatus (whole pot soil) were collected and homogenized separately, and a representative sample was taken for subsequent analysis. The distance between a midpoint in the outer cylinder and another located in the middle point between the apparatus and the pot wall (3.5 cm) was used for calculating the difference in P concentrations at the two points in the soil (Delta P), and they were assumed to correspond to P movement by diffusion from the fertilizer dissolution zone to the whole pot soil. The available soil P was determined by the anion-exchange resin method (van Raij *et al.*, 1987).

2.5. Statistical analysis and agronomic indices

Data were submitted to an analysis of variance, and the effects of fertilizer P rates and incubation time on dry matter, P uptake by maize, available P in soil and soil Delta P for each MAP fertilizer were assessed through a linear regression analysis. Multiple linear regressions using Akaike's Information Criteria (AIC) were used to define the best fit model for each MAP fertilizer. Statistical analyses were run using SAS (SAS Institute, Inc. 2001).

Applied fertilizer P and available soil P concentration in the soil corresponding to 90% of maximum dry matter production were estimated using the selected regression models. The indices of Agronomic Efficiency (AE) and Apparent P Recovery (AR) of a plant were calculated as the ratio of the increase in dry matter production and the P taken up by the plant over control (no added P) treatments to the applied rate of the nutrient, respectively, as in the following equations:

$$AE\ (mg\ mg^{-1}) = (Y_N - Y_O)\,/\,F_N \qquad \text{Equation 3.}$$

$$AR\ (\%) = [(U_N - U_O)\,/\,F_N]\,x\,100 \qquad \text{Equation 4.}$$

where Y_N and U_N are the dry matter production and P taken up by plants in a given treatment, respectively, Y_O and U_O are dry matter production and P taken up by plants in the control treatment without P application, respectively, and F_N is the amount of applied fertilizer P corresponding to 90% of the maximum dry matter production.

3. Results

3.1. Kinetics of P release from the fertilizer granule

Coated MAP fertilizer granules released P to percolating water slower and in smaller amounts than the uncoated MAP (MAP$_1$) (Figure 3). With percolating

water for 1320 min, approximately 96% of all the P was released from MAP$_1$. On the other hand, MAP$_4$ showed a distinctly slower release of P compared to MAP$_2$ and MAP$_3$ (Figure 3). MAP$_4$ had a t$_{1/2P}$ of 204 min, while for the t$_{1/2P}$ of MAP$_2$ and MAP$_3$ were 56 and 41 min, respectively. MAP$_1$ released approximately 50% of the initial P in only 13 min.

$$\hat{P}_{MAP1} = 92.89^{**}(1- e^{-0.0515^{**}})\ \ R^2 = 0.9519$$
$$\hat{P}_{MAP2} = 65.38^{**}(1- e^{-0.0123^{**}})\ \ R^2 = 0.9718$$
$$\hat{P}_{MAP3} = 69.13^{**}(1- e^{-0.0169^{**}})\ \ R^2 = 0.9954$$
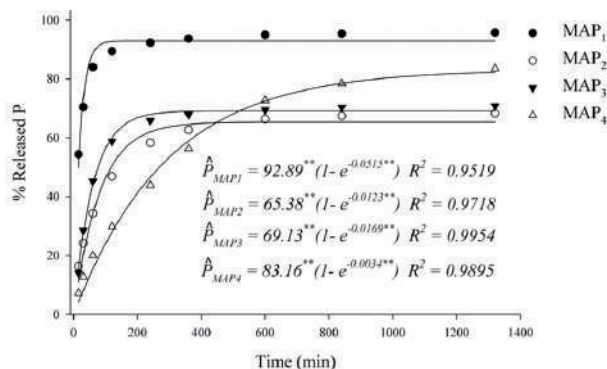$$\hat{P}_{MAP4} = 83.16^{**}(1- e^{-0.0034^{**}})\ \ R^2 = 0.9895$$

Figure 3. Release of P relative to total P released (%) from non-coated MAP (MAP$_1$) and coated MAP as a function of time (min) in a leaching column under water flow at 2 mL min^{-1}. MAP$_2$ is coated with a natural organic acid; MAP$_3$ is coated with a synthetic organic acid and MAP$_4$ is coated with a peat humic organic acid. Equations are adjusted according Lagergren. ** indicate significant coefficients at *p* < 0.01 by the t test.

