



Research article

Agronomic efficiency of phosphate fertilizers produced by the re-use of a metallurgical acid residue



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ABSTRACT

The production of fertilizers with industrial wastes reduces the environmental impacts of waste disposal and improves environmental sustainability by generating added-value products. Our objective with this study was to evaluate the agronomic performance and potential soil/plant contamination with heavy metals of alternative phosphate (P) fertilizers, obtained from the acidulation of phosphate rocks (PR) by a metallurgical acidic waste. Seven P fertilizers were evaluated: three PR (Araxá, Patos, and Bayóvar), their respective acidulated products (PAPR), and triple superphosphate fertilizer (TSP). A greenhouse trial was carried out to test the agronomic performances of fertilizers in a sequentially cultivated maize-soybean-white oat. The reaction of PR with acid waste was effective to increase their solubility and improve plant yield and P uptake compared to their natural PR. There was a cumulative recovery by plants of 1.4 and 8.1% of added P via PR and PAPR, respectively. No increase in heavy metal (Cd, Pb, Cr, and Ni) availability in soil or accumulation in shoots was observed, indicating that the PAPR were environmentally safe. The usage of acid waste to produce P fertilizers therefore represents a strategic way to employ marginal products for the production of fertilizers.

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1. Introduction

Phosphorus is one of the most limiting nutrients for plant growth in tropical soils, which must be fertilized regularly to sustain profitable crop yields. Brazil, for instance, like many other countries, is not self-sufficient on phosphate fertilizer production; in 2014, it imported more than 50% of the total P fertilizer marketed in the country (DNPM, 2015).

To meet this demand, phosphate rocks (PR) are the main P sources for fertilizer production. Phosphate rocks are composed of tricalcium phosphates, generically known as apatite minerals, which are ineffective as P fertilizer when employed *in natura*, mainly for short-cycle crops, due to their low reactivity (Friesen et al., 1987; Braga et al., 1991; Oliveira et al., 2008). Brazil's PR deposits are marginalized and underused because they are essentially low-reactivity apatite and composed of large amounts of

impurities, such as Fe-, Al-, and Si- minerals. These impurities decrease final fertilizer quality by decreasing its water solubility (Hammond et al., 1989; Prochnow et al., 2003a), often leading to a fertilizer that does not meet the requirements of the Brazilian market.

To produce high-grade P fertilizers, pure mineral acids, such as sulfuric and phosphoric acids, are used, aiming to transform apatites [$\text{Ca}_5(\text{PO}_4)_3(\text{F,OH,Cl})$] into a soluble P phase monocalcium phosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2$. Thereby, these acids represent an important portion of the production costs of soluble P fertilizers. On the other hand, the metallurgical industry of Ta and Nb produces an acidic waste with 5.8 mol L^{-1} of acidity, high S contents (Mattiello et al., 2016), and a pH of around 0 (Santos et al., 2016). Using such source of acid to solubilize Brazil's PR has a strong environmental and economic appeal. Not only that companies spend large sums on the disposal of this acidic residue, but also because of the environmental problems it might cause (Chien et al., 2011). Also, this new process represents a technological innovation in the production of P fertilizers with Brazilian PR, which has been shown in a recent publication from our research group (Mattiello et al., 2016;

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Santos et al., 2016). Therefore, in this work, we focused on the production and agronomic evaluation of P fertilizers obtained from the reaction of PR and a metallurgical acid waste.

2. Material and methods

2.1. Phosphorus fertilizers

We used phosphate rocks (PR) with different reactivities in this study. Araxá and Patos PR were obtained from igneous and sedimentary medium-grade metamorphic deposits, respectively, located in the state of Minas Gerais, Brazil. Bayóvar PR was obtained from a sedimentary deposit in the Sechura Desert in Peru.

A concentrated acidic waste (AW), obtained from a Ta and Nb metallurgical industry, was used as an alternative substrate to solubilize these PR, following the previous work by Mattiello et al. (2016). Briefly, the acidic waste ($\text{H}_2\text{SO}_4\text{--HCl--HF}$) was diluted with water to 23, 20, and 18% (v v⁻¹) and mixed with the Araxá, Patos, and Bayóvar PR, respectively. These concentrations lead to the highest solubilization of each PR, as defined earlier (Mattiello et al., 2016). The mixtures were placed in reactors with a 1:3 PR: acid solution ratio (w/v) and stirred at 80 oscillations for 1 h. Thus, the material was oven-dried at 65 °C for 24 h and powdered (<149 μm) for chemical analysis. The end products obtained nearly met the requirements for partially acidulated phosphate rock (PAPR), according to the Brazilian legislation (20% w w⁻¹ of total P, 45% soluble in neutral ammonium citrate and 25% soluble in water) (BRASIL, 2007). Triple superphosphate (TSP) was used as the reference of the soluble P source for comparison.

