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Characterization and agronomic efficiency of natural and recovered phosphates in tropical soil with corrected acidity

Jéssica Franciele Kaminski Ramos(1)*, Bruno José Rodrigues Alves(2), Jorge Makhlouta Alonso(3), Paulo César Teixeira(3) and Vinicius de Melo Benites(3)

(1) Universidade Federal Rural do Rio de Janeiro, Departamento de Solos, Programa de Pós-Graduação em Ciências do Solo, Seropédica, Rio de Janeiro, Brasil.
(2) Empresa Brasileira de Pesquisa Agropecuária, Embrapa Agrobiologia, Seropédica, Rio de Janeiro, Brasil.
(3) Empresa Brasileira de Pesquisa Agropecuária, Embrapa Solos, Rio de Janeiro, Rio de Janeiro, Brasil.

ABSTRACT: Demand for phosphate fertilizers in Brazil, combined with its reliance on external sources, highlights the need to explore alternative phosphorous (P) sources for limed cultivated soils. This study aimed to characterize and evaluate the agronomic performance of phosphates from various sources, including national sedimentary (Arraias, Bonito, and Pratápolis) and igneous deposits (Catalão and Registro) imported sedimentary sources (Algeria, Bayovar, and Morocco), and residue-recovered sources (Bonechar and effluent recovered phosphate – ERCP). Phosphates underwent mineralogical and chemical characterization, including P solubility in different extractant solutions. A greenhouse experiment was conducted using an Oxisol with pH corrected to 6.3 in a completely randomized design. The experiment tested P sources at a rate of 160 mg kg^{-1}, along with a treatment using triple superphosphate (TSP) as a reference source and a control without P addition. Two corn crops were grown for 45 days each, with measurements taken for P content and aboveground dry mass. Bonechar and ERCP exhibited high solubility in 2 % citric acid. Bonechar and sedimentary phosphates with solubility above 27 % in citric acid showed agronomic efficiency equivalent to TSP. In contrast, national phosphates subjected only to primary beneficiation processes displayed lower agronomic efficiency. The efficiency of low-water-soluble phosphates in soils with corrected pH is generally related to their solubility in citric acid, except for ERCP, which exhibited high solubility but low performance. This study highlights the potential of diverse phosphate sources to address P deficiency in Brazilian soils and emphasizes the importance of understanding their characteristics for effective fertilization strategies in agricultural soils.

Keywords: rock phosphate, corn, apatite, P solubility, P use efficiency.

*** Corresponding author:**
E-mail: j.kaminskiramos@gmail.com

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INTRODUCTION

Global demand for food continues to grow rapidly, driven by population increases and changes in consumption patterns, posing significant challenges to agricultural production (Valin et al., 2013). It is estimated that food production will need to increase by 70 % by 2050 to meet this demand (Lal, 2015; FAO, 2017). In this context, Brazil stands out as one of the world's largest producers and exporters of food, serving as a reference in tropical agriculture (Kucukvar et al., 2019).

Agricultural production in tropical soils faces the challenge of ensuring adequate phosphorus (P) availability, as these soils are naturally deficient in this essential element (Bernardi et al., 2002). In response, the widespread use of soluble phosphate fertilizers, such as superphosphates, has become a conventional practice to meet the P needs of crops (Bindraban et al., 2020). However, recent constraints on acquiring soluble fertilizers caused by internal economic crises or international conflicts have resulted in shortages and price increases. Consequently, alternative P sources, including phosphate rocks and animal-origin materials, have gained increasing attention as potential solutions (Lehr, 1980; Kaminski and Peruzzo, 1997).

Despite being one of the world's leading agricultural producers, Brazil faces significant limitations in its fertilizer production. According to ANDA (2023), the country imported 85 % of the fertilizers used in 2023. Phosphorus (P) importation is slightly lower than nitrogen (N) and potassium (K) but still substantial, with over 70 % of the P fertilizer used in 2020 coming from abroad (ANDA, 2023; Brasil, 2023). The National Fertilizer Plan 2050, published in 2023, emphasizes the need to increase domestic fertilizer production to ensure food security and support the agricultural sector, which is vital to the country's economy (Brasil, 2023). Additionally, the plan encourages the development of technologies to optimize fertilizer management and promotes the exploration of new manufacturing routes and raw materials for production (Brasil, 2023). Therefore, to reduce the country's dependence on foreign fertilizers, it is crucial to investigate the characteristics and optimal agricultural management practices for using Brazilian phosphates, as well as phosphorus sources derived from recycled or reused materials.

Brazil's agricultural lands are predominantly established on Oxisols and Ultisols, which correspond, respectively, to Latossolos and Argissolos in the Brazilian Soil Classification System (Santos et al., 2018). These soils exhibit high degrees of weathering, low cation exchange capacities, high exchangeable acidity, and high P fixation (Bernardi et al., 2002; Lopes and Guilherme, 2016; Santos et al., 2018). These challenging soil conditions require liming to improve agricultural productivity by neutralizing H^+ and Al^{3+} ions (Camargo et al., 2010; Xu et al., 2019), with approximately 77.1 million hectares of Brazilian soils undergoing pH correction to address these limitations (Conab, 2024). Soil pH influences the dissolution of apatite, a primary source of P in soils. In acidic soils, the low pH and, consequently, high concentration of H^+ ions increase apatite solubility, releasing more plant-available phosphorus and enhancing agronomic efficiency (Bolan and Hedley, 1990; Chien and Menon, 1995). Conversely, neutral or alkaline soils reduce apatite dissolution, lowering P availability due to the formation of insoluble compounds with calcium and other cations (Rajan and Ghani, 1997).

Phosphate rocks can be broadly classified into two main types, sedimentary and igneous, each with distinct characteristics influencing P availability (Mohammadkhani et al., 2011). Sedimentary deposits, formed over millions of years, contain apatite minerals such as fluorapatite and francolite, combined with accessory minerals like quartz, carbonates, and clay minerals (Seer et al., 2001; Abram et al., 2011; Pufahl and Groat, 2017). On the other hand, in igneous deposits originating from volcanic activity, apatite minerals are associated with silicates and iron (Fe) and aluminum (Al) oxides (Rajan et al., 1996; Azzone and Ruberti, 2010). The release and availability of P from these sources vary according to their origin and mineralogical properties, with factors such as the degree of isomorphous substitutions impacting crop productivity (Chien, 1993; Rajan et al., 1996).

In addition to phosphate deposits, agro-industrial by-products are emerging as potential phosphorus sources for agricultural fertilizers. Examples include Bonechar derived from slaughterhouses and precipitated calcium phosphate from swine effluents (Bauer et al., 2007; Laird et al., 2009; Siebers and Leinweber, 2013). Besides providing essential nutrients for plants, these animal-origin phosphates contribute to a circular economy by repurposing waste and mitigating the environmental impact associated with their disposal (Marcinczyk and Oleszczuk, 2022).

To assess the efficiency of these fertilizers, it is critical to consider their chemical composition, mineralogy, and release rates. Total P content quantifies the overall amount of P in a source, but its availability to plants depends on various factors. Assessing the immediate availability of P in the soil, whether derived from phosphate rocks or organic sources, involves the use of organic extractants. For example, 2 % citric acid is a regulated extractant in Brazil (Kaminski and Peruzzo, 1997). These assessments are important for developing more efficient phosphate fertilization strategies, considering the different P sources and their interactions with organic acids present in the soil and the rhizosphere (Vasconcelos et al., 1986; Van Hees et al., 2005; Pinheiro et al., 2013).