3.2. FTIR spectrum of organic acids

The FTIR spectrum of the organic acids used in the coating presented the following peaks in the wavenumbers with the possible assignment, respectively: 595 cm^{-1} ((δs(C-CO-C)) aldehydes); 717 and 827 cm^{-1} (γ(C-H) aromatic ring); 3350 cm^{-1} (ν_s(O-H) in hydrogen bonding (related to alcohol, phenols or carboxylic acids)); 2844 and 2913 cm^{-1} (ν_s(C-H, CH$_2$) and ν_s(C-H, CH$_3$)); 2350 cm^{-1} (νs(C$\equiv$C) conjugated alkynes); 2159 cm^{-1} (ν_s(C$\equiv$N) possibly in conjunction with other unsaturated groups); 1730 cm^{-1} (ν_s(C=O) aldehydes and ketones); 1570 cm^{-1} (ν_s(C=C) the benzene ring and the vibration of the aromatic skeleton; ν_{as} (COO$^-$) and ν_s(C=O) the COOH group due to the H bonded

OH; ν_s(C=C) overlaid with δ_{as}(C-H, CH$_3$); ring alkanes; ν_s(C=N) pyrimidine); 1380 cm^{-1} (δs(O-H), ν_s(C-O) phenol groups and the ν_{as}(COO$^-$)); 1365 cm^{-1} (δs(C-H, CH$_3$ or CH$_2$) aliphatic chains); 1157 cm^{-1} ((ν_s(C-CO-C)) aldehydes) and 1100 cm^{-1} (δs(O-H) and ν_s(C-O) coupled ν_s(C-C) secondary alcohols).

The peat humic acid used for coating the MAP$_4$ fertilizer had a lower density of aliphatic hydrocarbons (especially with smaller ramifications) and a greater density of -COO$^-$ and -OH groups when compared with the synthetic organic acid and the natural organic acid, respectively (Figure 1), giving it an intermediate hydrophobicity among the other organic acids. The synthetic organic acid (MAP$_3$) had a higher density

of aliphatic hydrocarbons, with the presence of ramifications, unsaturated bonds (C≡C) (Figure 1), and carbonyl groups (C=O) (Figure 1). Additionally, it had less intense bands related to stretches of the C=C aromatic ring (Figure 1) in its structure compared to the other organic acids. The presence of unsaturation promotes greater distortion in the molecule even if it has higher aliphatic chains. This feature and the greater number of carbonyl groups confer a higher permeability to water molecules. In contrast, the natural organic acid used for producing MAP_2 showed no C-H (CH_2) or C-H (CH_3) stretches, which are features of alkyl chains. Combined with the smaller abundance of -COO^- groups and larger bands for C=C stretches in the aromatic rings (Figure 1), this molecule displayed greater hydrophobicity.

3.3. Greenhouse pot experiment

Available P in soil

The uncoated conventional MAP (MAP_1) led to the lowest availability of P in the soil among all fertilizers when higher levels of P were applied (Figure 4). In this way, the maximum availability of P reached by applying uncoated MAP was 246 mg dm^{-3} when 1200 mg of fertilizer P dm^{-3} were applied 15 d before planting maize. The coated fertilizers favored greater availability of soil P over time. The coated MAP_2 provided a more constant concentration of available soil P over pre-incubation times among all fertilizers. The greatest availability of soil P when applying MAP_2

(267 mg dm^{-3}) occurred with 1200 mg of P dm^{-3} and no pre-incubation time (0 d) (Figure 4). A similar behavior of soil P availability over time was observed for both MAP_3 and MAP_4. The highest concentration of available soil P among all fertilizers was provided by MAP_3 (359 mg dm^{-3}) and followed by MAP_4 (324 mg dm^{-3}), both after 20 d of pre-incubation and with the application of the highest P dose - 1200 mg of P dm^{-3} (Figure 4).