2.2. Sequential cropping in greenhouse experiments

The performances of the P fertilizers were evaluated in a greenhouse pot experiment with a sequential cultivation of maize, soybean, and white oat. An Oxisol sample collected from the 0–30 cm layer was used to represent a typical highly weathered tropical soil with high P sorption capacity. 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), high P fixation capacity (12.7 mg L⁻¹ of remaining-P), 68% of clay, pH in water of 4.9, low exchangeable Ca²⁺ and Mg²⁺ (4.0 and 0.1 mmol_c dm⁻³, KCl 1.0 mol L⁻¹ extractor), and soil organic C of 24 g kg⁻¹ (Walkley and Black, 1934). The clay mineralogical composition of this soil is mainly kaolinite and gibbsite, with low contents of iron oxides (goethite and hematite; data not shown).

Samples of 4 dm³ of soil were placed in pots inside plastic bags. Lime (CaCO₃ and MgCO₃, at a Ca: Mg ratio of 4:1) was applied in order to reach 70% of base saturation and the soil was subsequently wetted to 80% of its field capacity and incubated for 15 d. After this period, the soil of each pot was air-dried and homogenized and powdered P fertilizers were thoroughly mixed with the soil before reporting. After planting, soils were wetted as required to maintain a moisture level of 70% of field capacity during the experimental period.

The experiment was composed of eight treatments, of which seven contained P fertilizers: natural PR (Araxá, Patos and Bayóvar), partially acidulated PR with acid waste – PAPR (PAPR-Araxá, PAPR-Patos, and PAPR-Bayóvar), and TSP; plus a control treatment without P application. The trial was carried out in a completely randomized design with four replications. Sources of P were evaluated in a sequential cultivation of maize, soybean, and white oat (cultivated for three cycles).

Six seeds of maize (DKB 390 commercial variety) were sown in each pot at a depth of 2 cm. After five days, seedlings were thinned

to the three most uniform ones in each pot. Solutions of NKS were added at 10, 20, and 30 d after planting, giving total rates of 350 mg dm⁻³ N, 150 mg dm⁻³ K, and 60 mg dm⁻³ S. Micronutrients were also applied 7 d after sowing at rates of 4 mg Zn dm⁻³, 0.8 mg B dm⁻³, 1.4 mg Cu dm⁻³, 1.6 mg Fe dm⁻³, 3.7 mg Mn dm⁻³, and 0.2 mg Mo dm⁻³. At 45 d after planting, plants were harvested by cutting the stems at the soil surface. The shoot was oven-dried at 70 °C for 72 h (constant weight), weighed, and milled for chemical analysis. Before seeding the soybean, 300 cm⁻³ of soil were sampled from the center of each pot using an appropriate auger. Soil samples were air-dried and homogenized before chemical analysis.

In sequence, nine seeds of soybean (variety UFV-16) were sown into undisturbed soil pots at a depth of 1 cm; after seedling emergence (10 d), the three best and most homogeneous seedlings were left in each pot. Seeds were inoculated with commercial *Bradyrhizobium* in order to fix and provide N to the soybean. Macronutrients (K and S) were added 15 and 30 d after planting, giving a total of 200 mg K dm⁻³ and 60 mg S dm⁻³. Phosphorus was not applied, requiring the soybean to use the residual P for its nutrition. Pots were wetted daily by weight with distilled water to maintain the water content at 80% of field capacity. After 55 d, the shoots were harvested by cutting the stems at the soil surface. The plant material was oven-dried at 70 °C for 72 h (constant weight), weighed and milled for chemical analysis, and the soil was collected as described above.

Lastly, twenty seeds of white-oat (IPR 126 cultivar) were sown in undisturbed soil pots at a depth of 2 cm and 10 d after sowing, each pot was thinned to 11 plants. Nutrients (NKS) were applied to provide a total of 50 mg N dm⁻³, 40 mg K dm⁻³, and 10 mg S dm⁻³, respectively. As for soybean cultivation, P was not re-applied. White oat was cultivated for three cycles, cutting the shoots every 30 d (total of 90 d of cultivation). The material was oven-dried at 70 °C for 72 h, weighed, and milled for chemical analysis. The soil was collected and prepared as described above.

