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Acid Ammonium Citrate as P Extractor for Fertilizers of Varying Solubility

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ABSTRACT: There are several globally accepted methods to chemically characterize P-fertilizers, but not all are suitable to predict the agronomic efficiency of the P sources in terms of plant nutrition. Our aim was to investigate the performance of P extractors for fertilizers, investigating the consistency of different methods for P sources of varying properties and the related plant responses. The experiment was carried out in a greenhouse, using corn as a model plant. Phosphorus values extractable in water, 2 % citric acid, 2 % formic acid, ammonium neutral citrate + water, and acid ammonium citrate were evaluated for eight P fertilizers of varied solubility and correlated with P uptake by corn. The extractors citric acid and formic acid recovered no predictive amounts of P from crystalline apatite sources (Araxá and Patos phosphate rocks, PRs). However, they showed a satisfactory performance for Bayóvar PR and partially acidulated PRs but extracted low amounts of P from soluble P sources such as superphosphates. Neutral ammonium citrate + water extractors could accurately predict the efficiency of soluble P sources but underestimated the performance of Bayóvar (a reactive PR). In contrast, the extractor acid ammonium citrate, AAC, (pH 3) accurately predicted the agronomic efficiency of all P fertilizers. We therefore suggest AAC as an effective predictor of the agronomic effectiveness of any inorganic phosphorus sources.

Keywords: phosphorus fertilizers, citric acid, ammonium neutral citrate.

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INTRODUCTION

Phosphorus is a limiting plant nutrient, especially in highly weathered soils with low P reserves and high sorption capacity, where P, even at high application rates, is unavailable for plant uptake. Therefore, the use of phosphate fertilizers of known agronomic performance is essential to ensure adequate P supply and high crop productivity (Novais and Smyth, 1999; Scholz and Wellmer, 2013). However, the use of finely ground phosphate rocks (PRs) is not commonly practiced in Brazil due to the lack of supporting information on their agronomic performance. Indeed, PRs show a high variation in physical, chemical, and mineral properties, affecting their solubility and reactivity as well as the characteristics of the produced P fertilizers.

The most common process to produce high-grade P fertilizers uses sulfuric or phosphoric acid to solubilize the apatite mineral present in PRs. However, the global resources of high-quality PR are limited (Cordell et al., 2009; Cooper et al., 2011; Scholz and Wellmer, 2013), forcing manufacturers to use PRs with a high degree of impurities, such as P-Fe or P-Al and Si phases. Due to the great variation in the composition of these P sources, the resulting P fertilizers, known as partially acidulated phosphate rocks (PAPRs), greatly vary in terms of solubility and have a low water solubility (Chien et al., 2009).

The solubility of P fertilizers is generally measured using extractors which simulate the extraction power of the roots in terms of available soil P (Binh and Zapata, 2002). In Brazil, neutral ammonium citrate (NAC) + water is used for superphosphates, ammonium phosphates, PAPR fertilizers, and thermophosphates, while 2 % citric acid is used for PRs (Brasil, 2016). In Europe and the USA, 2 % formic acid and NAC are used for PRs, respectively (Chien and Hammond, 1978; Binh and Zapata, 2002).

Extractors for phosphate fertilizers are important to predict their agronomic performance, to establish the doses of fertilizers, and to comply to the legislation. For instance, for PAPR, the Brazilian legislation has established a minimum of 20 % (w/w) of the total P_2O_5, at least 9 % of P_2O_5 soluble in NAC (NAC_P), and at least 5 % of water-soluble P_2O_5 (water_P). For non-reactive PRs, a minimum of 5 % (w/w) of the total P_2O_5, thereof at least 15 % of the specified concentration of P_2O_5 soluble in 2 % citric acid (CA_P), is compulsory. The chemical extractant 2 % citric acid has been used to discriminate reactive and non-reactive PRs, assuming that for reactive PRs, more than 30 % of the total P_2O_5 concentration are soluble in 2 % citric acid (Brasil, 2016). Therefore, reactive PRs may have, besides the above-mentioned citric acid solubility, a minimum of 27 % (w/w) of total P_2O_5, according to Brazilian legislation (Brasil, 2016). For soluble phosphate fertilizers such as MAP, a minimum of 48 % P_2O_5 soluble in NAC and at least 44 % of water-soluble P_2O_5 is required.

Several methods have been used to analyze phosphorus fertilizers, which vary greatly in their chemical composition and solubility. However, these variations are not necessarily related to the agronomic effectiveness (Chien and Hammond, 1978). Moreover, it is unclear which chemical extractant may be used when mixing different P sources in NPK mixtures. The use of multiple methods generally increases analysis costs. In this context, the objective of this study is to evaluate chemical extractants for P fertilizers, investigating the P extractability via plant responses.