3.4. Estimated P movement from the fertilizer granules into the soil

As expected, the Delta P (the difference in available soil P in the internal soil core in comparison to that in the external soil core) for all fertilizers increased with the applied level of P (Figure 5). The uncoated MAP showed a significant reduction in Delta P over time Table 1. The concentrations of available soil P were estimated to be similar for the two sampling points (Delta P: 0) after 33 and 85 d, by applying 100 mg dm^{-3} and 1200 mg dm^{-3}, respectively (Figure 5). However, even the high application doses of coated MAP_2, MAP_3 and MAP_4 were not sufficient to allow P movement from the internal core soil to the external core soil at the same magnitude as uncoated P. Thus, there was always a smaller amount of P movement in soil when coated MAP fertilizers were used compared to the uncoated conventional MAP. Nevertheless, it did not mean less P uptake and maize growth as one would initially suspect (see more details below).
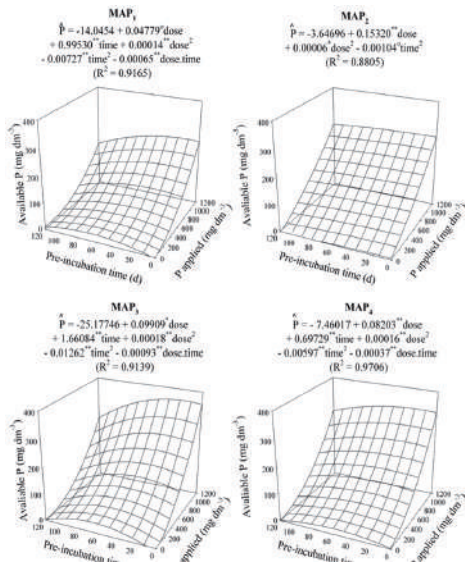
Figure 4. Available soil P extracted by anion-exchange resin (mg dm^{-3}) as a function of applied P rates (mg dm^{-3}) and pre-incubation times (d) of non-coated MAP (MAP$_1$) and coated MAP (MAP$_2$, MAP$_3$ and MAP$_4$). MAP$_2$ is coated with a natural organic acid; MAP$_3$ is coated with a synthetic organic acid; and MAP$_4$ is coated with peat humic organic acid. °, *, ** indicate significant coefficients at $p < 0.1$; 0.05 and 0.01 by the t test, respectively.

Figure 5. Differences between available P concentrations in the inner and outer soil compartments (Delta P - mg dm^{-3}) as a function of applied P rate (mg dm^{-3}) and pre-incubation time (d) of non-coated MAP (MAP$_1$) and coated MAP (MAP$_2$, MAP$_3$ and MAP$_4$). MAP$_2$ is coated with a natural organic acid; MAP$_3$ is coated with a synthetic organic acid; and MAP$_4$ is coated with a peat humic organic acid. °, *, ** indicate significant coefficients at $p < 0.1$; 0.05 and 0.01 by the t test, respectively.

3.5. Maize plants P uptake

The conventional uncoated MAP caused little variation in the uptake of P by the maize plant (Figure 6), regardless of the pre-incubation time. The maximum P uptake by the maize plant (98.2 mg pot^{-1}) was the lowest among all MAP fertilizers evaluated, and it was estimated to occur when 1080 mg dm^{-3} of P as MAP$_1$ was pre-incubated with the soil 120 d before planting (Figure 6). Interestingly, MAP$_4$ allowed the
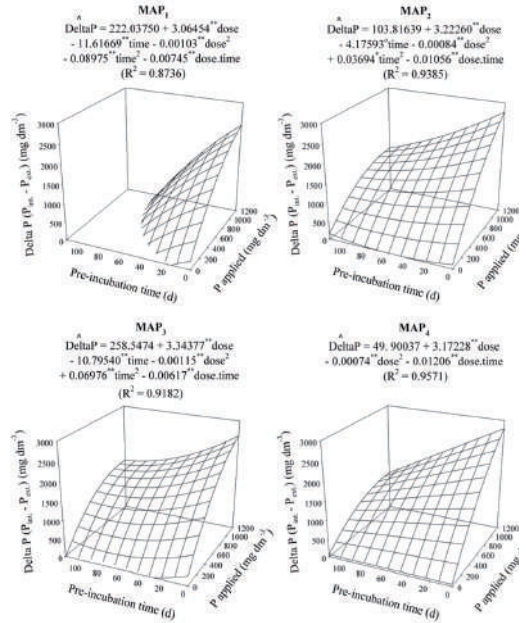
greatest P uptake by the maize plant (111.2 mg pot^{-1}). That uptake was estimated to occur with the application of 1080 mg dm^{-3} of P to the soil as MAP$_4$ 96 d prior to the planting. MAP$_2$ provided a P uptake by maize plants of 107 mg pot^{-1} when 1080 mg dm^{-3} of P pre-incubated with the soil during 84 d before planting. Finally, MAP$_3$ allowed the lowest P uptake by the plants (98.6 mg pot^{-1}) among all the coated fertilizers, which was estimated to occur with its application (960 mg dm^{-3}) to the soil 84 d before planting.