2.3. Chemical analysis

Total P, water-soluble P (P–H₂O), and neutral ammonium citrate soluble P + water (P_{NAC} + H₂O) in the fertilizers were determined as described by the Brazilian Ministry of Agriculture, Livestock and Food Supply Normative Instruction #28 (BRASIL, 2007). The contents of Cr, Ni, Pb, and Cd were determined in the extract for total P analysis. The results of chemical analysis of P fertilizers are presented in Table 1.

Plant samples were mineralized in an open-vessel-digestion system using a nitric-perchloric solution (3:1 v v⁻¹) (Miller, 1998).

Table 1

Total P, water-soluble P (P_{water}), P soluble in neutral ammonium citrate, soluble P + water (P_{NAC}), and heavy metal contents of phosphate fertilizer.

Fertilizer	P ₂ O ₅ Total g kg ⁻¹	P _{water}	P _{CNA}	Cr	Ni	Pb	Cd
			% (w/w) ^a		mg kg ⁻¹		
Araxá PR	300	0.2	3.0	37	69	52	1.1
Patos PR	290	0.3	2.7	16	5.5	29	0.1
Bayóvar PR	290	1.2	3.1	129	3.0	30	26
PAPR-Araxá	220	17	40	49	84	75	1.0
PAPR-Patos	230	18	42	35	46	29	0.5
PAPR- Bayóvar	220	16	40	143	30	37	18
Triple superphosphate	430	86	93	14	20	6.5	5.6

^a Percentage of total P (w/w). PAPR-Araxá, PAPR-Patos, and PAPR- Bayóvar are end-products from acidulation of Araxá, Patos, and Bayóvar phosphate rocks, respectively.

Soil samples were analyzed for Cr, Ni, Cd, and Pb extractable by Mehlich-3 solution.

Phosphorus concentration in all extracts (fertilizers, plants, and Mehlich-3 extracts) was measured using the colorimetric method, while concentrations of Cr, Ni, Pb, and Cd, except for white oat, were determined by atomic absorption spectroscopy (Agilent, Series AA Model 240 FS).

2.4. Data and statistical analysis

The relative agronomic effectiveness (RAE) of each P source was calculated using Equation (1):

$$\text{RAE (\%)} = [(P_i - P_0) / (P_{tsp} - P_0)] \times 100, \quad (1)$$

where P_i is shoot dry matter yield in treatments with added P fertilizers (g pot^{-1}); P_{tsp} is the shoot dry matter yield obtained by triple superphosphate (reference fertilizer, RAE = 100%) treatment; P_0 is the shoot dry matter yield without addition of P fertilizer (control).

The P uptake was calculated according to Equation (2):

$$\text{P uptake (mg pot}^{-1}\text{)} = \text{P in plant tissue (mg g}^{-1}\text{)} \times \text{dry matter yield (g pot}^{-1}\text{)} \quad (2)$$

The recovery rate of P (Rec P) for each treatment was calculated according to Equation (3):

$$\text{Rec P (\%)} = [(\text{P uptake in shoots in the treatments} - \text{P uptake in shoots in the control}) / \text{total P initially applied via fertilizer}] \times 100(3)$$

The parameters RAE, P uptake, Rec P, and concentration of heavy metals in plant tissue were submitted to one-way analysis of variance; the means were compared by Tukey's test ($p < 0.05$).

3. Results

3.1. Crop yield and P uptake

For maize (the first cultivation), supplying P as TSP resulted in higher shoot dry matter yield and P uptake compared with other P fertilizers (Table 2). Significant increases in dry matter yield and P uptake were observed when acidulated PR were applied compared to non-acidulated PR, except Bayóvar PR, for which acidification did not play a role. There was no significant effect of Araxá and Patos PRs application on shoot dry matter yield and P uptake by maize (Table 2).

Shoot dry matter yield of the soybean (second crop) was higher for acidified Araxá PR than for non-acidified PRs, but significantly lower than for the other acidified PR (PAPR) and TSP (Table 2). Araxá and Patos PR did not increase the dry matter production and P uptake by soybean as compared to the control. The P shoot content of soybean was similar between TSP and Bayóvar (both natural and acidified), which was higher than for the other acidified fertilizers.