MATERIALS AND METHODS

Phosphorus fertilizers of varying solubility

Two non-reactive PRs (Araxá and Patos) and one reactive PR (Bayóvar), as well as their partially acidulated phosphate rocks (PAPRs), and two fully acidulated phosphate fertilizers (SSP and TSP) were evaluated. Araxá PR is an apatite concentrate from igneous deposits, while Patos PR is obtained from a sedimentary medium-grade metamorphism

deposit; both can be found in the state of Minas Gerais, Brazil. The highly crystalline hydroxyapatites and fluorapatites are the most common P sources in Brazilian phosphates (Santos et al., 2016), considered to be low-reactive fertilizers for direct use (Barreto et al., 2018). In addition, the high occurrence of Fe-, Al-, and Si species in the deposits of these phosphates has prompted the industries to concentrate the apatite minerals prior to the production of P-fertilizers.

Bayóvar PR is a phosphorite mined in a marine sedimentary deposit in the Sechura Desert in Peru. The phosphate mineral contained in Bayóvar PR is mainly hydroxyapatite of high porosity (Baldoino, 2017) and low crystallinity (Santos et al., 2016).

Partially acidulated phosphate rocks (PAPRs) are produced by reaction of PRs with an acidic wastewater, as demonstrated by Barreto et al. (2018). The wastewater is highly acidic (pH ~ 0 and 5.75 mol L^{-1} H$^+$), with high concentrations of some plant nutrients, such as S-SO$_4^{2-}$ (791 g L^{-1}), N-NO$_3^-$ (18 g L^{-1}), Cl-Cl$^-$ (128 g L^{-1}), P-PO$_4^{3-}$ (19 g L^{-1}), Fe (13,595 mg L^{-1}), K (3,438 mg L^{-1}), and Mn (1,199 mg L^{-1}) (Santos et al., 2016).

Briefly, the wastewater was diluted with water to 23, 20, and 18 % (v/v) for Araxá PR, Patos PR, and Bayóvar PR, respectively. These concentrations were based on the results of preliminary studies and almost met the requirements for PAPR fertilizers (Brasil, 2016).

Eight samples of phosphate fertilizers of distinct solubility were evaluated in a greenhouse test with corn (Barreto et al., 2018); we investigated the consistencies of different methods to extract P of fertilizers and their correlations with plant uptake and dry matter production.

Greenhouse trial

Phosphate fertilizer performance was evaluated in a greenhouse pot experiment with corn cultivation for 45 days. An Oxisol (*Latossolo Vermelho-Amarelo*, LVA), collected from the 0.00-0.30-m soil layer, was used as an example of a typical highly weathered tropical soil. Samples were air-dried and passed through a 4-mm sieve for experiments and a 2-mm sieve for chemical and physical analyses. The soil presented low available P (1.8 mg dm^{-3}, Mehlich-1 extractor), 68 % of clay (Claessen, 1997), a pH(H$_2$O) of 4.9 (at a ratio of 1:2.5 v/v), low exchangeable Ca^{2+} and Mg^{2+} (4.0 and 0.1 mmol$_c$ dm^{-3}, respectively, KCl 1.0 mol L^{-1} extractor), low soil organic C [24 g kg^{-1}, Walkley and Black (1934)], and low remaining P [12.7 mg L^{-1}, Alvarez V. et al. (2000)]. The mineral-containing clay-fractions of this soil are mainly kaolinite and gibbsite as well as minor contents of Fe oxides, such as goethite and hematite (data not shown).

Soil samples of 4 dm^3 were placed in pots inside plastic bags. Lime (CaCO$_3$ and MgCO$_3$ at a Ca:Mg ratio of 4:1) was applied to reach 70 % base saturation. The soil was wetted to 80 % field capacity and incubated for 15 days. Subsequently, the soil of each pot was air-dried and homogenized, and the phosphate fertilizers (powder form) were thoroughly mixed in before repotting. Pots were wetted as required to maintain nearly 70 % of field capacity throughout the experimental period.

The experiment was designed in a factorial scheme (8 × 2) + 1, using eight phosphate fertilizers (Araxá PR, Patos PR, Bayóvar PR, their PAPR forms, single superphosphate, and triple superphosphate) at two P doses (300 and 600 mg dm^{-3}) and a control treatment without P application. The experiment was carried out in a completely randomized design with four replications.

Six seeds of corn (DKB 390 commercial variety) were sown in each pot at a depth of 0.02 m; at five days after seedlings emergence, they were thinned to obtain the three most uniform per pot. Solutions of N, K, and S were added at 10, 20, and 30 days after planting, with total rates of 350 mg dm^{-3} N, 150 mg dm^{-3} K, and 60 mg dm^{-3} S. Micronutrients were also applied at seven days after sowing at rates of 4 mg dm^{-3} Zn, 0.8 mg dm^{-3} B,

1.4 mg dm^{-3} Cu, 1.6 mg dm^{-3} Fe, 3.7 mg dm^{-3} Mn, and mg 0.2 dm^{-3} Mo. At 45 days after planting, plants were harvested by cutting the stems at the soil surface. The shoots were oven-dried at 70 °C for 72 h, weighted, and milled for chemical analysis. About 300 cm^{3} of soil were collected from the center of each pot with the use of an auger. Soil samples were air-dried and homogenized prior to chemical analysis.

