

# Phosphorus extractants for soils in the humid tropical region of Brazil<sup>1</sup>

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**ABSTRACT** - Given the heterogeneity of soils in Roraima state, Brazil, and the need for a phosphorus (P) extraction protocol, this study aimed to assess the efficiency of the Mehlich-1, Mehlich-3, Bray-1 extractants and anion exchange resin (AER) in determining available P in soils representative of the state. The chemical, physical and mineralogical attributes of seven soil classes were determined. The experiment was conducted in a greenhouse, using a randomized block design in a 7 x 5 factorial scheme with four repetitions. The first factor was the soils (LA (ITÃ), LV (ITÃ), LA (SERRA DA PRATA), LA (CCA), PA (CCA), FT (BONFIM), SN (SURUMU)), and the second P doses, estimated based on the maximum P-adsorption capacity (MPAC). A polyethylene pot containing 5 dm<sup>3</sup> of soil and five plants was defined as the experimental unit. The indicator species was corn grown in two 30-day phases. The P doses were applied using monopotassium phosphate. Soil samples were removed before planting to determine available P using the extractants. Corn dry weight was assessed at the end of the two-phase experiment. Correlation tests were performed for dry weight versus extractant and extractant versus extractant. The Mehlich-3 and Bray-1 extractants were the most sensitive to variations in soil attributes. The resin exhibited the greatest correlations with the different soils individually and combined, showing potential in determining available P in soils from the humid tropical region of the Brazilian Amazon.

**Key words:** Phosphorus extraction. Assessment methods. Corn. Available phosphorus.

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## INTRODUCTION

Soil available phosphorus (P) is typically evaluated using acid extractants, such as Mehlich-1, Mehlich-3 and Bray-1. In addition to chemical extractants, anion exchange resins (AERs) are also used in some Brazilian laboratories. The choice of extractant to determine available P depends on the degree of correlation between the P content of the extractant and that of the plant, whereby the greater the correlation, the more suitable the extractant (STEINER *et al.*, 2012). However, there is no consensus regarding the extractant that best expresses plant-available P, largely due to soil attributes that influence adsorption of this element (NUNES *et al.*, 2021; ROSA; SILVA; MALUF, 2018; WUENSCHER *et al.*, 2015; ZEHETNER *et al.*, 2018).

Acid extractants, such as Mehlich-1, facilitate the acquisition of clear liquids by decantation, enable low-cost analyses and are more feasible for routine use in laboratories (ZEHETNER *et al.*, 2018). These extractants act differently depending on soil type because of their different capacities to dissolve and solubilize P from phosphate compounds (NUNES *et al.*, 2021).

Mehlich-1 is restricted for use in clayey soils, especially when phosphates that are poorly soluble in water have been applied, due to excessive P-Ca extraction, which is unavailable to plants (MEDEIROS *et al.*, 2021; MUMBACH *et al.*, 2018). Additionally, the extractant may underestimate available P in clayey soils with a high pH because of extractant exhaustion resulting from high cation exchange capacity and ineffective extraction of P bound to Fe (P-Fe) and Al (P-Al) (ROY, 2017; VINHA *et al.*, 2021).

Bray-1 is recommended for soils with a wide range of chemical characteristics due to Al<sup>3+</sup> fluoride complexation (DARI *et al.*, 2019; ZEHETNER *et al.*, 2018). For acid soils, Mehlich-3 is more widely used for available P extraction because it is more economical and versatile than Bray-1 in that it can simultaneously extract other nutrients in addition to P (NUNES *et al.*, 2021). However, Penn *et al.* (2018) used this method and observed a decline in P extraction with increasing pH due to changes in P forms and the consumption of extractant fluoride by calcium minerals.

AERs have a number of favorable characteristics, particularly the high correlation between P uptake by the plant and that extracted from the soil and better theoretical basis for determining soil P content (SILVA; RAIJ, 1999). These resins simulate the behavior of root systems at P uptake and do not affect natural soil chemistry (GONÇALVES *et al.*, 2012).

Results differ in terms of extractant efficiency in determining soil-available P and demonstrate the

importance of these studies in establishing an extraction method for each region (DARI *et al.*, 2019; MEDEIROS *et al.*, 2021; RAIJ; FEITOSA, 1980; SANTOS; KLIEMANN, 2005; SILVA; RAIJ, 1999; STEINER *et al.*, 2012; WUENSCHER *et al.*, 2015). Moreover, although most research has concluded that ARTs exhibit the best correlation with Brazilian soils, chemical extractants have been used to estimate available P in humid tropical regions of the country.

As such, given the different findings obtained in establishing a P extractant and the small number of studies on this topic under humid tropical conditions in Brazil, this investigation aimed to assess Mehlich-1, Mehlich-3, Bray-1 and AER in determining available P in seven soil classes representative of Roraima state.