While much is known about the efficiency of phosphates in acidic soils, there is a gap in understanding how these phosphates behave in soils with corrected acidity. This study aims to characterize different P sources through mineralogical and chemical analyses, evaluate their agronomic efficiency, and assess P use efficiency in two successive corn crops in limed soil.

MATERIALS AND METHODS

Fertilizers used

This study analyzed eleven samples of phosphate fertilizers, including Brazilian, imported, residue-recovered, and soluble phosphates. Among the phosphate rocks of igneous origin, all were sourced from Brazil, specifically from the cities of Catalão, in the state of Goiás, and Registro, in the state of São Paulo. Sedimentary sources included those from Brazil, sourced from the cities of Arraias, in the state of Tocantins, Bonito, in the state of Mato Grosso do Sul, and Pratápolis, in the state of Minas Gerais, as well as those sourced from Morocco, Algeria, and Peru (Bayovar). These phosphates are respectively denoted as Catalão, Registro, Arraias, Bonito, Pratápolis, Morocco, Algeria, and Bayovar. Phosphate from Registro underwent thermal treatment at 250 °C, according to information provided by the company.

In addition to the phosphate rocks, the Bonechar derived from the pyrolysis of degreased bovine bones at 800 °C for 6 h and a swine effluent recovered calcium phosphate (ERCP) were also investigated. The ERCP was produced by chemically precipitating P with calcium hydroxide [$Ca(OH)_2$] from swine effluent, a process that is part of the ‘P’ module of SISTRATES® (Effluent Treatment System), a technology developed by Embrapa’s research unit for swine and poultry (Fernandes et al., 2012). Triple superphosphate (TSP) was used as a soluble reference source. Phosphatic concentrate from ‘Jacupiranga/SP’, with a certified content of 15.5 % P (IPT 18B reference material), was used as a reference in the P determination analyses.

Sample preparation

The phosphates were dried in an oven at 65 °C and ground until they passed through a 0.3 mm sieve, in accordance with the Manual of Official Analytical Methods for Fertilizers and

Amendments (Brasil, 2017). This particle size range was used for material characterization and the subsequent greenhouse experiment.

Mineralogical characterization of phosphate rocks by X-ray Diffraction

Determination and quantification of minerals were carried out using the X-ray diffraction (XRD) technique at the Mineral Technology Research Center (CETEM) in Brazil. X-ray diffractograms were obtained using the powder method on the Bruker-D8 Advance equipment, operating under the following conditions: CuKα radiation (40 kV), scan rate of 0.02° 2θ per step, with a counting time of 1 s per step, and collected from 5 to 80° 2θ. Obtained data was interpreted and refined by comparing them with standards saved in the Bruker DiffracPlus software. For quartz content quantification, as required by MAPA Normative Instruction No. 5 for phosphate rocks, the Rietveld method (Rietveld, 1969) was employed with the assistance of Bruker AXS Topas software, v. 30 (Brasil, 2017).

Determination of total and soluble P by the colorimetric method

Total P extraction was carried out in a 10 % HNO_3 solution by cold shaking (Ballotin et al., 2021). For soluble P in citric acid, the concentration of the citric acid solution was 2 %. All extractions, with HNO_3, citric acid, and water, were performed at a phosphate-to-extractant ratio of 1:100, with 0.4 g of fertilizer sample in 40 mL of solution. Fertilizer sample and the acidic matrix were added to a 50 mL Falcon tube and placed on an automatic horizontal shaker at 90 rpm for 12 h. After the agitation process, the samples were filtered using medium-grade qualitative filter paper (80 g m^{-2}) with a diameter of 12.5 cm.

The method employed for P determination was adapted from Murphy and Riley (1962). For the preparation of the working reagent, 70 mL of H_2SO_4 solution was dissolved in 500 mL of water (13.7 mol L^{-1}); 20 g of ammonium molybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$] in 500 mL of water (0.020 mol L^{-1}); 0.27 g of potassium antimony tartrate [$C_8H_4K_2O_{12}Sb_2.3H_2O$] in 100 mL of water (0.0034 mol L^{-1}); 1.76 g of ascorbic acid ($C_6H_8O_6$) in 100 mL of water (0.01 mol L^{-1}). All solutions were prepared in a volumetric flask using ultrapure water. A volume of 125 mL of sulfuric acid solution, 37.5 mL of ammonium molybdate solution, 12.5 mL of potassium antimony tartrate solution, and 75 mL of ascorbic acid solution were mixed to achieve a concentration of 0.041 mol L^{-1} in the final working reagent solution.

To produce a standard P curve, a stock solution of 1,000 mg L^{-1} of P was prepared using a high-purity KH_2PO_4 salt previously dried in an oven. This solution was diluted to 10 mg L^{-1} of P with distilled water, from which standard solutions with five P concentrations (0, 0.5, 1.0, 1.5, and 2.0 mg L^{-1}) were prepared for the analytical curve.

To determine P contents in the samples, a volume of 5 mL was adopted (4 mL of the diluted solution or standard curve and 1 mL of the working reagent solution). The colorimetric reaction time was 10 min. Absorbance readings were performed using the 'Nova 1600UV' Spectrophotometer (Nova Instruments, Piracicaba, SP) at a wavelength of 880 nm. All steps were conducted in triplicate, including extraction, determination, and readings.

Quantification of other chemical elements

Quantification of Ca, Mg, Cu, Fe, Mn, Zn, and Al content was conducted using the atomic absorption spectroscopy method, utilizing the 55B Agilent equipment. The volumetric method of D-mannitol was employed to determine Na content. Sulfur was quantified using the gravimetric method of barium sulfate. Potassium content was determined using the flame photometry method. All methodologies for characterizing chemical elements were conducted in accordance with the Manual of Official Analytical Methods for Fertilizers and Amendments (Brasil, 2017).

Evaluation of agronomic efficiency in greenhouse

The experiment was conducted in a greenhouse located at Embrapa Agrobiologia, in Seropédica, RJ, Brazil. Experimental units consisted of plastic pots containing 2 kg of soil samples classified as Ferralsol [Latossolo Vermelho-Amarelo distrófico típico, according to Santos et al. (2018)], collected at 0.00-0.20 m soil layer in the Avelar district of Paty do Alferes, Rio de Janeiro State. Initially identified as acidic with a pH (H_2O; 1:2,5) of 4.68, the soil underwent a correction process. Before the correction, the sample was subjected to air drying and subsequently sieved using a 4 mm sieve. Chemical and physical characterization of the soil was performed according to methods described in Teixeira et al. (2017), and the results are presented in table 1. Soil pH was measured using a combined electrode immersed in a soil/water suspension in a ratio of 1:2.5. Mehlich-1 extractant was used to determine the P, and K levels. The exchangeable cations (Al^{3+}, Ca^{2+}, and Mg^{2+}) were determined using a 1 mol L^{-1} KCl extractant solution. The extraction of soil potential acidity (H+Al) was carried out with buffered calcium acetate at pH 7.0 and volumetric determination with NaOH solution in the presence of phenolphthalein as an indicator. The sand was determined by sieving and weighing, and that of silt and clay was done by the pipette method using 1 mol L^{-1} sodium hydroxide solution.