Chemical analysis

Total P, water-soluble P (water-P), 2 % citric acid P (CA-P), and neutral ammonium citrate soluble P + water (NAC-P) in the fertilizers were measured as described by the Brazilian Ministry of Agriculture, Livestock, and Food Supply, Normative Instruction No. 28 (Brasil, 2007). We also determined soluble P in ammonium citrate (pH 3) (AAC-P) and 2 % formic acid (FA-P), following Chien and Hammond (1978) and Braithwaite et al. (1989), respectively.

The NAC extractor was prepared dissolving 370 g of citric acid (CAS: 77-92-9; $C_6H_8O_7.H_2O$) in 1.5 L of distillated water and adding 345 mL of ammonium hydroxide (CAS: 1336-21-6; NH_4OH). Solutions of 1+7 v/v of ammonium hydroxide and 10 % w/v citric acid were used to adjust the solution to pH 7. For the preparation of the AAC extractor, 180 g of citric acid were diluted in 500 mL of distilled water. Subsequently, a 25 % v/v solution of ammonium hydroxide was used to adjust the pH to 3.0, and the solution volume was then brought to 950 mL with distilled water. To re-adjust the pH to 3.0, while the solution was brought to a volume of 1,000 mL, we used a 10 % w/v solution of citric acid or a 25 % v/v solution of ammonium hydroxide.

The plant tissues were digested in an open-vessel-digestion system, using a nitric-perchloric solution 3:1 (v/v) (Miller, 1998). The P concentration in the extracts was measured via the colorimetric method (Braga and Defelipo, 1974).

X-ray diffraction analysis

The X-ray diffraction (XRD) in the powder analysis of fertilizers before and after acid solubilization was carried out using an X'Pert Pro MPD Panalytical diffractometer in the 10 to 60° -2θ range with Co-Ka radiation (l = 1.789 Å) at a rate of 0.02 °2θ^{-1} and a counting time of 1 s, operated at 40 kV and 30 mA. The samples were prepared by packing soil samples into aluminum holders.

Data analysis

The Mitscherlich equation approach (Equation 2) was fitted to the data of dry matter production, according to equation 1.

$$\hat{y} = Amax(1 - e^{-bx}) \hspace{4cm} \text{Eq. 1}$$

in which: ŷ is the dry matter production (g pot^{-1}) by shoots (mg pot^{-1}), Amax is the maximum of dry matter production, and b is a parameter related to the shape of the curve. The variable x corresponds to the dose of the added P, quantified by different extractors.

The solvent afforded adjustment coefficient of determination (R^2) greater than 0.8 and the lowest estimate standard error of adjustment were considered the best predictors of agronomic efficiency. The dose required to achieve 90 % of maximum yield (Amax × 0.9) was considered the maximum agronomic efficiency (MAE).

Data were submitted to one-way analysis of variance, and the means were compared by Tukey's test (p = 0.05). Regression analyses, including the Mitscherlich approach, were performed using the R environment (R Development Core Team, 2016). The XRD data were analyzed using the diffraction database of powder of the American Mineralogist Crystal Structure Database (AMCSD).

RESULTS

Mineral composition of P sources

As expected, X-ray diffraction analysis provided evidence that apatite is the main mineral present in all phosphate rocks (PRs). We did not detect P-Fe or P-Al minerals in the PR samples. Data of peak intensities and their widths at half height confirmed that Bayóvar PR contains the poorest crystalline apatite (Figure 1).

The treatment promoted partial dissolution of apatite rather than mineral alterations or breakdown of apatite structure. In fact, some apatite peaks remained after acid treatment, but with minor intensity. The mineral gypsum was detected in all PAPR products. The mineral quartz, already present in Patos PR, was also detected after the acid treatment. We did not find evidence of the formation of new phosphate minerals in PAPR products.

Chemical composition of P sources

The acid treatment of PRs partitioned the total P concentrations in their respective PAPR products, decreasing them by about 30 % w/w (Table 1). There were different trends for the P extraction among extractors and PRs. In general, P extractability in water and NAC was most significantly changed by acid treatment. The means of all PRs revealed that water_P and NAC_P values were increased by 30- and 13.8-fold in the PAPR products, respectively. For other extractors, Bayóvar PR differed from other PRs. Indeed, the CA_P value was increased by 2-fold for PAPR Patos or Araxá PRs, while there was almost no increase in the treated Bayóvar PR.