## MATERIAL AND METHODS

Seven soil classes were selected (Table 1) based on their agricultural importance to Roraima and classified according to the Brazilian Soil Classification System (EMBRAPA, 2018). Samples of each soil type were collected from the 0-0.20 m layer for chemical, physical, mineralogical and P adsorption analyses.

### Soil chemical, physical and mineralogical analysis

Chemical analysis of the soils consisted of pH in water, calcium, exchangeable magnesium and aluminum in 1 mol L<sup>-1</sup> KCl, available phosphorus and potassium using Mehlich-1, potential acidity with 0.5 mol L<sup>-1</sup> of calcium acetate and organic matter by determining organic carbon in 0.2 mol L<sup>-1</sup> potassium dichromate, in accordance with Embrapa (2009). The soil attributed sum of bases – SB (Ca<sup>2+</sup> + Mg<sup>2+</sup> + K<sup>+</sup> + Na<sup>+</sup>), total cation exchange capacity – T (SB + H + Al), effective cation exchange capacity – t (SB + Al), clay activity index (T/clay x 1000), base saturation – V% (SB/T x 100) and aluminum saturation – m% (Al<sup>3+</sup>/t x 100) were obtained from the results of the abovementioned analyses. The soil characterizations LA (CCA) and PA (CCA) were taken from Benedetti *et al.* (2011) and SN (SURUMU) from Schaefer *et al.* (1993). The results of these analyses are presented in Table 2.

Physical characterization consisted of determining the texture class of the soils based on granulometry, using the pipette method (EMBRAPA, 1997) and the soil texture triangle of the Brazilian Soil Classification System – SiBCS (EMBRAPA, 2018). The silt-to-clay ratio (SCR) was calculated by dividing the two soil fractions. The results are shown in Table 3.

Mineralogical analysis of the sand, silt and clay fractions (Table 4) was performed via X-ray diffraction (XRD), by adding around 100 mL of water

and 10 mL of 1 N NaOH solution to soil samples of approximately 100 g. After 24 hours, the samples were broken up (disaggregation) in a mechanical shaker for 10 min. The fractions were separated using 0.053 mm mesh sieves for sand and silt and 0.002 mm for silt and clay, with constant washing to remove any traces of NaOH

that might influence the diffractograms. After drying at ambient temperature, the soil fractions were macerated and fixed on glass slides with mineral oil for sand, and water for silt and clay. The X-ray diffractograms were obtained using a Shimadzu diffractometer with a cobalt tube, in a range of 7 to 70° and scan speed of 0.02°/sec.

**Table 1** - Soil classes of the samples collected in the 0-0.20 m layer for P extraction using different extractants

Soil	Acronym	Municipality	Coordinates			
			Latitude		Longitude	
Oxisol (LATOSSOLO AMARELO Distrófico petroplíntico)	LA (ITÃ)	Caracará-RR	01° 31' 36.8"	N	60° 45' 0.4"	W
Oxisol (LATOSSOLO VERMELHO Distrófico petroplíntico)	LV (ITÃ)	Caracará-RR	01° 30' 7.1"	N	60° 43' 13.7"	W
Oxisol (LATOSSOLO AMARELO Distrófico típico)	LA (SERRA DA PRATA)	Mucajá-RR	02° 22' 20.3"	N	60° 59' 54.0"	W
Oxisol (LATOSSOLO AMARELO Distrófico típico)	LA (CCA)	Boa Vista-RR	02° 52' 15.9"	N	60° 42' 40.2"	W
Ultisol (ARGISSOLO AMARELO Distrocoeso típico)	PA (CCA)	Boa Vista-RR	02° 52' 22.9"	N	60° 42' 41.8"	W
Oxisol (PLINTOSSOLO ARGILÚVICO Distrófico abruptico)	FT (BONFIM)	Bonfim-RR	03° 32' 14.0"	N	60° 0' 33.3"	W
Alfisol (PLANOSSOLO NÁTRICO Órtico plintossólico)	SN (SURUMU)	Pacaraima-RR	04° 11' 33.2"	N	60° 46' 19.5"	W

**Table 2** - Chemical characterization of soil samples (0-0.20 m layer) from seven classes for P extraction using different extractants

Soil	Chemical Analysis														
	pH	M.O.	P	Ca	Mg	K	Na	Al	H+Al	SB	t	T	m	V	
	g kg <sup>-1</sup>	mg kg <sup>-1</sup>	cmol <sub>c</sub> dm <sup>-3</sup>						----- % -----						
LA (ITÃ)	5.0	19.5	12.2	1.8	1.5	0.0	-	0.2	4.3	3.4	3.6	7.7	5.9	45.3	
LV (ITÃ)	5.5	28.1	20.5	4.8	1.9	0.5	-	0.1	3.2	7.2	7.3	10.4	2.0	68.4	
LA (SERRA DA PRATA)	5.7	12.3	29.2	1.7	1.0	0.0	-	0.0	2.3	2.7	2.7	5.0	0.0	54.0	
LA (CCA)*	4.7	8.9	0.4	0.1	0.0	0.0	-	0.7	2.3	0.1	0.9	2.4	84.1	5.8	
PA (CCA)*	5.0	8.3	0.5	0.0	0.0	0.0	-	0.4	1.7	0.1	0.5	1.8	85.4	3.9	
FT (BONFIM)	5.3	15.4	55.0	2.5	0.9	0.2	-	0.1	2.8	3.6	3.7	6.4	2.7	55.9	
SN (SURUMU)**	5.4	19.0	-	0.2	0.5	0.1	0.1	0.1	1.2	1.0	1.1	2.2	8.8	46.2	