Based on preliminary testing, the soil was incubated with $CaCO_3$ at a rate of 1.5 g kg^{-1} for 45 days, with soil moisture maintained at approximately 70 % of field capacity. At the end of this period, the pH value was 6.3.

The experiment was arranged in a completely randomized design with 12 treatments and four replications, totaling 48 experimental units. Previously described phosphate rocks (Catalão, Registro, Bonito, Pratápolis, Arraias, Morocco, Algeria, and Bayovar) and animal-origin phosphates (Bonechar and ERCP) were included as treatments. Triple superphosphate (TSP) and a control without a P source were included as a reference. All treatments received 320 mg pot^{-1} of P (equivalent to 160 mg kg^{-1} of P) in a single application, which was mixed into the total soil volume before sowing. This P rate was determined in a preliminary experiment using similar procedures as the current experiment and including the same soil but under six different P rates (0, 40, 80, 120, 160, and 200 mg kg^{-1} soil) using TSP as the P source. The chosen P rate resulted in 80 % of the maximum dry matter production obtained with the growth response curve of the corn (*Zea mays* L.) hybrid AG 8740 PRO3 at 45 days after planting.

One week after planting, thinning was performed, leaving only one plant per pot. A nutrient solution was applied on the day of planting, excluding P, and supplying 200 mg kg^{-1} of K, 200 mg kg^{-1} of N, 80 mg kg^{-1} of S, 200 mg kg^{-1} of Mg, 0.8 mg kg^{-1} B, 0.15 mg kg^{-1} of Mo, 4 mg kg^{-1} of Zn, 3.6 mg kg^{-1} of Mn, 1.5 mg kg^{-1} of Fe, and 1.3 mg kg^{-1} of Cu. These nutrients were supplied using, respectively: KCl, urea, $(NH_4)_2SO_4$, $MgSO_4.7H_2O$, H_3BO_3, $Na_2MoO_4\cdot 2H_2O$, $ZnSO_4.7H_2O$, $MnCl_2.4H_2O$, $FeCl_3.6H_2O$, and $CuSO_4.5H_2O$.

The nutrient solution and the P treatments were applied at the beginning of the experiment. Twenty days later, a second fertilization with N and K was carried out using a solution with half of the initial concentration. To ensure soil moisture, pots were weighed every two to three days, and when necessary, the volume was replenished with water to approximately field capacity.

Table 1. Chemical and physical characteristics of the soil used in the experiment

P(1)	K(1)	Ca^{2+}(2)	Mg^{2+}(2)	Al^{3+}(2)	H+Al(3)	pH(H_2O)(4)	C(5)	Sand	Silt	Clay
mg dm^{-3}		cmol$_c$ dm^{-3}					%	g kg^{-1}		
1.59	39.9	0.19	0.11	1.45	3.37	4.68	0.39	770	70	160

Soil samples were collected at a layer of 0.00-0.20 m. P: phosphorus; K: potassium; Ca^{2+}: exchangeable calcium; Mg^{2+}: exchangeable magnesium; Al^{3+}: exchangeable aluminum; H+Al: potential acidity; pH: hydrogen ion concentration; C: organic carbon; Sand, silt and clay represent soil texture components. Methods: (1) Mehlich-1; (2) Titration with EDTA; (3) NaOH titration; (4) (1:2.5 soil: solution ratio); (5) Walkley-Black; Soil particle-size distribution was determined using the pipette method.

The experiment was conducted for two successive crops, each lasting 45 days. After this period, the aboveground parts of the plants were collected. The samples were dried in a forced-air oven at a temperature of 65 °C until reaching a constant weight, at this point, the shoot dry mass (SDM) was measured. The dried material was ground in Wiley mills and further powdered in a ball mill to analyze P content. The analysis was performed through nitro-perchloric digestion, as described in the Manual of Soil, Plant, and Fertilizer Chemical Analysis (Silva, 2009).

To assess the agronomic efficiency of the different phosphate sources, the Relative Agronomic Efficiency Index (RAE; Equation 1) and Phosphorus Efficiency (PE; Equation 2) were calculated:

$$RAE(\%) = \frac{Dry\ matter\ under\ P\ source - Dry\ matter\ without\ P}{Dry\ matter\ under\ TSP - Dry\ matter\ without\ P} \times 100 \qquad \text{Eq. 1}$$

$$PE(\%) = \frac{P\ accumulation\ under\ P\ source - P\ accumulation\ without\ P}{P\ accumulation\ under\ TSP - P\ accumulation\ without\ P} \times 100 \qquad \text{Eq. 2}$$

The statistical analysis and data visualization were performed using the R software (R Development Core Team, 2024). The “ggplot2” package (Wickham, 2016) was used to elaborate the graphics. The Shapiro-Wilk test assessed the normality of the residuals, and the Bartlett test verified the homoscedasticity of variances, both with a significance level of 5 %. In cases where the data did not meet the necessary assumptions (normality and homoscedasticity), the log transformation was applied to adjust the data. The analysis of variance (ANOVA) was performed, and when the difference between means was observed ($p<0.01$), they were compared using the Scott-Knott test ($p<0.01$), with the help of the “easyanova” package (Arnhold, 2013).

RESULTS

Mineralogical and chemical characterization of phosphate fertilizers

Apatite was identified as the main mineral component in the various phosphate samples (Table 2). Additionally, the phosphate rocks from Bonito, Pratápolis, and Arraias were found to be more closely associated with quartz (SiO_2). These materials also contained phyllosilicate minerals such as kaolinite [$(Al_4(SiO_{10})(OH)_8$] and muscovite [$(KAl_2(AlSi_3O_{10}(OH)_2$].

Table 2. Percentage of different mineral phases in the composition of the phosphate rocks evaluated in the study

Minerals Phases	Catalão	Registro	Bonito	Pratápolis	Arraias	Morocco	Algeria	Bayovar
	%							
Apatite	84.7	68.9	48.3	41.6	51.6	87.9	92.7	92.8
Quartz	7.8	0.8	39.1	36.9	35.8	3.9	1.6	1.6
Kaolinite	-	-	4.2	4.3	4.9	-	-	-
Muscovite	-	-	5.3	13.2	7.8	-	-	-
Calcite	-	3.1	2.3	-	-	3.7	-	-
Dolomite	-	0.1	0.8	4.1	-	4.5	5.6	5.6
Chlorite	3.9	-	-	-	-	-	-	-
Goethite	3.5	6.5	-	-	-	-	-	-
Barite	-	14.9	-	-	-	-	-	-
Gorceixite	-	5.6	-	-	-	-	-	-

Mineral quantification was performed using X-ray diffraction (XRD) and the Rietveld method (Rietveld, 1969) for quartz content analysis.