Extractable P in AAC was increased by 3.6-, 4.6-, and 1.4-fold in the PAPR Araxá, PAPR Patos, and PAPR Bayóvar products. For the FA extractor, only for Araxá and Patos PRs, there was an expressive increase in extractable P.

Plant growth and P uptake

The P fertilizers performed differently in terms of corn dry matter production and P uptake (Table 2). Plants fertilized with SSP or TSP had higher shoot dry matter yields and P uptake
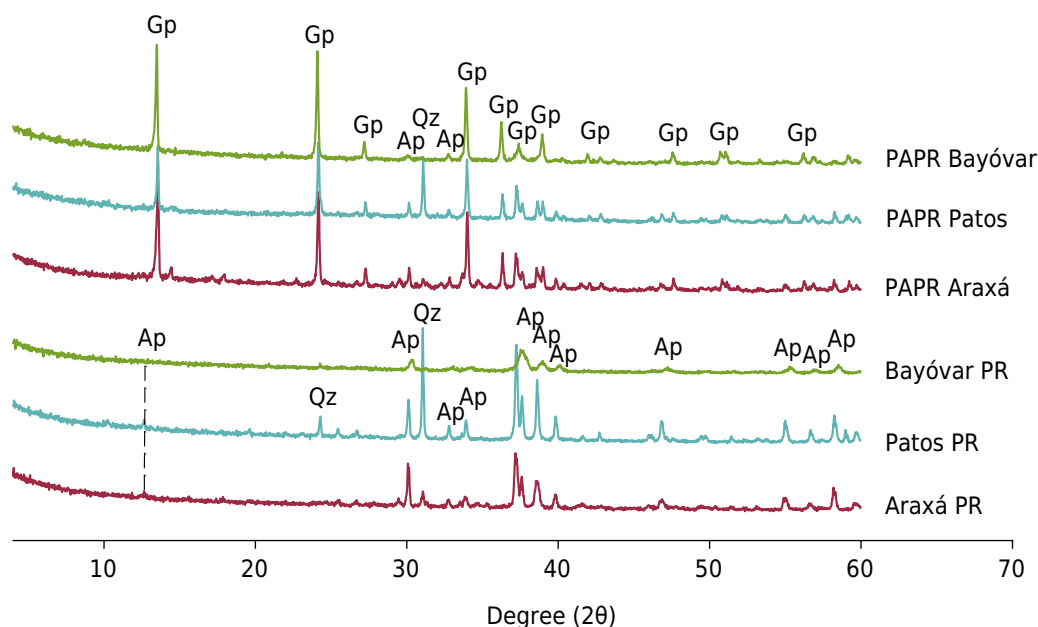

Figure 1. X-ray diffraction patterns from phosphate rocks (Araxá PR, Patos PR, and Bayóvar PR) and their respective partially acidulated forms (PAPRs), using a wastewater diluted in water to 18, 20, and 25 % (v/v), respectively. Ap = apatite; Gp = gypsum; Qz = quartz. Data were collected using Co-$_{Ka1}$ radiation (1.789 Å).

values compared with plants from the other treatments (Table 2). On the other hand, Araxá PR and Patos PR had a lower agronomic performance, but were highly superior compared to their PAPR products. Corn dry matter production and P uptake increased by about 20 and 25-fold, respectively, when PAPR-Araxá and PAPR-Patos were used compared to their natural PRs. However, there were no statistical differences between Bayóvar PR and its PAPR in terms of agronomic performance (Table 2).

Table 1. Total P content and its soluble portion in water (water-P), neutral ammonium citrate pH 7 (NAC-P), 2 % citric acid (CA-P), acid ammonium citrate pH 3 (AAC-P), and 2 % formic acid (AF-P)

Fertilizer	Total P-P_2O_5 (w/w)	Water-P	NAC-P	CA-P	AAC-P	FA-P
		total P (w/w)				
		%				
Araxá PR	30	0.2	3.0	10.1	7.6	13.0
Patos PR	29	0.3	2.7	13.0	5.8	16.2
Bayóvar PR	29	1.2	3.1	43.0	28.0	49.3
PAPR Araxá	22	16.6	40.3	20.9	27.2	28.1
PAPR Patos	23	18.2	41.6	25.6	26.8	37.0
PAPR Bayóvar	22	16.3	40.0	33.9	38.3	44.1
SSP	20	80.0	90.0	79.7	99.2	78.9
TSP	43	86.0	92.6	84.1	88.8	83.7

PAPR = partially acidulated phosphate rock; SSP = single superphosphate; TSP = triple superphosphate. Data were obtained from four replications. Total P, water-soluble P (water-P), 2 % citric acid P (CA-P), and neutral ammonium citrate soluble P + water (NAC-P) in the fertilizers were measured as described by the Brazilian Ministry of Agriculture, Livestock, and Food Supply, Normative Instruction No. 28 (Brasil, 2007). Soluble P in ammonium citrate, pH 3 (AAC-P) and 2 % formic acid (FA-P), were measured following Chien and Hammond (1978) and Braithwaite et al. (1989), respectively. Total P-P_2O_5, water-P, and NAC-P data, except for SSP fertilizers, were compiled from Barreto et al. (2018).