Where: OM: organic matter; SB: sum of bases; t: effective cation exchange capacity; T: total cation exchange capacity; m: aluminum saturation; V: base saturation. \*Adapted from Benedetti *et al.* (2011). \*\*Adapted from Schaefer *et al.* (1993)

**Table 3** - Physical characterization of soil samples (0-0.20 m layer) from seven classes for P extraction using different extractants

Soil	Physical Analysis				
	Sand	Silt	Clay	Silt/Clay	Texture Class
	g kg <sup>-1</sup>				
LA (ITÃ)	610.92	91.60	297.48	0.31	Sandy clay loam
LV (ITÃ)	402.96	177.21	419.83	0.42	Clay
LA (SERRA DA PRATA)	595.22	147.38	257.40	0.57	Sandy clay loam
LA (CCA)*	647.00	79.00	274.00	0.29	Sandy clay loam
PA (CCA)*	869.00	21.00	110.00	0.19	Loamy Sand
FT (BONFIM)	588.85	289.15	122.00	2.37	Sandy loam
SN (SURUMU)**	760.00	120.00	120.00	1.00	Sandy loam

\*Adapted from Benedetti *et al.* (2011). \*\*Adapted from Schaefer *et al.* (1993)

### Extracting available P

Available P was extracted from the soil samples using Mehlich-1 (0.05 mol L<sup>-1</sup> HCl + 0.0125 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>), Mehlich-3 (0.015 mol L<sup>-1</sup> NH<sub>4</sub>F + 0.2 mol L<sup>-1</sup> CH<sub>3</sub>COOH + 0.25 mol L<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub> + 0.013 mol L<sup>-1</sup> HNO<sub>3</sub> + 0.001 mol L<sup>-1</sup> EDTA), Bray-1 (0.025 mol L<sup>-1</sup> HCl + 0.03 mol L<sup>-1</sup> NH<sub>4</sub>F) and AER as extractants. P was extracted from the samples at the end of the experiment.

Extraction with Mehlich-1 and Mehlich-3 followed the methodology described by Embrapa (2009), Bray-1 in accordance with Bray and Kurtz (1945) and AER as reported by Raij *et al.* (2001).

Available P in the samples was determined based on a soil:extractant ratio of 1:10 (5 cm<sup>3</sup> of TFSA and 50 mL of extracting solution) and its content was estimated by molecular absorption using an ultraviolet-visible (UV-Vis) spectrophotometer.

### Greenhouse experiment

The experiment was conducted in a greenhouse at the Agricultural Sciences Center (CCA) of the Federal University of Roraima (Cauamé Campus), in Boa Vista, Roraima state, Brazil. A randomized block design was used, with a 7 x 5 factorial scheme and four repetitions. The first factor consisted of seven soil classes (LA (ITÃ), LV (ITÃ), LA (SERRA DA PRATA), LA (CCA), PA (CCA), FT (BONFIM) and SN (SURUMU)) and the second of five P doses (0, 25, 50, 75 and 100% of maximum P adsorption capacity - MPAC) per soil type, as reported by Matos *et al.* (2017) (Table 5).

### Preparing the experimental unit

A 5 kg sample of each soil class, collected from the 0-0.20 m layer, was previously sieved (4 mm mesh) and placed in 5 L polyethylene pots. Soil chemical analysis indicated the need for liming to raise base saturation to 60% for corn cultivation (RIBEIRO; GUIMARÃES; ALVAREZ, 1999). The soils were incubated with CaCO<sub>3</sub> (TNP 100%) and irrigated daily with distilled

**Table 4** - Mineralogical characterization of soil samples (0-0.20 m layer) from seven classes representative of Roraima state

Soil	Mineralogical Analysis		
	Sand	Silt	Clay
LA (ITÃ)	Gt, Qz	Gt, Qz	Kln, Gt
LV (ITÃ)	Gb, Gt, Hm, Qz	Gb, Gt, Hm, Qz	Kln, Gb, Gt, Hm
LA (SERRA GRANDE)	Gt, Qz	Gt, Qz	Kln, Gt
LA (CCA)*	Gt, Qz	Gt, Qz	Kln, Gt
PA (CCA)*	Gt, Qz	Gt, Qz	Kln
FT (BONFIM)	Mi, Qz	Mi, Qz	Kln, Mi
SN (SURUMU)**	Fd, Mi, Pg, Qz	Fd, Mi, Pg, Qz	Kln, Es, It