Chlorite [$(Mg,Fe)_3(Al,Si)_4O_{10}(OH)_2(Mg,Fe)_3(OH)_6$], a typical micaceous mineral found in igneous rocks, was only observed in the concentrate from Catalão. In the Registro phosphate, significant levels of barite ($BaSO_4$) and gorceixite [$BaAl_3(PO_4)(PO_3OH)(OH)_6$] were detected. Additionally, traces of quartz, calcite ($CaCO_3$), and dolomite [$CaMg(CO_3)_2$] carbonate minerals were observed. Dolomite mineral phase was also identified in the sedimentary phosphates from Morocco (4.5 %), Bayovar (5.6 %), Algeria (5.6 %), Pratápolis (4.1 %), and Bonito (0.8 %). Goethite [$FeO(OH)$] was the only iron mineral identified, present in the concentrates from Registro (6.5 %) and Catalão (3.5 %).

Apart from being a P source, the phosphates in this study showed differences in other elements, classified as macro- or micronutrients for plants (Table 3). The Ca content of phosphate rocks directly correlated with the apatite content ($R^2 = 0.978$; $p<0.0001$). Sedimentary phosphates from Morocco, Algeria, and Bayovar, as well as the igneous phosphate from Catalão, exhibited the highest Ca concentrations, exceeding 30 %. Similarly, Bonechar also showed a Ca content above 30 %, which was higher than the average of the other sources.

Nitrogen content ranged from 0.16 to 0.22 % across all sources of phosphate rocks, with ERCP, Bonechar, and TSP showing much higher concentrations, particularly the latter two at 1.31 and 1.59 %, respectively. Regarding the Mg content, ERCP presented a concentration of 11.5 %, significantly higher than the other sources, which had 1 % or less. No significant differences were observed for sodium. Sulfur was detected in imported phosphates but at low concentrations. Iron and Al were more abundant in Brazilian phosphate rocks than other P sources. Among the micronutrients, Mn is notable, as Brazilian phosphate rocks had much higher concentrations compared to the other P sources, except for ERCP and TSP, which exhibited intermediate Mn concentrations.

Total P content varied among the different sources, ranging from 3.71 to 20.48 % P (Table 4), with the highest concentration in TSP and the lowest in ERCP. Igneous phosphate from Catalão and the Bonechar were among the richest, each containing approximately 15 % P. In contrast, the igneous phosphate from Registro contained 11 % in total P. The imported sedimentary phosphates, such as Bayovar, contained around 13.61 % of P. Brazilian sedimentary phosphates had lower P contents than the imported sedimentary phosphates, with Bonito, Pratápolis, and Arraias having 7.9, 7.64, and 8.95 % of P, respectively.

Table 3. Chemical characterization of the different phosphorus sources evaluated in the study

P source	N	P	Ca	Mg	S	Na	Fe	Al	Mn	Cu	Zn
	%								mg L^{-1}		
Catalão	0.16	15.05	30.02	0.49	-	0.13	5.12	0.59	2400	378	209
Registro	0.16	11.08	21.80	0.10	-	0.19	7.18	1.77	8200	49	148
Bonito	0.16	7.89	15.11	0.29	-	-	2.73	4.74	624	38	121
Pratápolis	0.16	7.64	14.61	0.44	-	-	5.20	1.59	3900	49	429
Arraias	0.16	8.95	17.04	0.20	-	-	1.54	2.33	1100	127	344
Morocco	0.22	13.17	33.88	0.79	0.51	0.99	0.29	0.38	13	43	330
Algeria	0.16	12.18	34.28	1.00	1.17	0.88	0.27	0.24	32	13	155
Bayovar	0.16	13.61	34.29	0.90	0.65	0.89	0.29	0.24	76	94	150
ERCP	0.57	3.71	23.49	11.46	-	0.13	0.19	0.10	322	199	-
Bonechar	1.31	15.06	31.92	0.50	-	0.53	-	-	-	-	100
TSP	1.59	20.48	13.97	0.61	1.38	0.33	0.70	0.20	285	68	252

Element quantification was performed using the following methods: N Kjeldahl method; P adapted colorimetric method; Atomic Absorption Spectroscopy for Ca, Mg, Cu, Fe, Mn, Zn, and Al; Flame Photometry for K; D-mannitol for Na; Gravimetric method for S. The acronyms correspond to TSP: triple superphosphate; ERCP: swine effluent recovered calcium phosphate; Bonechar: pyrolyzed degreased bovine bones; Control: no P fertilizer application; and the other P sources are identified by their origin.

Table 4. Phosphorus content and solubility of phosphates in 2 % citric acid solution and water

P source	Total P[1]	Citric acid[2]	Water[3]
	%	% relative to total P content	
Catalão	15.05	11.73	0.02
Registro	11.08	18.10	0.24
Bonito	7.89	20.02	0.04
Pratápolis	7.64	18.34	0.11
Arraias	8.95	26.04	0.04
Moroccos	13.17	26.05	0.00
Algeria	12.18	29.91	0.08
Bayovar	13.61	27.03	0.48
ERCP	3.71	99.25	0.06
Bonechar	15.06	45.77	0.08
TSP	20.48	87.72	79.59

(1) Total: digestion in a nitric acid solution (10 %); (2) Citric acid: digestion in a citric solution (2 %); (3) Water: no digestion, only water addition. The P determination was performed using the adapted colorimetric method. The acronyms correspond to TSP: triple superphosphate; ERCP: swine effluent recovered calcium phosphate; Bonechar: pyrolyzed degreased bovine bones; Control: no P fertilizer application; and the other P sources are identified by their origin.

P solubility

The highest solubility of P in 2 % citric acid relative to total P was observed for ERCP, followed by TSP and Bonechar (Table 4). Among the sedimentary phosphates, Pratápolis, Bonito, Arraias, Morocco, Algeria, and Bayovar exhibited citric acid solubility values ranging between 18.3 and 29.9 % in relation to their total P content. In contrast, the Catalão phosphate showed the lowest solubility in citric acid. Generally, phosphate rocks and phosphates of animal origin proved to be practically insoluble in water, with solubility levels varying from 0.004 to 0.48 % (Table 4).

Agronomic efficiency of P fertilization

There were significant differences in the SDM production of corn for both crops in response to fertilization with different phosphate sources (Figure 1). In the first crop cycle, Bonechar and the sedimentary phosphates from Algeria and Bayovar provided SDM production equivalent to the reference source (TSP). Fertilization with the sedimentary phosphates from Bonito and Pratápolis did not improve growth compared to the control treatment (-P), while the other fertilizers yielded intermediate results.

All P sources in the second crop cycle resulted in significantly higher production than the control treatment. Although productivity was lower in this crop cycle, the highest shoot dry mass was observed with the sedimentary phosphates from Algeria and Bayovar, and the animal-origin phosphate Bonechar, which demonstrated similar performance to TSP. Six distinct groups were observed for the accumulated SDM over two crop cycles (Figure 1). All tested P sources resulted in significantly higher production compared to the control treatment. The highest SDM production was achieved using the Bonechar, which presented values similar to those of the TSP.

In the first crop cycle, Bonechar showed superior performance to TSP in terms of RAE (Figure 2). The sedimentary phosphates from Algeria and Bayovar showed similar performance to each other. In contrast, the phosphates from Bonito and Pratápolis were inert as sources of P in the crop's first cycle.