Table 2. Effects of P fertilizers of different solubilities and P doses on dry matter production and P uptake by corn

P dose	DMP	P uptake
	g pot^{-1}	mg pot^{-1}
300 mg dm^{-3}		
Araxá PR	1.6 a	0.9 a
Patos PR	1.4 a	0.7 a
Bayóvar PR	32.7 b	28.1 b
PAPR Araxá	25.9 b	19.0 b
PAPR Patos	26.9 b	20.2 b
PAPR Bayóvar	28.1 b	20.1 b
TSP	55.6 c	58.8 c
SSP	56.1 c	61.5 c
600 mg dm^{-3}		
Araxá PR	2.4 a	1.8 a
Patos PR	1.6 a	0.8 a
Bayóvar PR	45.1 b	48.8 b
PAPR Araxá	44.9 b	37.1 b
PAPR Patos	41.9 b	36.9 b
PAPR Bayóvar	50.8 bc	46.2 b
TSP	61.1 d	111.1 c
SSP	57.9 cd	113.2 c

DMP = dry matter production; P uptake in the control treatment (no P applied) were 1.1 ± 0.1 g pot^{-1} and 0.6 ± 0.1 g pot^{-1}, respectively. PAPR = partially acidulated phosphate rock; SSP = single superphosphate; TSP = triple superphosphate. Data were obtained from four replications.

Phosphorus extractors

The Mitscherlich equation approach revealed significant predictions (p≤0.01) for all extractors and P sources in terms of corn dry matter production (Figure 2). However, the performances of the extractors differed. The statistical parameters R^2 (determination coefficient) and SEE (standard error of estimation) indicated that the AAC extractor was the most predictive one, followed by FA, CA, water, and NAC. Comparison between the estimation of maximum dry matter production (Amax), provided by the Mitscherlich
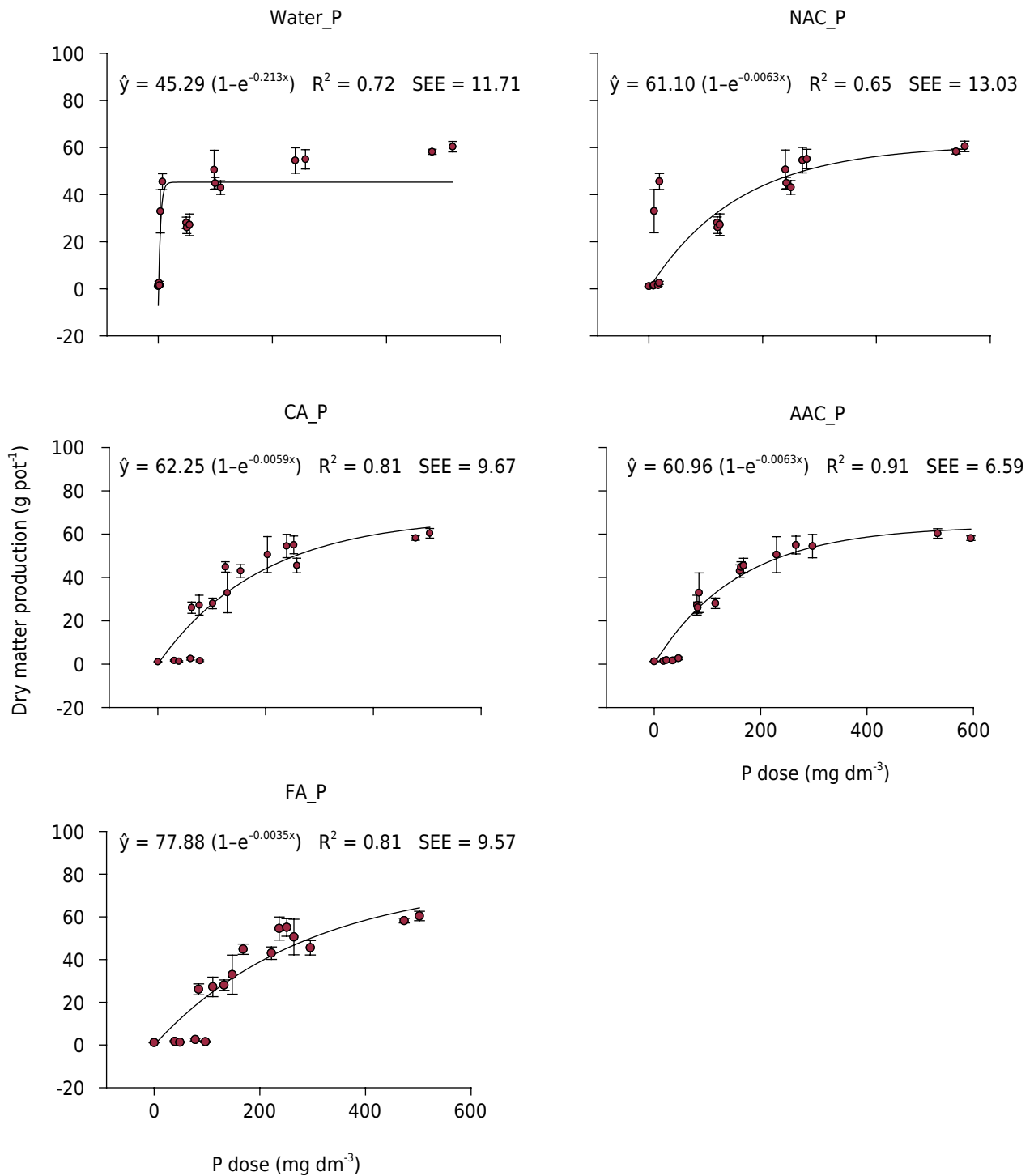
Water_P