Where: Kln: kaolinite; Ep: secondary expandable mineral; Fd: feldspar; Gb: gibbsite; Gt: goethite; Hm: hematite; It: illite; Mi: mica; Qz: quartz. \*Adapted from Benedetti *et al.* (2011). \*\*Adapted from Schaefer *et al.* (1993)

**Table 5** - P doses (0, 25, 50, 75 and 100%) based on the MPAC of the soils studied

Soil	MPAC*	P Doses (% MPAC)				
		0	25	50	75	100
----- g kg <sup>-1</sup> -----						
LA (ITÃ)	244.74	0	61.185	122.37	183.555	244.74
LV (ITÃ)	389.2	0	97.3	194.6	291.9	389.2
LA (SERRA GRANDE)	282.77	0	70.6925	141.385	212.0775	282.77
LA (CCA)	298.72	0	74.68	149.36	224.04	298.72
PA (CCA)	77.24	0	19.31	38.62	57.93	77.24
FT (BONFIM)	527.93	0	131.9825	263.965	395.9475	527.93
SN (SURUMU)	14.5	0	3.625	7.25	10.875	14.5

Where: MPAC: maximum phosphorus absorption capacity. \*Taken from Matos *et al.* (2017)

water to maintain 70% field capacity. Incubation ended after 20 days, when the soils reached pH greater than 6. Corrective fertilization was performed for N, K, S and Zn for the corn crop, in accordance with Ribeiro, Guimarães and Alvarez (1999).

The P doses for each treatment in the different soil types was incorporated into the soil in the pots in the form of a monopotassium phosphate ( $\text{KH}_2\text{PO}_4$ ) solution.

Five days later, 200 g of soil was collected from each experimental unit using a Dutch auger to remove soil across the entire profile. The samples were taken to the drying area and prepared for chemical analysis.

### Greenhouse experiment

Corn (*Zea mays* L.) was cultivated in two successive 30-day cycles, totaling 60 days. The 30F35YH corn hybrid was used (Pioneer, Brazil). Eight seeds were planted in each experimental unit, leaving five plants per pot after thinning.

Topdressing containing N and K in the form of solution was applied 12 days after emergence in both cycles (RIBEIRO; GUIMARÃES; ALVAREZ, 1999). No pest control was needed. Irrigation was performed daily with distilled water to maintain field capacity at 70%.

The plants were cut at ground level 30 days after emergence, with replanting five days after the first phase. The plant material collected in both cycles was placed in paper bags and dried in a forced air oven at 60 °C until constant weight and its mass measured for use in correlation analyses with P extracted via the Mehlich-1, Mehlich-3, Bray-1 and AER methods.

### Statistical analysis

The linear correlation coefficient was determined for extractant x dry weight and extractant x extractant, considering the soils individually and grouped according to the amount of P extracted with the increase in dry weight (SANTOS; KLIEMANN, 2005). All the parameters were compared using the t-test at 5% probability and classified according to Larson and Farber (2015).

## RESULTS AND DISCUSSION

### Relationship between the P doses applied and P extracted using the different methods

The relationship between the P doses applied to the soils and the maximum P content extracted by Mehlich-1, Mehlich-3, Bray-1 and AER was explained by linear functions. The maximum P contents extracted, angular and linear coefficients and coefficients of determination of each function are shown in Table 6.

With the exception of NP, which exhibited the highest angular coefficient, AER was the method that extracted the most P from the soils, with 373.50 mg dm<sup>-3</sup> in LA (ITÃ), 427.25 mg dm<sup>-3</sup> in LV (ITÃ), 286.75 mg dm<sup>-3</sup> in LA (SERRA DA PRATA) and 395.50 mg dm<sup>-3</sup> in LA (CCA) (Table 6). The factors that most influenced this variation were MPAC, soil texture and pH. Due to the increase in pH from liming, part of the P in the soil bonds to calcium (PENN; CAMBERATO, 2019), a non-labile form that is not available to plants (MATOS *et al.*, 2021;

**Table 6** - Coefficients of the linear equations for P extraction by Mehlich-1, Mehlich-3, Bray-1 and AER for the different P doses applied to the soil classes

Soil	Extractant	Y = A*X+B			Max extractable P mg dm <sup>-3</sup>
		A	B	R <sup>2</sup>	
LA (ITÃ)	Mehlich-1	1.733	-4.735	0.982**	169.26
	Mehlich-3	3.271	4.793	0.986**	323.35
	Bray-1	1.137	-8.217	0.964**	109.23
	Resina	3.545	27.650	0.976**	373.50
LV (ITÃ)	Mehlich-1	1.683	0.911	0.887**	197.04
	Mehlich-3	2.967	3.508	0.993**	288.68
	Bray-1	2.976	9.720	0.991**	293.36
	Resin	3.917	28.050	0.975**	427.25
LA (SERRA DA PRATA)	Mehlich-1	0.851	10.849	0.959**	88.93
	Mehlich-3	2.511	-1.179	0.990**	246.40
	Bray-1	0.719	9.129	0.969**	76.99
	Resin	2.948	-3.083	0.991**	286.75