The RAE for SDM accumulated over the two crop cycles followed a trend similar to that observed in the first crop. Bonechar achieved 123 % RAE, surpassing TSP. Phosphates from Bayovar and Algeria demonstrated similar efficiencies, with RAE values of 72 and 71 %, respectively (Figure 2). In contrast, phosphates from Pratápolis and Bonito showed slightly better performance than the control treatment.

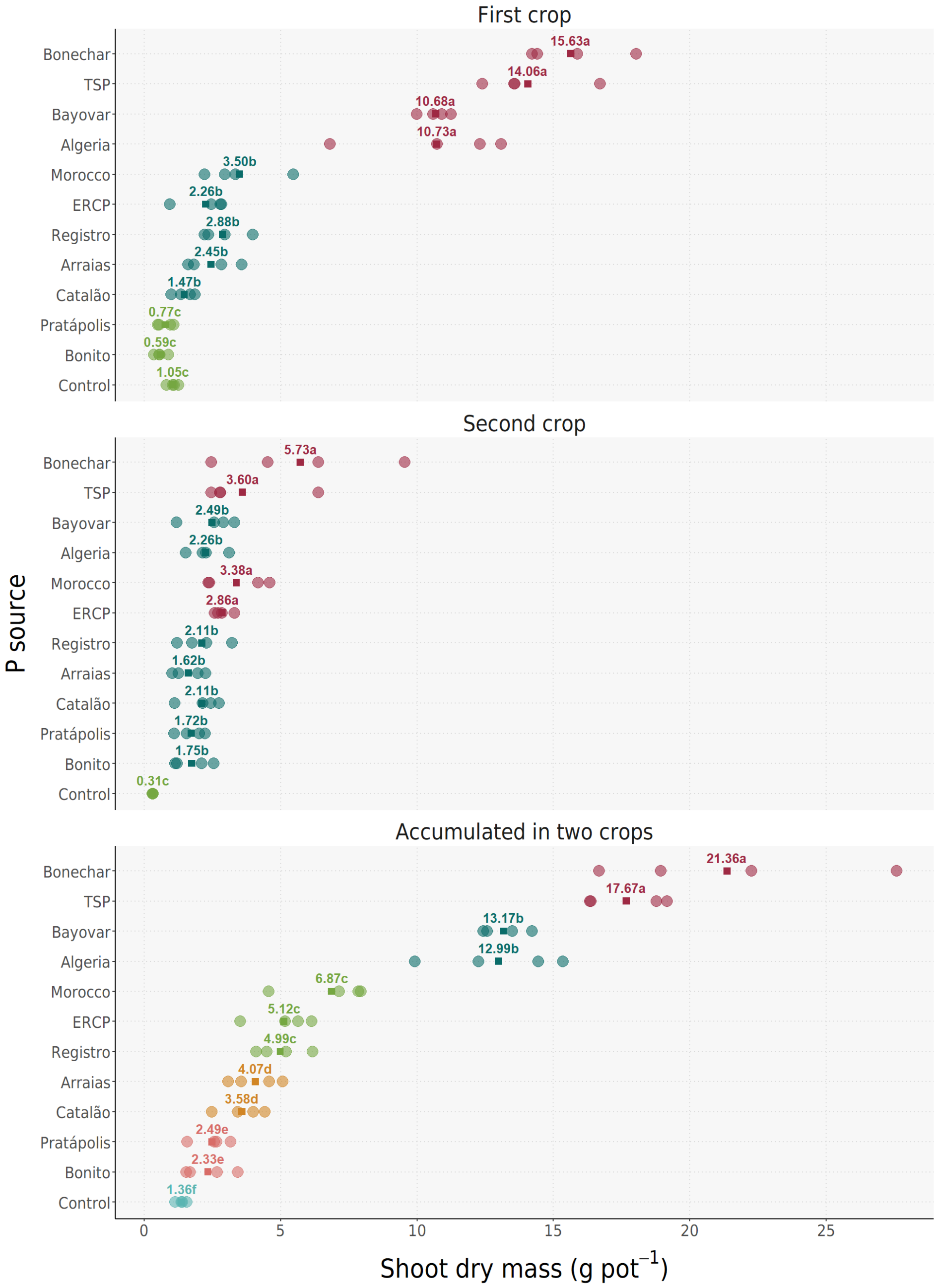

Figure 1. Shoot dry mass of corn in the first and second crops, and the accumulated over two crops in response to different phosphorus fertilization sources. For each crop, P sources identified by the same color and letter do not exhibit statistically significant differences, as assessed by the Scott-Knott test at a 1 % significance level. The means for P sources are identified by their value and a square point, while circular points represent the values of each replication for each P source. TSP: triple superphosphate; ERCP: swine effluent recovered calcium phosphate; Bonechar: pyrolyzed degreased bovine bones; Control: no P fertilizer application; and the other P sources are identified by their origin.

P recovery efficiency

Application of Bonechar and phosphates from Algeria and Bayovar led to a significant accumulation of P in corn plants, reaching values equivalent to those of TSP after the first cycle (Figure 3). All treatments accumulated more P than the control, with P amounts ranging from 8.5 mg to 0.7 mg per pot (Figure 3). After the second crop cycle, Bonechar and ERCP, along with the phosphate from Morocco, resulted in the highest P accumulation in corn plants, similar to TSP. There was a notable difference in the responses of the different phosphate fertilization sources compared to the control (Figure 3). The other treatments showed intermediate values, ranging from 4.2 mg to 3.8 mg of P per pot.