Table 1. Estimated values of P applied (mg dm^{-3}) as uncoated (MAP$_1$) and coated MAP (MAP$_2$, MAP$_3$ and MAP$_4$) and time of pre-incubation (d) to reach 90% of dry matter production (DMP, g pot^{-1}) of maize growth by 35 d in a pot experiment, and the corresponding available soil phosphorus concentration (Avail. soil P, mg dm^{-3}), Delta P (mg dm^{-3}), agronomic efficiency (AE, mg mg^{-1}) and apparent recovery (AR, %)

Fertilizers	90% DMP	P applied	Pre-incubation time	Avail. soil P	Delta P	Agronomic efficiency (AE)	Apparent recovery (AR)
	... g pot^{-1}...	... mg dm^{-3}...	...... d	... mg dm^{-3}...	... mg dm^{-3}...	.... mg mg^{-1}	.... % ....
MAP$_1$	30.41	1116	79	190	234	8.95	3.3
MAP$_2$	23.87	765	69	144	1410	9.18 (+ 3%)	4.92 (+ 49%)
MAP$_3$	26.85	840	55	195	1589	10.08 (+ 13%)	4.36 (+ 32%)
MAP$_4$	26.61	825	53	173	1632	9.92 (+ 11%)	4.65 (+ 41%)

MAP$_1$ uncoated MAP; MAP$_2$ is coated with a synthetic organic acid; MAP$_3$ is coated with a natural organic acid and MAP$_4$ is coated with a peat humic organic acid.
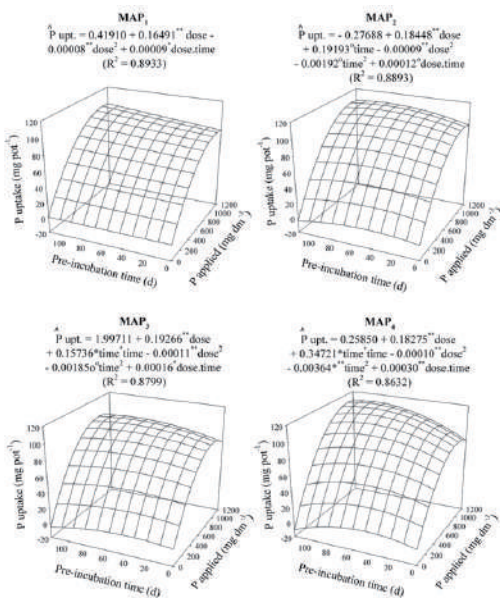

Figure 6. Phosphorus uptake (mg pot^{-1}) by maize plants as a function of applied P rate (mg dm^{-3}) and pre-incubation time (d) of non-coated MAP (MAP$_1$) and coated MAP (MAP$_2$, MAP$_3$ and MAP$_4$). MAP$_2$ is coated with a natural organic acid; MAP$_3$ is coated with a synthetic organic acid; and MAP$_4$ is coated with a peat humic organic acid. °, *, ** indicate significant coefficients at $p < 0.1$; 0.05 and 0.01 by the t test, respectively
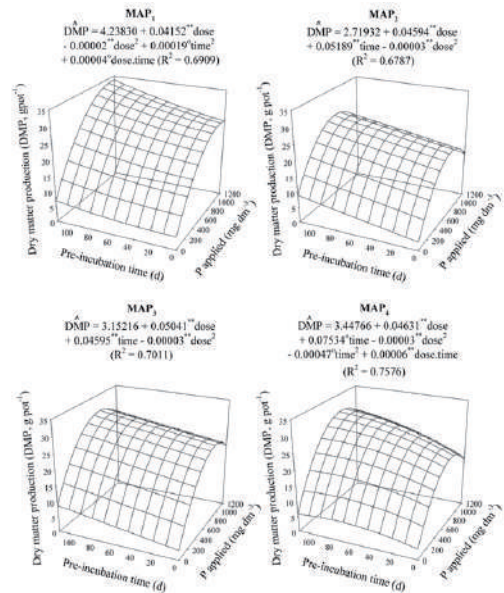
Figure 7. Dry matter production (DMP, g pot^{-1}) of maize plants as a function of applied P rate (mg dm^{-3}) and pre-incubation time (d) of non-coated MAP (MAP$_1$) and coated MAP (MAP$_2$, MAP$_3$ and MAP$_4$). MAP$_2$ is coated with a natural organic acid; MAP$_3$ is coated with a synthetic organic acid; and MAP$_4$ is coated with a peat humic organic acid. °, *, ** indicate significant coefficients at $p < 0.1$; 0.05 and 0.01 by the t test, respectively.