For white oat cultivation, there was no significant difference in shoot dry matter yield when TSP, PAPR, and Bayóvar PR were used as fertilizers (Table 2). White oat total dry matter production, as expected, showed similar responses to P fertilizers as for maize and soybean. The TSP led to the highest dry matter production, followed by Bayóvar PR, PAPR, and non-treated Araxá and Patos PR.

Comparing the effects of the P fertilizers on P accumulation by maize, soybean, and white oat crops, their performances were similar to those demonstrated by the dry matter production. The Bayóvar PR was more effective than Araxá or Patos PR, regardless of

Table 2

Shoot dry matter production, shoot P uptake, and percentage of P recovery in shoots of a sequential crop cultivation (maize/soybean/white oat) as affected by P fertilizers.

Fertilizer	Maize	Soybean	White oat	Total
Shoot dry matter (g/pot)				
Control	1.09 a	1.19 a	2.20 a	4.5 a
Araxá PR	1.66 a	2.42 a	17.76 b	21.8 b
Patos PR	1.28 a	1.42 a	8.79 ab	11.5 ab
Bayóvar PR	32.93 b	18.06 c	40.36 c	91.4 d
PAPR-Araxá	26.06 b	11.72 b	40.29 c	78.1 c
PAPR-Patos	27.21 b	18.82 c	36.52 c	82.6 cd
PAPR-Bayóvar	28.03 b	21.35 c	41.54 c	90.9 cd
Triple superphosphate	55.04 c	21.51 c	39.32 c	115.9 e
P uptake (mg/pot)				
Control	0.57 a	0.78 a	1.53 a	2.9 a
Araxá PR	0.94 a	2.65 a	22.27 a	25.9 a
Patos PR	0.67 a	1.18 a	10.37 a	12.2 a
Bayóvar PR	28.10 b	36.33 bc	70.75 b	135.2 c
PAPR-Araxá	19.04 b	18.83 ab	60.33 b	98.2 b
PAPR-Patos	20.18 b	27.90 b	54.61 b	102.7 bc
PAPR-Bayóvar	20.06 b	34.15 bc	70.62 b	124.8 bc
Triple superphosphate	58.81 c	47.06 c	66.50 b	172.4 d
P recovery (%)				
Araxá PR	0.03 a	0.16 a	1.73 a	1.92 a
Patos PR	0.01 a	0.03 a	0.74 a	0.78 a
Bayóvar PR	2.29 b	2.96 cde	5.77 bc	11.02 c
PAPR-Araxá	1.54 b	1.50 b	4.90 b	7.94 b
PAPR-Patos	1.63 b	2.26 bc	4.42 b	8.31 bc
PAPR-Bayóvar	1.62 b	2.78 bcd	5.76 bc	10.16 bc
Triple superphosphate	4.85 c	3.86 de	5.41 bc	14.12 d

Mean values appended by a different letter indicate significant differences within the column, as determined by Tukey's test ($p = 0.05$). PAPR Araxá, PAPR Patos, and PAPR Bayóvar are end-products from partial acidulation with acid waste of Araxá, Patos, and Bayóvar phosphate rocks, respectively.

the acidification. It was also as effective as PAPR in terms of shoot P content for all evaluated crops. Moreover, Bayóvar PR showed the same efficiency as TSP in the soybean and white oat crops (Table 2). Applying P as TSP resulted in higher shoot P contents compared to the other fertilizers for all three crops (Table 2). In contrast, when P was supplied as Araxá or Patos PR, P uptake by crops was similar to that in the control (without P application).

The addition of PAPR increased total dry matter yield and P uptake compared to the addition of natural PR (Table 2). These results are consistent with the increase of solubility, in terms of extractable P, when acid waste was used. Both P_{water} and $P_{\text{NAC+H}_2\text{O}}$ were considered to be low in non-reacted PR ($\leq 1.2 \text{ w w}^{-1}$), but were increased by up to 30- and 10-fold after acidification, respectively (Table 1). Compared to the soluble P source (TSP), the PAPR resulted in lower performances, but in white oat cultivation, there were no significant differences among these sources (Table 2).