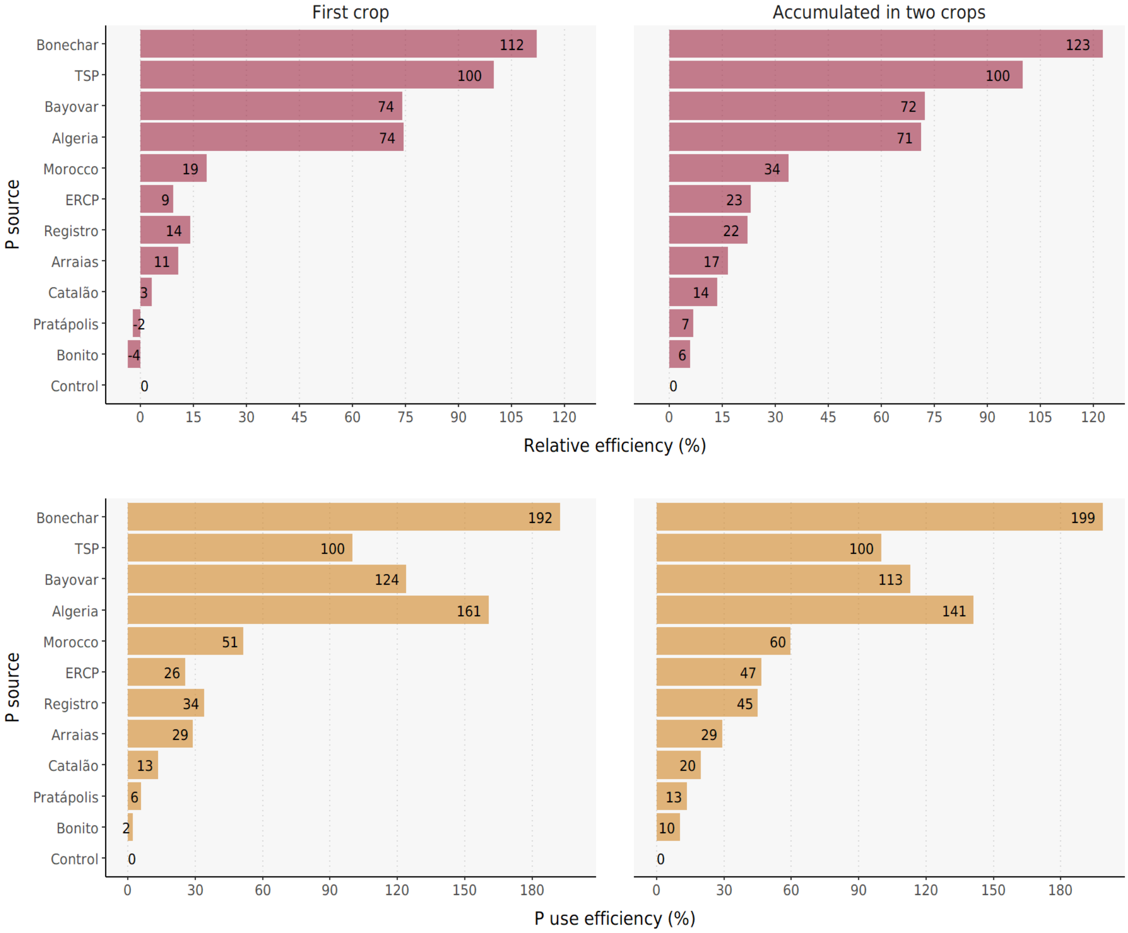

Figure 2. Agronomic efficiency and phosphorus use efficiency for corn in the first crop and accumulated over two crops in response to different phosphorous fertilizer sources. TSP: triple superphosphate; ERCP: swine effluent recovered calcium phosphate; Bonechar: pyrolyzed degreased bovine bones; Control: no P fertilizer application; and the other P sources are identified by their origin.

Over the two crop cycles, all phosphate sources differed from the control, forming six distinct groups in terms of P accumulation by plants (Figure 3). The highest total P accumulation was obtained with Bonechar (39.8 mg per pot). The second group included TSP and phosphates from Algeria and Bayovar. The third group comprised phosphates from Morocco (12.4 mg per pot), ERCP (9.9 mg per pot), and Registro (9.6 mg per pot), followed by the fourth group with phosphates from Arraias (6.4 mg per pot) and Catalão (4.6 mg per pot). The fifth group, with the lowest P accumulation, consisted of phosphates from Pratápolis (3.4 mg per pot) and Bonito (2.7 mg per pot).

Regarding P efficiency, in the first crop cycle, Bonechar and the phosphates from Algeria and Bayovar showed superior P uptake efficiency compared to TSP. This trend continued in the cumulative results of the two cycles, where the application of Bonechar and the phosphates from Algeria and Bayovar resulted in more efficient P accumulation than TSP.

DISCUSSION

Mineralogical and chemical characterization

Sedimentary phosphates from Morocco, Algeria, and Bayovar consist mainly of apatite concentrates, which undergo mechanical and chemical processes to remove impurities such as silica, clay, and carbonates (Hakkou et al., 2016; Boumaza et al., 2021). Chemical analysis confirmed their high apatite contents and low quartz presence (less than 10 %).

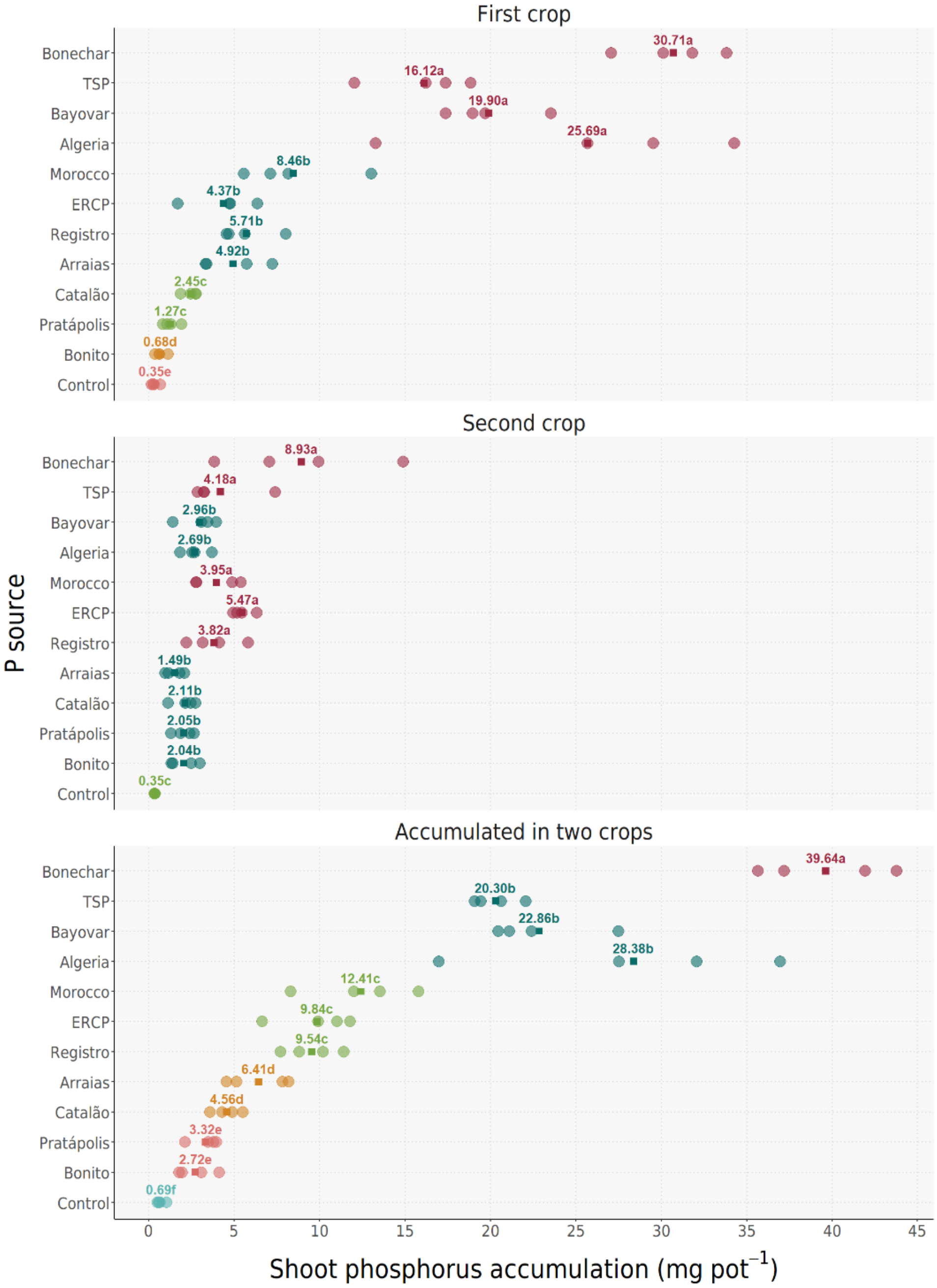

Figure 3. Shoot phosphorus accumulation of corn in the first and second crops and accumulated over two crops in response to different phosphorus fertilization sources. For each crop, phosphorus sources identified by the same color and letter do not exhibit statistically significant differences, as assessed by the Scott-Knott test at a 1 % significance level. For each crop, P sources identified by the same color and letter do not exhibit statistically significant differences, as assessed by the Scott-Knott test at a 1 % significance level. The means for P sources are identified by their value and a square point, while circular points represent the values of each replication for each P source. TSP: triple superphosphate; ERCP: swine effluent recovered calcium phosphate; Bonechar: pyrolyzed degreased bovine bones; Control: no P fertilizer application; and the other P sources are identified by their origin.