$\hat{y} = 45.29\,(1-e^{-0.213x})$ $R^2 = 0.72$ SEE = 11.71

NAC_P

$\hat{y} = 61.10\,(1-e^{-0.0063x})$ $R^2 = 0.65$ SEE = 13.03

CA_P

$\hat{y} = 62.25\,(1-e^{-0.0059x})$ $R^2 = 0.81$ SEE = 9.67

AAC_P

$\hat{y} = 60.96\,(1-e^{-0.0063x})$ $R^2 = 0.91$ SEE = 6.59

FA_P

$\hat{y} = 77.88\,(1-e^{-0.0035x})$ $R^2 = 0.81$ SEE = 9.57

Dry matter production (g pot^{-1})

P dose (mg dm^{-3})

Figure 2. Mitscherlich function fitted to shoot dry matter production of corn depending on doses of soluble P in water (Water_P), neutral ammonium citrate (NAC_P), citric acid (CA_P), acid ammonium citrate (AAC_P), and formic acid (FA_P). Mitscherlich equation model: $\hat{y} = Amax(1 - e^{-bx})$, in which *Amax* is the maximum dry matter production and *b* is a parameter related to the shape of the curve. The variable *x* is the added P dose (mg dm^{-3}). SEE = standard error of estimation of the model. * All adjustments were significant at p<0.01.
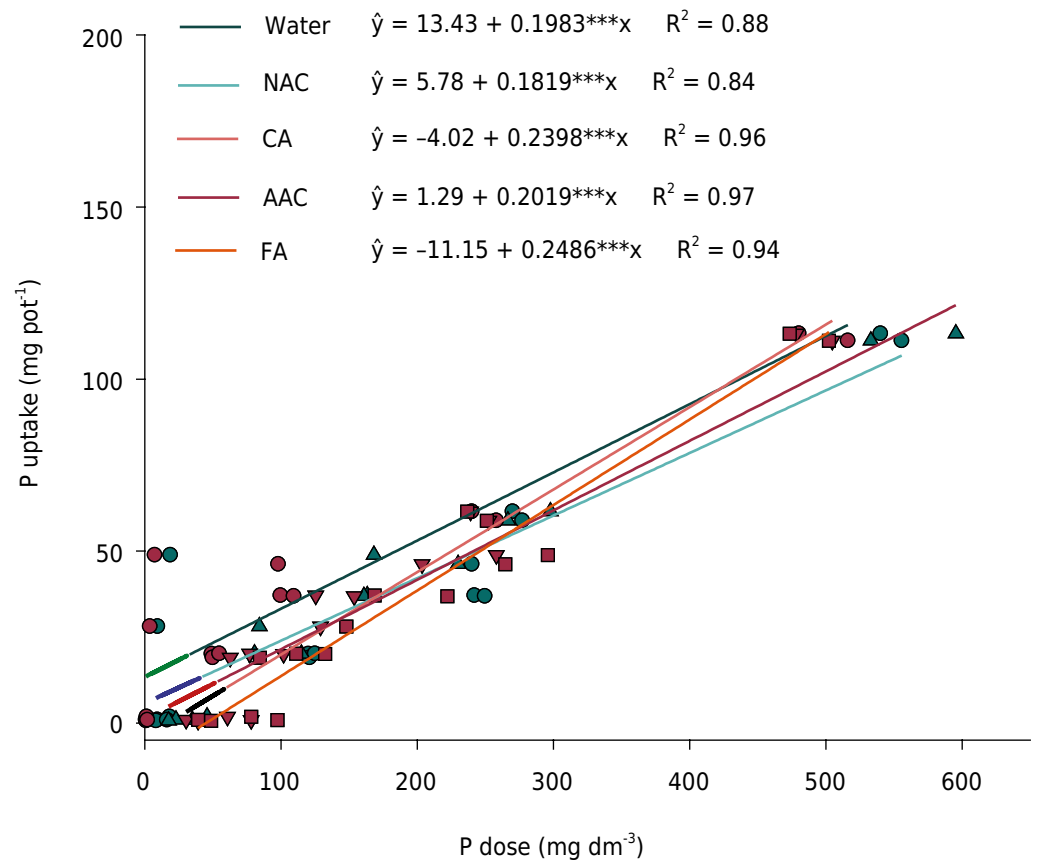
Figure 3. Phosphorus accumulation by corn as a function of P doses and P extractors (water; NAC, neutral ammonium citrate; CA, citric acid; AAC, acid ammonium citrate pH 3; FA, 2 % formic acid).