Continuation Table 6

LA (CCA)	Mehlich-1	1.581	-4.996	0.991**	154.21
	Mehlich-3	3.473	10.183	0.995**	351.79
	Bray-1	1.343	-5.797	0.983**	130.97
	Resin	4.050	9.650	0.990**	395.50
PA (CCA)	Mehlich-1	0.481	15.080	0.825**	52.75
	Mehlich-3	0.696	13.516	0.956**	75.77
	Bray-1	0.378	13.114	0.816**	42.30
	Resin	0.683	4.800	0.998**	74.00
FT (BONFIM)	Mehlich-1	3.578	-32.933	0.900**	355.67
	Mehlich-3	1.393	10.734	0.886**	134.20
	Bray-1	3.329	-29.888	0.901**	325.93
	Resin	8.190	-62.300	0.928**	852.50
SN (SURUMU)	Mehlich-1	0.104	2.374	0.862**	14.39
	Mehlich-3	0.086	2.203	0.876**	12.19
	Bray-1	0.097	1.976	0.888**	12.99
	Resin	0.062	1.850	0.806**	9.50

Where: A: angular coefficient; B: linear coefficient; R<sup>2</sup>: coefficient of determination; Max extractable P: maximum extractable phosphorus. \*\*Significant at 1% probability

SILVA; RAIJ, 1999; VINHA *et al.*, 2021). AER cannot extract this form of P, justifying the smaller amounts extracted in LA (SERRA DA PRATA) when compared to the other yellow latosols with similar MPAC. In Itã soils, AER was the most sensitive to texture variations in latosols (Table 6), with a lower available P content in sandy clay loam (373.50 mg dm<sup>-3</sup>) and higher in clayey soil (427.25 mg dm<sup>-3</sup>), as also reported by Santos and Kliemann (2005) and Mumbach *et al.* (2018, 2020).

Mehlich-3 extracted similar values to those observed for AER at most doses (Table 6), with maximum values of 323.35 mg dm<sup>-3</sup> in LA (ITÃ), 288.68 mg dm<sup>-3</sup> in LV (ITÃ), 246.40 mg dm<sup>-3</sup> in LA (SERRA DA PRATA) and 351.79 mg dm<sup>-3</sup> in LA (CCA). Both methods extract similar P forms in these classes, particularly those bound to Fe and Al (ROY, 2017). Mumbach *et al.* (2018) observed similar P extraction efficiency with Mehlich-3 and AER in four different soil texture classes. Steiner *et al.* (2012) reported greater extraction capacity for Mehlich-3 than AER, with a strong correlation between the P extracted and that absorbed by soybean. Nunes *et al.* (2021) studied P extractants in yellow latosol and haplic gleysol and found that although AER was a more efficient extractant, Mehlich-3 is less costly and faster, justifying its use. Dari *et al.* (2019) observed greater extraction capacity for Mehlich-3 compared to other extractants in alkaline soils from Idaho in the United States.

The Mehlich-1 and Bray-1 extracted the least P from latosols (Table 6), with values of 197.04 and

293.36 mg dm<sup>-3</sup>, respectively, in LV (ITÃ). The clayey texture of LV (ITÃ), concomitant to the presence of Fe- and Al-bound P, compromised the efficiency of Mehlich-1, which has a low extraction capacity for these P forms. This result is corroborated by other authors who analyzed the P extraction efficiency of Mehlich-1 (MEDEIROS *et al.*, 2021; NUNES *et al.*, 2021). On the other hand, Bray-1, which preferentially extracts Fe- and Al-bound P (RAIJ; FEITOSA, 1980; SILVA; RAIJ, 1999), showed increased extraction. In LA (ITÃ) without hematite (iron oxide), Mehlich-1 exhibited greater extraction than Bray-1. Wuenschel *et al.* (2015) obtained different results, with Bray-1 performing better in soils from Central Europe than the other chemical methods studied. Dari *et al.* (2019) reported that Bray-1 exhibits limited P extraction in alkaline soils from Idaho, unlike the acidic soils studied here.