3.6. Dry matter production (DMP)

The highest DMP among all fertilizers (33.8 g pot^{-1}) was estimated to occur when 1158 mg of MAP$_1$ dm^{-3} was applied to the soil 120 d ahead of maize planting For the same fertilizer pre-application period of 120 d, the required doses of MAP$_3$, MAP$_4$ and MAP$_2$ would be 840, 891, and 765 mg dm^{-3} for DMPs of 29.8, 29.5 and 26.5 g pot^{-1}, respectively (Figure 7).

4. Discussion

4.1. Kinetics of fertilizer P release in water

In summary, the water solubility test that we carried out with the distinctly coated MAPs demonstrated that the P release from fertilizer granules could be related to the hydrophilicity or hydrophobicity of the coating material. Thus, the molecular characteristics of the humic acid (MAP$_4$), with an intermediate hydrophobicity, provided a more gradual release of P over time compared to the organic acids-coated fertilizers (MAP$_2$ and MAP$_3$).

Recent studies using NPK fertilizer coated with different materials corroborate our findings of slower releases of coated MAPs. Lubkowski (2014) observed that the release of P from uncoated NPK was six times faster than from oligochitosan-coated NPK. Likewise, Lubkowski *et al.* (2015) observed that the t$_{1/2P}$ of NPK coated with different amounts of biodegradable poly (butylene succinate) was 100 to 1000 times slower than that of uncoated NPK (55-60 min). Noppakundilograt *et al.* (2015) evaluated the solubility of P in water from trilayer-coated NPK with poly(vinyl alcohol)/cross-Chitosan/poly(acrylic acid-co-acrylamide) and observed that only 12% of P was released over 30 days, while conventional NPK released 100% in 12 min.

The relationship between the hydrophilicity of the polymer coating and the release of P from the fertilizer granule to an aqueous medium is well known. Hana *et al.* (2009) examined a biodegradable starch/polyvinyl alcohol film as a coating for fertilizers and found higher water permeability through the coating with a higher proportion of polyvinyl alcohol. This effect can be partially explained by the increased hydrophilicity of the polyvinyl alcohol provided by the increasingly abundant -OH groups. Noppakundilograt *et al.* (2015), in a previous study of coated NPK fertilizer, observed that the increase of hydrophilic groups allowed a greater expansion of the hydrogel poly(vinyl alcohol)/cross-Chitosan/poly(acrylic acid-co-acrylamide) and higher water absorption. However, the hydrophilicity of the polymer coatings may depend on the pH of the surrounding solution (Ahmad *et al.*, 2015).

The slower P release rates of the coated fertilizer are usually a result of physical and chemical barriers. According to Wu and Liu (2008) the dissolution mechanism of coated fertilizers includes three stages: 1) the water penetrates through the porous coating; 2) the nutrients are gradually dissolved in the solution; and 3) the solution diffuses through the porous coating. Thus, issues such as porosity (Tomaszewska and Jarosiewicz, 2004; Silva *et al.*, 2012), thickness of the coating layer (Jia *et al.*, 2013; Lubkowski, 2014; Lubkowski *et al.*, 2015), and composition of the organic polymer (Wu and Liu, 2008; Tyliszczak *et al.*, 2009; Hana *et al.*, 2009) determine the P diffusion coefficient from the granule to the soil (Du *et al.*, 2006; Lubkowski, 2014; Ahmad, 2015).