3.2. Relative agronomic effectiveness (RAE) and P recovery

The RAE significantly increased for all three crops when PAPR-Araxá and PAPR-Patos were applied to the soil compared with their non-treated PR (Fig. 1). For maize, RAE increased from 1.1% in Araxá PR to 46% in PAPR-Araxá and from 0.36% in Patos PR to 48% in PAPR-Patos. For soybean, RAE increased from 6.1% in Araxá PR to 51.9% in PAPR-Araxá and from 1.1% in Patos PR to 86.8% in PAPR-Patos. For white oat, RAE increased from 43.7% in Araxá PR to 104.5% in PAPR-Araxá and from 18.1% in Patos PR to 94.4% in PAPR-Patos. The RAE of Bayóvar PR for all crops was higher than for Araxá and Patos PR and equivalent to PAPR or TSP, evidencing its natural high value as fertilizer (Figs. 1 and 2 SM).

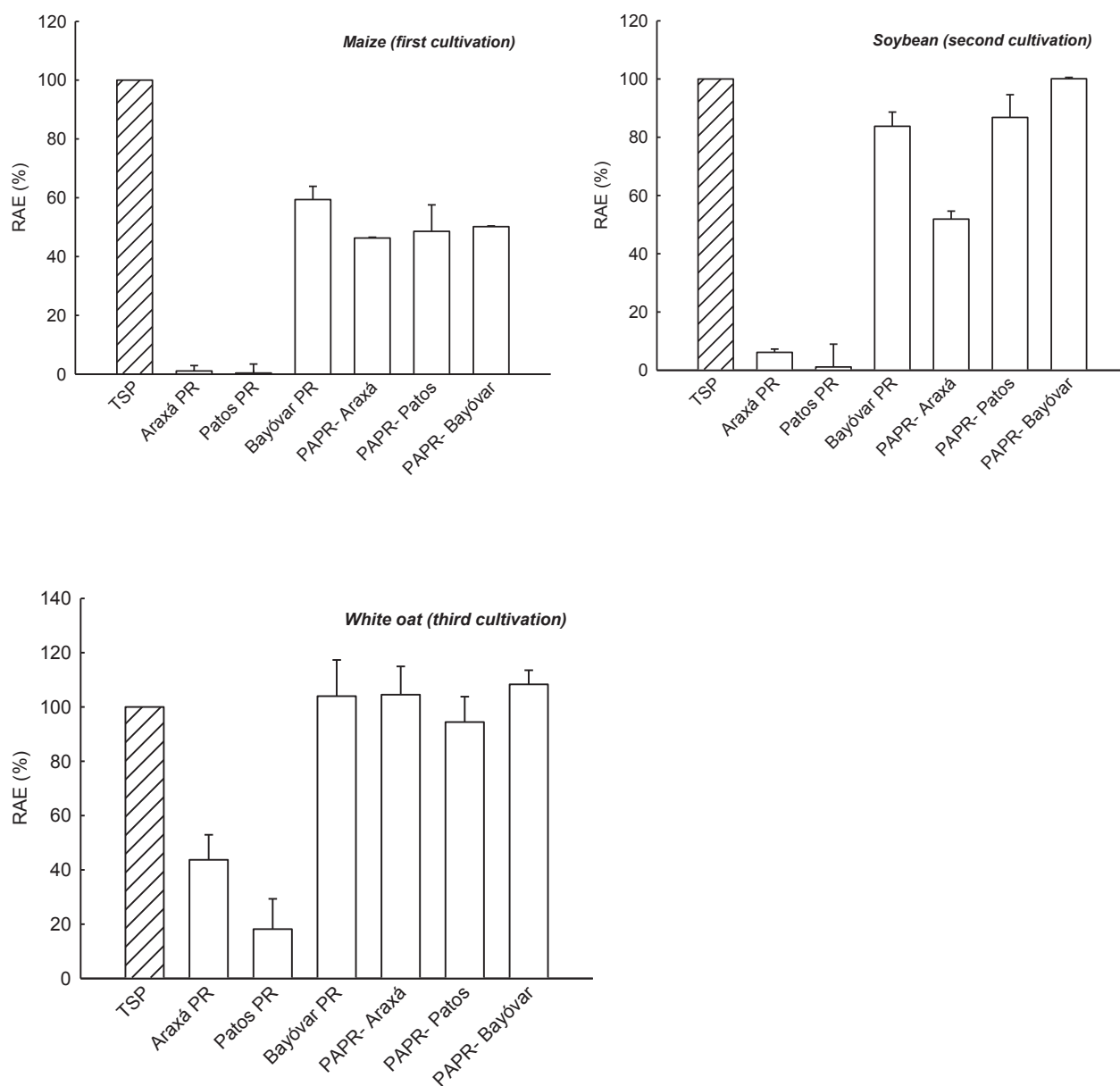


Fig. 1. Relative agronomic effectiveness (RAE) of phosphate fertilizers in a successive cultivation of maize-soybean-white oat. Means followed by the same letter do not differ statistically by Tukey's test at 5%. For the P reference fertilizer, the triple superphosphate (TSP), RAE = 100% (cross hatched bars). PAPR- Araxá, PAPR-Patos, and PAPR-Bayóvar are end-products from acidulation of Araxá, Patos, and Bayóvar phosphate rocks, respectively. Vertical bars (I) represent the standard error with four replications.