In sandy soils with a clay content lower than 150 g kg<sup>-1</sup> in the surface horizon, extraction was influenced by factors such as MPAC, mineralogy and soil pH (Table 3, 4 and 6). In FT (BONFIM), which has the highest MPAC of the soils studied and contains 2:1 clay, extractants based on strong (Mehlich-1) or weak acids (Mehlich-3 and Bray-1) are hampered by the high cation exchange capacity of these soils, thus exhausting the extractants due to the consumption of anions, sulphates and fluorides by aluminum or calcium present in the soil not bound to P (GONÇALVES *et al.*, 2012). As a result, P extraction using these methods was inferior to AER, with

maximum values between 134.20 and 355.67 mg dm<sup>-3</sup> for the acid extractants and 852.50 mg dm<sup>-3</sup> for AER, which simulates the P uptake behavior of the root, extracting large amounts of the element through ligand exchange between bicarbonate and dihydrogen phosphate (SILVA; RAIJ, 1999; VINHA *et al.*, 2021).

PA (CCA) and SN (SURUMU) exhibited similar maximum P extraction values for the different methods tested due to their similar clay contents and basically kaolinitic mineralogy (Tables 3, 4 and 6). Thus, phosphate in its different forms has lower binding energy with its active sites, making it easily dissociated even by extractants with a low dissociation capacity for P-Al, P-Fe (Mehlich-1) and P-Ca (Mehlich-3 and Bray-1). The maximum P extracted remained below 75.77 mg dm<sup>-3</sup> for Mehlich-3 in PA (CCA) and 14.39 mg dm<sup>-3</sup> for Mehlich-1 in SN (SURUMU). Similar results were reported by Raji and Feitosa (1980) in red podzolic soils (red argisols according to SiBCS (EMBRAPA, 2018)) with 14% clay. Rosa, Silva and Maluf (2018) reported high extractable P with the addition of humic acids to quartzarenic neosols containing 4% clay, due to the increase in P adsorption sites. In turn, Mumbach *et al.* (2020) reported superior extraction power for Mehlich-1 when compared to Mehlich-3 in soils with different clay contents.

#### Correlation between the amount of P extracted via the different methods and corn dry weight produced in the different soil classes

In this section, the soils were assessed individually and together considering the amount of P extracted with the increase in dry weight. Correlations between P extracted by Mehlich-1, Mehlich-3, Bray-1 and AER and corn dry weight produced in the soil classes individually and grouped together according to the amount extracted are shown in Tables 7 and 8.

Considering each soil type individually, the amount of P extracted by all the methods shows a strong correlation with the dry weight produced (Table 8). Strong correlations (> 0.78) were observed between the extractants and dry weight in the medium-textured and clayey soils. Bray-1 exhibited greater amplitude between soil correlations, possibly due to its increased sensitivity to iron and aluminum oxide, clay and calcium contents (DARI *et al.*; 2019; ZEHETNER *et al.*, 2018). Matos *et al.* (2021) found that the combination of different soil chemical, physical and mineralogical characteristics in humid tropical regions may explain the high correlations and small amplitudes between soil classes.

Despite the superior P extraction power of Mehlich-3 when compared to Mehlich-1, the correlation with dry weight was similar for all the latosols, indicating that both methods are suitable for estimating available P in this soil class (Tables 7 and 8). Several authors have reported similar results (MUMBACH *et al.*, 2018; NUNES *et al.*, 2021; STEINER *et al.*, 2012). Dari *et al.* (2019) concluded that Mehlich-3 is most adequate in the correlation between soil

**Table 7** - Coefficients of the linear equations for P extraction by Mehlich-1, Mehlich-3, Bray-1 and AER correlated with corn dry weight produced in the soils studied

Extractant															
Mehlich-1				Mehlich-3				Bray-1				Resin			
A	B	R <sup>2</sup>	CV%	A	B	R <sup>2</sup>	CV%	A	B	R <sup>2</sup>	CV%	A	B	R <sup>2</sup>	CV%
LA (ITÃ)															
0.56	47.35	0.75**	10.65	0.14	40.51	0.72**	15.31	0.38	46.42	0.61**	12.89	0.14	36.13	0.81**	14.42
LV (ITÃ)															
0.56	47.35	0.75**	10.65	0.32	46.88	0.69**	20.29	0.31	45.04	0.84**	18.28	0.27	35.26	0.84**	11.39
LA (SERRA DA PRATA)															
0.67	23.46	0.92**	16.68	0.22	31.57	0.86**	23.38	0.77	24.58	0.89**	18.20	0.20	30.85	0.92**	13.55
LA (CCA)															
0.13	23.15	0.70**	23.69	0.06	21.73	0.72**	23.17	0.14	24.10	0.63**	26.63	0.05	21.25	0.79**	21.68
PA (CCA)															
0.32	15.98	0.63**	22.50	0.24	17.10	0.63**	28.15	0.40	15.84	0.61**	18.09	0.29	17.18	0.80**	15.47
FT (BONFIM)															
0.02	34.08	0.56**	17.72	0.06	32.51	0.64**	17.74	0.02	34.40	0.48**	29.99	0.01	33.06	0.81**	14.05
SN (SURUMU)															
0.46	12.82	0.52**	34.84	0.55	12.76	0.51**	35.52	0.44	13.30	0.45**	39.96	1.00	11.40	0.81**	23.54