Based on these studies and our own findings, it can be hypothesized that the humic acid coating allowed an initial hydration of the coating, but in a following phase, the dissolution of the MAP fertilizer may have been slowed down by the thin film of soy oil previously adsorbed to the fertilizer granules. Thus, it appears

that instead of searching for compounds of variable composition and hydration capacities, it may be more effective and practical to use more than one coating material sequentially applied to the fertilizer granule. The products we use for the MAP$_4$ coating offer the advantage of being natural, biodegradable products that offer no environmental risks. Furthermore, they are readily available products and can be acquired at competitive prices worldwide. The use of peat humic acid may be questioned on the grounds of possible environmental impacts derived from its extraction/ mining from nature. However, such a limitation can possibly be overcome by using natural humic-like substances that are chemically similar to humic acids and can be synthesized from industrial, plant-derived biochar (Trompowski *et al*., 2005).

4.2. Greenhouse pot experiment

The uncoated MAP has a high rate of P release (Figure 3), and it leads to a fast increase in the concentration of P in the soil solution (Silva *et al*., 2012). Nevertheless, the quick release may be followed soon afterwards by low P availability due to the rapid adsorption and the low reversibility of the bonding of phosphate ions to Al and Fe-hydroxy (oxides) (Parfitt, 1989; Novais and Smyth, 1999; Khatiwada *et al*., 2012; Abdala *et al*., 2015a), which is particularly the case in acid tropical soils.

The coated fertilizers we evaluated provided greater soil P availability over time (Figure 3). The release of P from the polymer-coated fertilizer when in contact with the soil may also be influenced by the biodegradability of the polymer (Ao *et al*., 2013; Jia *et al*., 2013; Lubkowski *et al*., 2015) and by the characteristics of the soil solution surrounding the granule (ionic strength; temperature; pH conditions) (Hanafi *et al*., 2000; Tyliszczak *et al*., 2009; Ahmad *et a*l.,

2015). This fact contributes to the delayed release of the coated P fertilizers.

The dissolution of a P fertilizer creates two distinct zones around the granule as it is dissolved by the soil solution (Hedley and McLaughlin, 2005). For uncoated highly soluble fertilizers like MAP$_1$, it is likely that the rapid hydration and dissolution increased the concentration of P in the soil solution in close proximity to the granule, saturating the absorbent surface and thus allowing quickly diffusion of P towards the bulk soil. In this P-saturated zone, P precipitates are likely to form, thus reducing its solubility. Even in acid soils it appears that Ca-P, in addition to Fe-P and Al-P, precipitates are formed, and this is an important way of interfering with P availability (McLaughlin *et al*., 2011; Khatiwada *et al*., 2012). Further away from the fertilizer granule, a P-unsaturated zone exists, where the P concentration in solution is below the soil maximum adsorption capacity. Specific high-energy adsorption reactions of P with soil minerals dominate in this region and are intensified with increasing P contact time with the inorganic soil components, especially with mineral non-silicate clay (Fe and Al oxides), providing a form of P that is unavailable to plants.

In our double-walled apparatus used for preventing direct contact of fertilizer-P with the soil, the first P-saturated region was likely to occur in the internal soil core, and the P-unsaturated region could be formed in the external bulk soil. Assuming so, the slower release of P from the granules by our MAP-coated fertilizers may have reduced the formation of P precipitates in the P-saturated zone and favored a more continuous movement of P from the inner soil core to the bulk soil. This is supported by the fact that the Delta P values for the uncoated MAP$_1$ were lower than those found for MAP$_2$, MAP$_3$ and MAP$_4$ (Figure 4). Therefore, the gradual solubilization of the coated MAPs allowed a greater difference in concentrations of P between the internal and external soil cores, thus providing a more

constant supply of P towards the bulk soil where the maize roots were developing.

Phosphorus uptake and maize plant dry matter accumulation were significantly affected by the doses and pre-incubation times of MAP fertilizers (Figure 5 and 6). In general, CSRFs favored P uptake, plant growth and P use efficiency. Several studies with different plants have shown that when the P source is coated, there is greater P uptake by plants, similar to the findings of our study. Pauly *et al*. (2002) found that after 45 days of barley cultivation, MAP coated with polyethylene film favored 4.21% more P uptake by the plants in comparison to uncoated MAP. Chagas *et al*. (2015) studied MAP coated with soluble anionic polymers and found 31.2% more P uptake by lettuce plants with respect to uncoated MAP. The experimental evidence with plants has not always shown consistent results. Figueiredo *et al*. (2012) working with uncoated MAP and coated MAP (Kimcoat®) found higher productivity and DMP of maize plants for coated MAP. Silva *et al*. (2012) found no difference in the DMP of maize plants with different doses of P using MAP coated with a polymer (Phosmax®) and uncoated MAP. Such inconsistencies may have resulted from the distinct effectiveness of the coating material, initial soil P levels, fertilizer type and dose, and the soil mineralogy.