The PAPR-Araxá in soybean crop had a lower RAE (52%) compared to other PAPR and the TSP. On the other hand, the RAE values for PAPR-Bayóvar (100%), PAPR-Patos (86.8%), and Bayóvar PR (84%) were equal or close to the soluble P source (TSP, RAE = 100%).

In the third crop (white oat), similar RAE values for TSP, PAPR, and Bayóvar PR were observed (Fig. 1). The RAE values for Araxá, Patos, and Bayóvar PRs and for PAPR-Araxá, PAPR-Patos, and PAPR-Bayóvar were 44, 18, 104, 105, 94, and 108%, respectively.

Acidification of Brazilian PR (Araxá and Patos) using acid waste was effective to increase P recovery by plants, and no significant differences were observed between them in all crops (Table 2). On average, 1.6, 1.9, and 4.7% of added P were recovered in maize,

soybean, and white oat crops, respectively, resulting in a cumulative recovery of 8.1% over the three crops. Using such natural PRs, P recovered in maize, soybean, and white oat was only 0.02, 0.1, and 1.24% of added P, respectively, resulting in a cumulative recovery of 1.4% over the three crops. On the other hand, acidification of Bayóvar PR did not increase P recovery by plants, and the results were similar to PAPR and significantly lower than TSP.

For the TSP fertilizer, about 4.8, 3.8, and 5.4% of added fertilizer P was recovered in maize, soybean, and white oat, respectively (Table 2). Such results were significantly higher than for other P fertilizers, resulting in a cumulative recovery of 14.0% over the three crops (Table 2).

3.3. Concentrations of heavy metals in soil and plants

The concentrations of Cr, Ni, Cd, and Pb in soil, extracted by Mehlich-3 solution, were low for all treatments and below the detection limits of 0.20, 0.10, 0.18, and 0.24 mg dm⁻³ for Cr, Ni, Cd, and Pb, respectively. We only detected traces of Cr (0.35 mg dm⁻³) after the maize crop for the treatment corresponding to Bayóvar PR, which was lower than in the control treatment (0.56 mg dm⁻³). Accordingly, there was no significant effect of P application by all studied fertilizers on heavy metal concentrations in shoots of maize or soybean (Table 3).

4. Discussion

4.1. Agronomic performance of P fertilizers

The reaction of phosphate rocks with acid waste was effective based on the increasing extractable amount of P (P_{water} , P_{NAC}), strongly improving the value as P fertilizers of the acidulated PR. The soluble P fraction of fertilizers is closely related with dry matter yield and P uptake. Phosphate fertilizers produced through a chemical reaction between Bayóvar PR and a similar acid waste had P soluble amounts in NAC and in citric acid comparable to those of commercial phosphate fertilizers, which contain a monocalcium phosphate phase (Santos et al., 2016).

The increased solubility of P was a result of the conversion of apatite to more soluble phosphates. An increase of soluble P by reaction of PR with an acid waste is due to the conversion of apatite to amorphous iron(III) phosphate (AIP), amorphous Ca-phosphate, dicalcium phosphate (DCP), and monocalcium phosphate (MCP), with AIP being the main P species found as analyzed by P K-edge XANES (Santos et al., 2016). Since there is a remaining acidity from the reaction in the end product, we hypothesized that such acidity solubilizes the AIP in the soil, thus forming more soluble P forms such as MCP. In fact, PAPR had equivalent performances to STP, which is composed mainly of MCP.

Acid waste is an environmental liability that requires expensive processes for neutralization and disposal. On the other hand, the Patos and Araxá PR studied here, which occur in large amounts across the Brazilian territory, have low agronomic efficiencies as P fertilizers when applied *in natura* (non-treated). The usage of acid waste to produce P fertilizers therefore represents a strategic way to use marginal products for fertilizer production.