Where: A: angular coefficient; B: linear coefficient; R<sup>2</sup>: coefficient of determination; CV%: Coefficient of variation. \*\*Significant at 1% probability

**Table 8** – Coefficient of linear extractant x dry weight correlation for each soil individually and grouped according to the amount of P extracted

Soil	Extractant			
	Mehlich-1	Mehlich-3	Bray-1	Resin
Individual Soils				
LA (ITÃ)	0.85**	0.82**	0.78**	0.90**
LV (ITÃ)	0.83**	0.86**	0.83**	0.92**
LA (SERRA DA PRATA)	0.93**	0.96**	0.94**	0.96**
LA (CCA)	0.85**	0.83**	0.79**	0.89**
PA (CCA)	0.79**	0.79**	0.78**	0.90**
FT (BONFIM)	0.80**	0.75**	0.69**	0.90**
SN (SURUMU)	0.72**	0.72**	0.67**	0.90**
Group 1				
LA (CCA) + FT (BONFIM)	0.64**	0.55	0.60**	0.73**
Group 2				
LA (ITÃ) + LV (ITÃ) + LA (SERRA DA PRATA) + LA (CCA) + SN (SURUMU)	0.83**	0.83**	0.85**	0.92**

and plant-available P in alkaline soils in the United States. However, Penn *et al.* (2018) reinforced the sensitivity of these extractants with high soil pH. Despite the strong correlations observed for all the extractants, the authors recorded higher values for AER, indicating more uniform P extraction versus dry weight produced.

Considering the soils with a sandy textured surface (PA (CCA), FT (BONFIM) and SN (SURUMU)), AER exhibited a higher correlation when compared to the other extractants, with a value of 0.90 for these three soil classes (Tables 7 and 8). With the exception of AER, similar correlations were observed for all the extractants, ranging from 0.72 to 0.80 to Mehlich-1, 0.72 to 0.79 for Mehlich-3 and 0.67 to 0.78 for Bray-1. The high CV% of the data obtained for these extractants demonstrates the variable extraction capacity for a same P dose applied to the soil, compromising the correlation between these data with dry weight. On the other hand, Wuenscher *et al.* (2015) studied 14 P extraction methods in 50 soils from Central Europe and observed a greater correlation for Mehlich-3 and Bray-1 when compared to AER. Culman *et al.* (2020) also observed a strong correlation between Mehlich-3 and Bray-1 and dry weight, although the former extracted 35% less P than the latter.

In a bibliographic review of extractant efficiency analyses, Silva and Raij (1999) found that AER was the most suitable method for a wide variety of soils. Several recent studies have reported similar findings (MEDEIROS *et al.*, 2021; MUMBACH *et al.*, 2018; NUNES *et al.*, 2021). By contrast, the results obtained here differ from those of other authors who used AER (DARI *et al.*; 2019; MUMBACH *et al.*, 2020),

which indicates a unique dynamic for phosphate in terms of the heterogeneity of the physical, chemical and mineralogical properties of Brazilian soils and the importance of these studies in different regions.

With regard to soils grouped according to the amount of P extracted in the different classes (Table 8), Group 1 showed a strong correlation only for AER (0.73), with lower values for the remaining extractants (0.64, 0.55 and 0.60 for Mehlich-1, Mehlich-3 and Bray-1, respectively). For Group 2, a strong correlation was observed for all the extractants (0.83 to 0.92), with the highest value recorded for AER. According to Santos and Kliemann (2005), the factors that influence this correlation are unclear, since soils with different characteristics that affect extraction are grouped together. However, the authors defend clustering as a means of validating the correlation indices, given the increased number of points in determining the linear correlation for each group. These results make AER an adequate extractant for determining available P considering the soil classes separated by common characteristics, such as clay content, OM and total cation exchange capacity (T) or the amount of P extracted. Given the difficulties involved in determining fertilization levels for each soil class and its variations, in order to be feasible an extractant should exhibit a correlation with soil groups as opposed to a single class.

#### **Correlation between P contents extracted for the Mehlich-1, Mehlich-3, Bray-1 and AER methods.**

The correlations between Mehlich-1, Mehlich-3, Bray-1 and AER for each soil class are presented in Table 9.