An intriguing finding of our study is the fact that at short pre-incubation times and high MAP doses, the uncoated MAP fertilizer led to a greater DMP by maize plants than the coated MAP fertilizers. This effect might be related to the pulse of P into the soil solution on the very first day (short pre-incubation time and high dose) by the uncoated fertilizer, favoring initial plant P uptake and growth. When lower P doses were used and there were longer P contact times with the soil, the conversion of available P to less available P forms is expected, particular in soil zones more distant from the fertilizer granule (Khatiwada *et al*.,

2011). Detailed studies of the P forms in this soil using synchrotron K-edge XANES found that most P in a non-calcareous soil was bound to Fe, and a small proportion was bound to Ca. At longer incubation times (6 months), less P was found in adsorbed, plant available forms, and more stable P minerals were observed in the granular MAP treatment broadcast onto the soil surface. At the other end of the spectrum, the lowest DMP among the coated fertilizers was found for the plants of the MAP_2 treatment, which may have resulted from it having the slowest P release kinetics. This too slow release likely resulted from its high hydrophobicity and may have limited P movement from the granule into the bulk soil when MAP_2 had shorter pre-incubation times (high initial plant demand was not met by the initial slow P release). Therefore, limited P movement occurred into the inner soil core and then into the outer soil core where maize roots were growing.

Among the three major nutrients (N, P and K), P is the only one that is non-renewable and has no alternative sources, except the management of biogeochemical cycling (Childers *et al*., 2011; Alamgir and Marschner, 2016). Taken together with this fact, the current use and rate of P application can cause a peak of production by 2030 (Cordell *et al*., 2009). Thus, more efficient handling and environmentally safe and sustainable P use is required. The efficient management of P may be achieved through distinct ways involving strategies in the plant/rhizosphere/soil continuum (Shen *et al*., 2011), and it may also be improved by the use of CSRFs (McLaughlin *et al*., 2011).

In the current study, it was observed that the maximum economical production efficiency (90% DMP) was obtained by the conventional uncoated MAP; however, it was reached at a cost of a much higher P dose (1116 mg dm^{-3}). Plants fertilized with coated MAP fertilizers accumulated slightly less DMP than those fertilized with MAP_1, but they required lower

P doses to do so (MAP$_2$: 765 mg dm^{-3}; MAP$_3$: 840 mg dm^{-3} and MAP$_4$: 825 mg dm^{-3}). Additionally, CS-RFs showed agronomic efficiencies varying from 3 to 13% greater than MAP$_1$, and the recovery of applied P by maize plants ranged from 32 to 49% higher than MAP$_1$ (data not shown). This might have occurred because lower doses of coated MAP warranted a more gradual but more constant release of P into the soil, thus promoting a more efficient use of P by the plants . The distinct agronomic performances obtained by applying MAP fertilizers before planting suggest a management strategy more operationally efficient to be further analyzed by farmers that are used to broadcasting soluble fertilizers on the soil surface well ahead of the planting time. Despite the fact that MAP$_1$ provided 90% DMP by the maize plant when it was applied 79 d before planting (for coated MAPs it varied from 53 to 69 d), the dose required to obtain this effect was considerably higher because there is the need to saturate the soil minerals so that subsequent P released from the granule will be more available to plants. This strategy, however, undermines P use efficiency by plants and is less sustainable in the long term. Higher surface applied P doses also offer greater risk of losses of dissolved reactive P through runoff and the eutrophication of surface water bodies (Shoumans *et al*., 2013)

5.Conclusions

Overall, the coating of granular monoammonium phosphate (MAP) fertilizer with organic acids modifies the pattern of P release, the movement from the fertilizer granule to the soil and P availability to plants over time. This resulted in greater P use efficiency by plants fertilized by coated MAP most of the time. The longer pre-incubation of MAP fertilizers may result in less P availability and plant growth, especially of uncoated MAP. This will probably be

magnified in broadcast applications in clay, oxidic soils with low initially available P. By choosing coatings with distinct characteristics, it is possible to modulate P release by soluble P fertilizers such as MAP and to favor plant uptake over the formation of less available P forms, thus improving the efficiency of use of soluble fertilizer P.

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