The best performance of Bayóvar PR, compared to non-treated PR or PAPR, suggests that physical and chemical features of this P source, such as its higher specific surface and higher isomorphous

substitution of CO₃²⁻ for PO₄³⁻ in the apatitic structure, resulted in higher P availability when compared with Araxá and Patos PR. Isomorphous substitution is the most important property that affects the agronomic performance of PR (Faria and Guardieiro, 2011). Although Bayóvar PR was less efficient than TSP as a P source for maize (as first cultivation crop), it could be considered as a direct source of P fertilizer, keeping its production costs low. Additionally, as a P fertilizer, Bayóvar PR has an effective residual effect on sequential cropping.

The strong soil P-buffering capacity of Brazilian oxisols more significantly decreased available P contents over time in the soluble sources than in PAPR and pristine PR. Regardless of the source, P recovery by crops was minimal (less than 15% of applied P). This buffering effect in tropical soils is commonly observed under field conditions because even in soils with phosphate fertilizer legacy, P fertilization is required to obtain high crop yields (Santos et al., 2008, 2011). Rodrigues et al. (2016) evaluated P availability in Brazilian soils of the cerrado cultivated with soybean-millet and cotton and found that even after 20 years of cultivation with high fertilization levels, the soils did not reach the critical value of P extractable by anion exchange resin (Raj, 1991), demonstrating the high P fixation capacity of these soils.

Partially acidulated Patos and Bayóvar PR in soybean crop showed RAE values similar to that of soluble fertilizer. The soil-plant interaction facilitates the acidification of the rhizosphere due to biological fixation of N₂, and the increased demand for Ca by soybeans can favor the dissolution of these fertilizers and, consequently, increase P uptake by plants, as reported previously (Aguilar and Diest, 1981; Illmer et al., 1995).

The lowest RAE value in soybean crop with PAPR Araxá suggests a less efficient solubilization treatment with the acid waste in this rock, likely due to high levels of impurities, mainly Fe minerals, which are usually found in high contents in this pristine PR (Beisiegel and Souza, 1986). For this PR, there was a reduced efficiency of acid solubilization (Prochnow et al., 2003a), which confirmed the need for a better quality of raw materials for the manufacturing of highly soluble P fertilizers (Prochnow et al., 2003b). The greater efficiency of white oat in the P uptake after the maize and soybean crops demonstrates the ability of this plant to acquire nutrients from lower liability forms (Hinsinger and Gilkes, 1996, Table 2). White oat, as well as black oat, are cover crops able to increase P cycling rates, thereby favoring subsequent crops, given the greater availability of P in the system from the crop residue (Vos and Van Der Putten, 2000; Crusciol et al., 2008).

Evaluating soybean growth, especially over the white oat harvesters in the treatment without P fertilization, lower P liability fractions could be responsible for adequate plant nutrition, based on dry matter production and P uptake. Rodrigues et al. (2016) highlighted the increase of moderately labile P fractions and organic P compounds over time with fertilizations, and these P fractions as responsible for plant nutrition.

The greater performance of TSP for maize was expected as this fertilizer is composed of monocalcium phosphate, a soluble P form readily available for plant uptake. However, as the performance of TSP was equivalent to that of PAPR and Bayóvar PR for soybean (second one) and white oat (third one) crops, we can assume that, even in soils with high P-fixing capacity, the residual effect of a soluble P source is comparable to those of less soluble P sources, which need more time to be solubilized in the soil. In addition, Araxá and Patos PRs showed low efficiency when applied *in natura*. However, their acidification using acid waste is an efficient and alternative way to produce P fertilizers.

Table 3
Trace elements in dry matter of the shoots of maize and soybean crops.

Fertilizer	Maize				Soybean			
	Cr	Ni	Cd	Pb	Cr	Ni	Cd	Pb
	mg kg ⁻¹							
Control	0.07	0.10	0.03	0.53	0.10	0.09	0.02	0.60
Araxá PR	0.08	0.11	0.03	0.46	0.08	0.10	0.03	0.68
Patos PR	0.06	0.11	0.03	0.54	0.09	0.10	0.03	0.68
Bayóvar PR	0.06	0.10	0.03	0.53	0.09	0.09	0.02	0.61
PAPR-Araxá	0.06	0.10	0.02	0.51	0.09	0.10	0.03	0.65
PAPR-Patos	0.05	0.09	0.03	0.49	0.09	0.12	0.03	0.71
PAPR-Bayóvar	0.06	0.10	0.03	0.48	0.09	0.11	0.03	0.74
Triple superphosphate	0.05	0.09	0.02	0.48	0.09	0.09	0.02	0.56

PAPR-Araxá, PAPR-Patos, and PAPR-Bayóvar are end-products from acidulation of Araxá, Patos, and Bayóvar phosphate rocks, respectively. Data were obtained from four replications.