**Table 9** – Linear correlation coefficients for extractant x extractant in each soil type studied

Extractant	Extractant			
	Mehlich-1	Mehlich-3	Bray-1	Resin
LA (ITÁ)				
Mehlich-1	-	0.986**	0.990**	0.945**
Mehlich-3	-	-	0.977**	0.959**
Bray-1	-	-	-	0.929**
LV (ITÁ)				
Mehlich-1	-	0.895**	0.888**	0.953**
Mehlich-3	-	-	0.999**	0.957**
Bray-1	-	-	-	0.959**
LA (SERRA DA PRATA)				
Mehlich-1	-	0.959**	0.986**	0.958**
Mehlich-3	-	-	0.951**	0.971**
Bray-1	-	-	-	0.959**
LA (CCA)				
Mehlich-1	-	0.965**	0.981**	0.975**
Mehlich-3	-	-	0.938**	0.978**
Bray-1	-	-	-	0.952**
PA (CCA)				
Mehlich-1	-	0.955**	0.997**	0.875**
Mehlich-3	-	-	0.952**	0.948**
Bray-1	-	-	-	0.865**
FT (BONFIM)				
Mehlich-1	-	0.763**	0.988**	0.918**
Mehlich-3	-	-	0.740**	0.846**
Bray-1	-	-	-	0.883**
SN (SURUMU)				
Mehlich-1	-	0.987**	0.987**	0.591**
Mehlich-3	-	-	0.975**	0.577**
Bray-1	-	-	-	0.554**

The extractants exhibited a high correlation for the latosol and argisol classes. This demonstrates proportionality between the methods in terms of extraction capacity, suggesting that all four extractants removed similar amounts of different P forms from the soil. Given that the efficiency of chemical extractants is limited to a certain type of phosphate bonding (P-Ca for Mehlich-1 and P-Al and P-Fe for Mehlich-3 and Bray-1), it can be inferred that each extractant counterbalances the minimal dissolution of its non-extractable P forms with larger amounts of the more accessible fraction, as observed by Penn *et al.* (2019). Thus, Mehlich-1 extracted more P-Ca, while Mehlich-3 and Bray-1

preferred P-Al and P-Fe, maintaining extraction proportional to the variation in P doses in the soil. It is important to note that this correlation does not indicate analogous extraction capacities for latosols and argisols, only that the methods extract similar amounts of P at the element concentrations studied (WUENSCHER *et al.*, 2015).

In the case of FT (BONFIM), lower indices were obtained for Mehlich-1 x Mehlich-3 (0.76) and Mehlich-3 x Bray-1 (0.74). In this case, although both have similar principles, the preferred bonding of fluoride with high-valence elements such as Al<sup>3+</sup> and the low

acidity of Mehlich-3 indicates that this extractant is not always efficient at extracting P bound to Ca, with reasonable amounts of the latter element present in the soil in question. These findings are corroborated by Penn *et al.* (2018). The fluoride ion present in both solutions forms a complex with  $Al^{3+}$  in particular and, to a lesser extent,  $Ca^{2+}$ , releasing phosphate which precipitates in the form of calcium fluoride (MEDEIROS *et al.*, 2021; ZEHETNER *et al.*, 2018). Despite the presence of fluoride in both extractants, its higher concentration in Bray-1 (0.03 N  $NH_4F$ ) in relation to Mehlich-3 (0.015 N  $NH_4F$ ) maintained the complexing power of  $Ca^{2+}$  and  $Al^{3+}$  in the former, an important feature in soils with a high concentration of expandable clay minerals, which consume a large part of the fluoride ions due to their elevated T. Different results were reported by Culman *et al.* (2020), with a strong correlation between extraction by Mehlich-3 and Bray-1 in alkaline soils from Ohio, Indiana and Michigan. Mehlich-1, in turn, preferentially removes P-Ca due to the presence of two strong acidic solutions, namely 0.05 mol  $L^{-1}$  HCl and 0.0125 mol  $L^{-1}$   $H_2SO_4$ , with Mehlich-3 extracting higher values in soils containing P-Ca (MEDEIROS *et al.*, 2021).

Correlations between the chemical extractants and AER were low for SN (SURUMU). The selectivity of chemical extractants means they remove phosphate bound to different cations in labile and nonlabile forms (SOUZA; PEGORARO; REIS, 2017; ZEHETNER *et al.*, 2018), whereas AER uses a similar process to that of roots, via porous material with a high bicarbonate-form anion exchange, responsible for P dissolution and subsequent adsorption to AER (GONÇALVES *et al.*, 2012; SILVA; RAIJ, 1999). In less acidic soils with low T, chemical extractants may overestimate plant-available P, extracting nonlabile forms present in the soil. Under these conditions, AER is better suited to extracting P amounts consistent with those available to plants.

## CONCLUSIONS

1. Extraction by Mehlich-1, Mehlich-3, Bray-1 and RTA was strongly correlated with the dry weight produced in the latosols and argisols analyzed, with superior results for AER in FT (BONFIM) and SN (SURUMU);
2. There was a strong correlation between extractants for latosols and argisols. Mehlich-3 exhibited lower correlations with Mehlich-1 and Bray-1 in FT (BONFIM). For SN (SURUMU), the extraction capacity of AER differed from that of the chemical extractants;
3. The resin method is the most appropriate for determining available P in soils from the Brazilian humid tropical

region, showing low sensitivity to variations in the characteristics of the soils studied.

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