approach, and the observed data indicated that the extractors NAC, AAC, and CA were most predictive.

With increasing P doses, for all P fertilizers and extractors, we observed a linear positive P accumulation in corn (Figure 2), with a high statistical significance ($p \leq 0.01$). In addition, the R^2 values of the models also revealed that the extractors AAC, CA, and AF promoted the best adjustments, followed by water and NAC.

Relating the soluble P fraction for each extractor within the P sources (Table 1) to dry matter production or P uptake by corn (Table 2), we observed that the performance of the extractors depended on the P source characteristics. As expected, water and NAC extraction were predictive in terms of plant P availability when the P sources were acidified, such as PAPR, SSP, and TSP fertilizers, while CA was a less suitable indicator. Both FA and CA overestimated the fertilizer values for Araxá PR and Patos PR, but adequately predicted that of Bayóvar PR. Acid ammonium citrate was the most balanced extractor to predict plant P availability for all fertilizers. For instance, P analysis using the extractor AAC showed less (non-reactive PRs), medium (Bayóvar PR and PAPRs), and high (SSP and TSP) available P values, comparable to plant uptake (Table 2 and Figure 3).

DISCUSSION

There are several methods to extract P from fertilizers (Chien et al., 1990; Brasil, 2016), and ideally, they provide a first approach of P availability assessment in fertilizers, thereby helping to select the most suitable source for each crop system. Furthermore, extractable P values are indicators of the standardization and quality of P-fertilizers

and used for fertilizer regulations. Our study shows that the extractor acid ammonium citrate best predicted the agronomic effectiveness of P fertilizers of varying solubility. This is especially important considering that many new fertilizers contain P forms of different solubilities and reactivities (e.g., NPK mixtures composed of concentrate PRs and superphosphates), and there are no defined official methods for these fertilizers. Alternatively, multiple sequential extractions can be adopted (Chien et al., 2011), but such an approach is relatively time- and cost-consuming. While formic acid or citric acid are the extractors most used for PRs, neutral ammonium citrate solution is the preferred extractor for soluble P fertilizers globally and in Brazil (Binh and Zapata, 2002; Chien et al., 2011; Brasil, 2016).

For P extractability in all used extractors, the acid treatment of Araxá and Patos PRs showed to be effective in increasing the fertilizer quality of their end products (PAPR), especially for water-P, CNA-P, and CA-P (Mattiello et al., 2016; Santos et al., 2016; Barreto et al., 2018), but also for FA_P and AAC_P. This increase in the solubility of PAPR products was due to the transformation of apatite minerals into new P species, supposedly non-crystalline iron and calcium phosphate as well as monocalcium phosphate and dicalcium phosphate, as reported by Santos et al. (2016). In addition, the combination of XRD and P extractability data suggests that all PRs were partially solubilized by acid treatment. The detection of gypsum ($CaSO_4 . 2H_2O$) in the XRD spectra, as a new mineral in PAPR products, followed by the decrease in the intensity of the main reflection peaks of the apatite minerals, reveals that sulfate from sulfuric acid, present in the waste, reacted with Ca from PRs (e.g., $2\ Ca_5(PO_4)_3\ OH + 7\ H_2SO_4 \rightarrow 3\ Ca\ (H_2PO_4)_2 + 7\ CaSO_4 + 2H_2O$), reinforcing previous studies developed by Mattiello et al. (2016) and Santos et al. (2016). The detection of remaining apatite peaks in all PAPR products indicates that the solubilization of the apatite minerals was not complete.

Despite increasing the P extractability for Bayóvar PR after acidification, especially for water_P and NAC_P, the agronomic performances of these P sources (Bayóvar PR and PAPR-Bayóvar) were equivalent. Based on this trend, we reinforce here that for natural phosphates, water and NAC are not suitable extractors to predict P plant availability. For natural phosphates containing carbonates, such as those from sedimentary ores, the prediction capacity of the extractor NAC may be increased when it is used in a second extraction, because carbonates are more soluble than apatite in neutral ammonium citrate solution, decreasing apatite solubilization in the first extraction (Chien and Hammond 1978; Chien et al., 2010).