These results were similar to those of the Brazilian phosphate rock of Catalão, an igneous deposit containing apatite, goethite, quartz, and traces of chlorite (Azzone and Ruberti, 2010), which is concentrated through flotation (Monte and Pimentel, 2021). The Registro phosphate exhibited a higher gangue mineral content, including goethite, barite, and gorceixite. According to the manufacturer, this is attributed to its beneficiation process, which involves crushing, grinding, magnetic separation, desliming, and drying at 250 °C to remove fine silica fractions. Mineralogical characterization of the Juquiá residual apatite phosphate deposit, where the Registro phosphate is mined, revealed the presence of dolomitic limestone and minerals of Fe (goethite), Al (gorceixite), and barite (Alcover Neto and Toledo, 1993), consistent with the findings of this study.

In contrast, sedimentary phosphates like Bonito, Pratápolis, and Arraias exhibit lower apatite content (<50 %) and higher quartz content (>35 %), originating from the Neoproterozoic era (~600 million years ago) in formations like the Bambuí Group's Sete Lagoas Formation (Bizzi et al., 2003; Abram et al., 2011; Ribeiro, 2016). Bonito phosphate, from the Bodoquena Plateau, includes Neoproterozoic metasediments, microphosphorites, silicified dolomites, stromatolites, and algal laminations, deposited in a coastal environment influenced by marine currents (Lacerda Filho et al., 2006).

Solubility of natural and organic phosphate fertilizers

One advantage of processing igneous phosphates is their lower impurity content, such as carbonates, which facilitates flotation and ensures a final phosphate material with higher P content compared to sedimentary phosphates. This was observed in total P determination analyses (Table 4), where igneous phosphate concentrates reached P levels of up to 15 %, while the average values for sedimentary phosphate concentrates were 6.5 % P (Pufahl and Groat, 2017; Silva et al., 2018).

Raw igneous phosphates generally have lower total P content before beneficiation, ranging from 2.2 to 6.5 %, with an average of 3.9 % P at the Catalão mine (Santos et al., 2002; Pufahl and Groat, 2017). In contrast, sedimentary phosphates tend to have higher P levels, ranging from 6 to 13 % of their total weight. These sedimentary phosphates undergo physical beneficiation processes such as grinding, classification, gravity concentration, and magnetic separation. These processes enhance their suitability for direct soil application without the need for flotation, potentially reducing beneficiation costs (Kaminski and Peruzzo, 1997; Souza and Fonseca, 2009), which can be assumed for the phosphate rocks from Arraias, Bonito, and Pratápolis.

Apatite solubility is dependent on the degree of isomorphic substitution between phosphate (PO_4^{3-}) and carbonate (CO_3^{2-}) and is proportional to the CO_3^{2-}/PO_4^{3-} molar ratio (Chien and Menon, 1995). Carbonate presence destabilizes the mineral structure of apatite, shortening the a-axis and interfering directly with chemical bonds and crystallography, which increases the dissolution rates of the material (Chien, 1993). Generally, sedimentary phosphates are more reactive than igneous phosphates due to their higher carbonate content, which replaces phosphate in the apatite structure, making it more soluble (Oxmann and Schwendenmann, 2014).

Igneous phosphates, such as those from Catalão and Registro, feature lower carbonate substitutions compared to sedimentary phosphates, resulting in lower solubility in 2 % citric acid (Rajan et al., 1996). Despite having the same origin as these igneous phosphates, the thermal treatment of Registro phosphate can significantly alter its structure, increasing its solubility. Elevated temperatures induce greater atomic vibration and thermal expansion of the crystalline structure, affecting the P stability and solubility (Roy et al., 2023).

Animal-derived phosphates such as Bonechar contain apatite in a different form derived from hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] (Zimmer et al., 2018). Analyzing the P in ERCP, resulting from chemical precipitation with $Ca(OH)_2$, Fernandes et al. (2012) identified hydroxyapatite as the predominant form of P. Based on the chemical composition and total P levels quantified, potential Ca phosphate formations could be primarily hydroxyapatite or tricalcium phosphate [$Ca_3(PO_4)_2$] due to the high concentrations of Ca (23 %) and P (3.9 % P). However, the alkaline pH of ERCP (9.6) favors the formation of hydroxyapatite, which is more stable under alkaline conditions, unlike tricalcium phosphate, which forms at a more acidic pH (Thurmer et al., 2011).

Agronomic and P use efficiency

Bonechar is characterized by a structure rich in calcium phosphate, particularly hydroxyapatite (Zwetsloot et al., 2015), and has proven to be a highly efficient source of P to corn. Zimmer et al. (2019) evaluated the influence of Bonechar fertilization on the dry mass production of ryegrass (*Lolium multiflorum* L.) over seven cuts. The results indicated that using Bonechar led to accumulated biomass production similar to that of TSP, showing that both P sources were equally effective across different crops. In studies on the dissolution of Bonechar, phosphate rocks, and TSP in different soils, Warren et al. (2008) observed a satisfactory response from Bonechar, even in soils with higher pH, where the application of phosphate rocks had reduced efficiency. The dissolution of Bonechar was more significant in the first 20 days after application, followed by a gradual release of P over time, revealing its potential agronomic performance.

Phosphates from Algeria and Bayovar demonstrated high agronomic efficiency, even in soil with a pH corrected to 6.3. These phosphates, originating from sedimentary deposits, have lower crystallization and are considered more reactive and easily hydrolyzable compared to Brazilian igneous phosphates (Leon et al., 1986; Chien et al., 1990), such as those from Catalão and Registro. Even though there are chemical and mineralogical similarities, the Morrocco phosphate showed reduced agronomic efficiency compared to Algeria and Bayovar. According to the manufacturer, the batch of Morrocco phosphate evaluated in this study was imported to Brazil to produce soluble P fertilizers through the acidulation process. This suggests that, beyond the analyses conducted in this study, other factors may have influenced the P availability of this source. Phosphate minerals are highly complex, with the PO_4 radical capable of combining over 30 chemical elements to form various phosphate minerals (Loureiro et al., 2008). This leads to numerous possible ionic substitutions and structural variations, which can significantly affect solubility (Chien et al., 1990). One possible explanation for the difference between these imported phosphates may be the presence of different types of apatite minerals in these materials. Since some apatite minerals are more soluble than others (Vieillard and Tardy, 1984), this variability could impact the phosphates' agronomic efficiency.