4.2. P fertilizers and heavy metals

A concern with using acid mining wastes to produce fertilizers is the potential incorporation of heavy metals to the end product and, ultimately, to the soil. A comparison among concentrations of trace elements of the native PR and the respective acidified products revealed a slight enrichment for Cr (up to 2.2-fold for Patos PR) and Pb (up to 1.4-fold for Araxá PR). The greatest enrichment was observed for Ni in PAPR Bayóvar (10-fold) and PAPR Patos (8.4-fold), mainly because of the lowest native concentrations of these elements and the high Ni contents in acid waste. A chemical characterization of this waste showed concentrations of Ni, Cr, Pb, and Cd of 126, 59, 56, and 11 mg L⁻¹, respectively (Mattiello et al., 2016). In addition, for all P sources, including those acidulated, the concentrations of Cd, Pb, and Cr did not exceed the maximum allowable concentrations of 4, 20, and 40 mg kg⁻¹, respectively, per percentage (1% w w⁻¹) of P₂O₅ content, according to standards adopted in Brazil for phosphate fertilizers (BRASIL, 2007), which do not include a tolerable limit for Ni.

The difference between supplied amounts of trace elements by acidified PR and their respective PR, for the used P dose (300 mg dm⁻³), indicated additions of up to 0.14, 0.12, 0.11, and 0.001 mg dm⁻³ of Cr, Ni, Pb, and Cd, respectively. According to the background contents of these heavy metals in representative oxisols of Minas Gerais state, Brazil, of 197.3, 53.5, 1.4, and 0.4 mg kg⁻¹ of Cr, Ni, Pb and Cd, respectively (Caires, 2009), the inputs through the application of PAPR fertilizers would increase about 0.071, 0.22, 7.28, and 0.25% the contents of these metals in the soil, respectively. These amounts represent a negligible environmental risk. In fact, no P fertilizers increased the availability of these trace elements in soil (by Mehlich 3 test) or their concentrations in plant tissues (Table 3), even under greenhouse conditions, where the root system is confined and elemental uptake is increased compared to field conditions. Moreover, under field conditions, much lower P doses are applied to the soil as compared to the doses applied in this study. Even in Brazilian soils under long-term application of high doses of P fertilizers (containing Cd), the levels of Cd in the edible parts of potato cultivars were safe (Corguinha et al., 2012).

Cadmium is a toxic metal that occurs naturally in PRs deposits (Roberts, 2014). For igneous or metamorphic phosphate deposits, as those found in Brazil, Cd concentration tends to low compare to sedimentary deposits (Roberts, 2014; Santos et al., 2016), corroborating with our data, that demonstrated the Bayóvar PR as the most Cd rich PR compared to others. The Cd concentration in the Bayóvar PR was up to 260-fold higher than in Patos PR.

The single (SSP) or triple superphosphate (TSP), which are produced by reacting PR with sulfuric acid and phosphoric acid, respectively, contain all of the trace elements present in their phosphate rock concentrate. According to Van Kauwenbergh (2001), SSP fertilizers can contain from 2 to more than 40 mg kg⁻¹ and TSP can have from less than 10 to over 100 mg kg⁻¹ Cd. In our work, the concentration of Cd in commercial TSP was up to 11-fold higher than PAPR-Araxá or PAPR-Patos.

A joint evaluation of our data, including Mattiello et al. (2016) and Santos et al. (2016), has provided supporting evidences of the feasibility and beneficial re-use of acid waste from the metallurgical industry, with positive environmental impacts in terms of waste disposal and production costs of P fertilizers by replacement of pure acid for PR solubilization. In addition, the agronomic performances of the acidulated P fertilizers indicate that acidification is more required for Patos and Araxá PR (igneous PR source) as compared with Bayóvar PR (sedimentary PR source), which has an inherent high quality as P fertilizer.

5. Conclusions

This study demonstrates that acidifying non-reactive phosphate rocks such as Patos and Araxá PRs through the re-use of an acid industrial waste is an effective and safe way to increase agronomic performance. The end products from acidification of phosphate rocks have low concentrations of toxic metals, and no accumulation was observed in shoots of sequential maize-soybean-white oat crops.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jenvman.2017.11.075>.

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