The lower crystallinity of apatite most likely increases the agronomic performance of the PRs. In this way, despite the lower P extractability for Bayóvar PR compared to PAPR fertilizers, it contains the poorly crystalline apatite (Santos et al., 2016) and promotes equivalent dry matter production or P uptake in corn (Barreto et al., 2018). Moreover, when the performance of Bayóvar PR (poorly crystalline apatite), which contains about 46 % of the total P soluble in 2 % citric or formic acid, was compared with that of Brazilian phosphates (highly crystalline apatite), which showed medium extractable P values with the same extractors (~13 % of the total P), its performance was considerably higher. This leads us to infer that the reactive PRs are predictive for both 2 % citric acid and 2 % formic acid, but not for highly crystalline apatite. As required by the Brazilian legislation for non-reactive and reactive PRs, at least 15 and 30 %, respectively, of their total P must be soluble in 2 % citric acid (Brasil, 2016). The solubility of igneous is lower than that of sedimentary PRs because their geometric surface determines the rate of dissolution (Gholizadeh et al., 2009). For crystalline structures, which are typically found in igneous PRs, there is basically no available internal surface for dissolution reactions, unlike for sedimentary PRs. These differences in the physical properties of PRs due to their geologic origins may affect both the extractability of the P forms and, consequently, agronomic effectiveness, as demonstrated in this work.

Brazilian PRs, directly applied, are relatively unsuitable in terms of supplying plants with P; they are therefore used in the production of fully acidulated fertilizers, especially SSP. However, due to the concentration of impurities, including Mg, Fe-Al, and Si phases, obtaining the minimum content of soluble P in NAC and water, as required by the current legislation, is challenging. This forces the industry to mix phosphorus sources in order to reach the target soluble content of P or, alternatively, to obtain partially acidulated fertilizers, which are less water-soluble. Thus, a universal chemical extractant, such as AAC, may provide more reliable information on available P contents from phosphate fertilizers.

Soluble P sources (SSP and TSP) were more effective in terms of dry matter production or P uptake compared to other sources for both used doses (300 and 600 mg dm^{-3}). However, the differences among these P sources significantly decreased with increasing P doses, revealing that there is a trend of converging over increasing P doses. This behavior indicates the need of key extractors to estimate P fertilizer doses according to their P extractabilities. Studies on the effects of P doses on plant yields, comparing P sources of different solubility, will be essential for this recommendation approach.

With increasing P doses for all extractors, we observed linear increases in P accumulation, with a high statistical significance (0.1 %) and R^2 (≥0.88); however, the statistical approach considering linear regression models for P accumulation is not suitable to select predictive P extractors. The Mitscherlich fitting for dry matter production as a function of P dose ranked AAC as the best extractor, followed by CA and FA. Chien and Hammond (1978) found good correlations between the amounts of P extracted by AAC and FA and plant growth, even for P fertilizers containing high concentrations of impurities.

In general, CA and FA performed satisfactorily in terms of correlations with plant growth or P uptake, but they extracted less than 85 % of the total P from soluble P sources and recovered high P contents from the P sources with low reactivity (Araxá PR and Patos PR). As reported by Binh and Zapata (2002), these extractors usually recover more P from PRs because of their high acidity (pH ~ 2.0). For Rajan and Watkinson (1992), FA was the best P extractor compared to CA and NAC in terms of predicting the agronomic effectiveness of PRs, regardless of their particle size, while CA, which is used in Brazil and New Zealand, showed to be a poorer indicator of the reactivity of the PRs. In addition, Mackay et al. (1984) reported that for Fe or Al phosphate, FA might underestimate the agronomic effectiveness. For fully acidulated P fertilizers, such as TSP and SSP, the values of soluble P in water and in NAC can be related to agronomic effectiveness. The water-insoluble, but citrate-soluble P forms in these P fertilizers, such as amorphous Fe- and Al-phosphates, do have agronomic value as fertilizers (Chien et al., 2011). The Brazilian legislation recommends these extractors for fully and partially acidulated P fertilizers, ammonium phosphates, and thermophosphates (Brasil, 2016).

Our research represents a first approach towards using AAC as a P extractor for fertilizers of varied compositions and reactivities. In our experiments, AAC was a highly effective predictor of agronomic effectiveness of the different phosphorus sources.

CONCLUSIONS

Contrasting the biological response of corn in terms of dry matter production and P uptake as well as the amount of supplied P as water-P, NAC-P, AAC-P, and FA-P, the method using ammonium citrate (pH 3) showed to be predictive for short-term P availability from phosphate fertilizers varying in solubility, including natural phosphates of different origins and partially or fully acidulated fertilizers. Therefore, our research represents an approach towards using AAC as a broad P extractor for mineral fertilizers.

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