Brazilian sedimentary phosphates, represented by Bonito, Pratápolis, and Arraias, showed lower agronomic efficiency in the current conditions of soil pH corrected to 6.3. According to Novais et al. (2007), the effective application of less reactive natural phosphates, which are insoluble in water, depends on soil acidity (protons) to initiate P dissolution. Thus, liming can reduce the dissolution rate of phosphate rocks, impacting their agronomic efficiency (Sale and Mokwunye, 1993). Considering these factors, the pH correction performed in this study may have affected the agronomic performance of some P sources, particularly the less reactive Brazilian sedimentary phosphates.

Agronomic efficiency of Brazilian phosphates was higher for the igneous phosphates of Catalão and Registro compared to the sedimentary phosphates of Bonito and Pratápolis. It is worth noting that Registro phosphate showed similar solubility in 2 % citric acid when compared to sedimentary phosphate from Arraias. However, it is crucial to consider that solubility analyses in organic acids are only one aspect to be considered in evaluating phosphate efficiency. Registro phosphate underwent thermal treatment, which may have influenced its solubility in the soil and absorption by plants (Francisco et al., 2007).

The ERCP, obtained from swine effluents, undergoes a P removal process where $Ca(OH)_2$ is added to precipitate the phosphate (Fernandes et al., 2012), resulting in a by-product with high Ca content. The high solubility of ERCP in citric acid is due to the presence of tricalcium phosphates, as stated by Fernandes et al. (2012) in their evaluation of this material. Tricalcium phosphates generally have a higher solubility than natural apatite and hydroxyapatites (Dorozhkin, 2015; Laskus and Kolmas., 2017). However, despite their high solubility, these phosphates are more effective as fertilizers in acidic soils with a high H^+ ion content (Cabeza et al., 2011; Pearson and Rueda-Ayala, 2022). In soil with slightly acidic or higher pH, the agronomic efficiency of these phosphates tends to be lower compared to mineral P sources (Römer and Steingrobe, 2018). The presence of high concentrations of Ca and Mg in ERCP, along with the high exchangeable Ca levels present in the soil after liming, can lead to the formation of insoluble calcium phosphate compounds, which reduces the immediate availability of P for plants at pH levels above 7.0 (Andersson et al., 2015; Maluf et al., 2018). This limitation is a possible explanation for the results observed in the present study, as soil acidity was corrected before the experiment began.

The variation in the behavior of P accumulation and recovery among different sources over the two consecutive crop cycles can be attributed to the specific characteristics of each source. The sedimentary phosphates of Bayovar and Algeria and the Bonechar source demonstrated the ability to release P quickly, providing immediate plant availability in the first crop. Ensuring adequate P availability in the early stages of plant development is crucial, as its limitation can interrupt root growth and induce lateral root formation (Péret et al., 2014; Fageria et al., 2016). The increase in root length plays a crucial role in the efficient absorption of nutrients like P, which has low mobility in the soil and depends on direct contact with roots through diffusion (Xiang et al., 2017). On the other hand, less reactive sources, like the Brazilian phosphates from Catalão, Pratápolis, Bonito, can act as slow-release phosphorus sources, as stated by Novais et al. (2007). The authors explain that while P from soluble sources tends to be adsorbed in the soil when not absorbed by plants, the slower dissolution of natural phosphates promotes gradual P release and a greater residual effect. This was observed in the second crop of the present study, where the SDM (although low) for these phosphates was higher than in the first crop and greater than in the control.

The study of phosphate rocks, especially Brazilian inputs, aligns with the directive to explore new sources and methods to promote fertilizer production in Brazil, as outlined in the National Fertilizer Plan 2050 (Brasil, 2023). This is especially emphasized in Action 15, which underscores the need to promote agronomic studies to identify the potential of regional phosphate rocks. To reduce the country's dependence on foreign P fertilizers, it is crucial to research how Brazil can optimize its phosphate resources, both in the industry for better input manufacturing and in the field for more efficient input use (Oliveira et al., 2019; Raniro et al., 2023). While it was observed that phosphate rocks did not perform well in limed soils, other studies have reported better results in non-limed tropical soils (Novais et al., 2007). Therefore, the use of phosphate rocks should be carefully coordinated with liming to achieve optimal results from both practices.

On the other hand, the results for Bonechar highlight the potential of using this P source as a fertilizer in limed soils. Brazil has the largest livestock herd in the world, estimated at 175 to 190 million heads (ABIEC, 2022), which generates a significant amount of carcass residues that can be repurposed for Bonechar production. As noted by Withers et al. (2018), bioresources are an underexplored P source in Brazil, with the recovery from animal residues playing a crucial role in addressing the country's agricultural P demand. Additionally, recovering P from waste avoids the environmental impacts associated with phosphate mining (Dias and Lajolo, 2010). Finally, recovering nutrients from animal wastes enhances resource circularity and aligns with the UN Sustainable Development Goals (SDGs), particularly Goal 12, which emphasizes responsible consumption and production (Ortiz-de-Montellano et al., 2023), contributing to making Brazilian agriculture even more sustainable.

CONCLUSION

Significant differences were observed in the mineralogical and chemical characteristics of sedimentary phosphates from different regions, which have implications for their agronomic efficiency and suitability for various agricultural applications.

Different phosphate sources exhibit varying degrees of effectiveness in supplying P to corn plants. Natural phosphates with a relative solubility in 2 % citric acid below 27 % do not demonstrate good agronomic efficiency in soils with corrected acidity. In contrast, Bonechar has shown agronomic efficiency comparable to that of triple superphosphate, while also promoting resource circularity and being produced from readily available residues in Brazil.

DATA AVAILABILITY

The dataset is available in Ramos et al. (2024) at https://doi.org/10.5281/zenodo.14247219. The R script used for the statistical analyses and plot generation can be found in the same repository or at: https://github.com/jmalonso55/fosfatos/blob/main/An%C3%A1lise_fosfatos_g.md.

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AUTHOR CONTRIBUTIONS

Conceptualization: Bruno José Rodrigues Alves (equal) and Vinicius de Melo Benites (equal).

Data curation: Jorge Makhlouta Alonso (lead).

Formal analysis: Jorge Makhlouta Alonso (equal), Jéssica Franciele Kaminski Ramos (equal) and Vinicius de Melo Benites (equal).

Funding acquisition: Bruno José Rodrigues Alves (equal) and Vinicius de Melo Benites (equal).

Investigation: Jéssica Franciele Kaminski Ramos (equal) and Vinicius de Melo Benites (equal).

Methodology: Jéssica Franciele Kaminski Ramos (equal) and Vinicius de Melo Benites (equal).

Project administration: Vinicius de Melo Benites (lead).

Resources: Bruno José Rodrigues Alves (equal) and Vinicius de Melo Benites (equal).

Supervision: Bruno José Rodrigues Alves (equal) and Vinicius de Melo Benites (equal).

Validation: Bruno José Rodrigues Alves (equal), Paulo César Teixeira (equal) and Vinicius de Melo Benites (equal).

Visualization: Jorge Makhlouta Alonso (equal) and Jéssica Franciele Kaminski Ramos (equal).

Writing – original draft: Jéssica Franciele Kaminski Ramos (lead).

Writing – review & editing: Bruno José Rodrigues Alves (equal), Jorge Makhlouta Alonso (equal), Jéssica Franciele Kaminski Ramos (equal), Paulo César Teixeira (equal) and Vinicius de Melo Benites (equal).

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