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Use and recovery of P reserves in Southern Brazil Oxisols under no-till with low and high P availability

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ABSTRACT: The accessibility of soil P reserves by plants on highly weathered Brazilian soils remains unclear. In this study, we assessed the contribution of soil P fractions to P uptake by soybean plants in two no-till Oxisols (Latossolos), with low and high initial content of available P. The recommended P rates (viz., 153 and 50 kg ha-1 yr-1 in the low-P and high-P soil, respectively) were applied in the form of triple superphosphate (TSP) or Bayovar rock phosphate (BRP) plus a treatment without fertilizer. Yields of winter cereals and soybean on the studied soils were examined over a period of three years. Soil samples were collected in the 0.00-0.10 m soil layer and subjected to sequential chemical fractionation of P. In the last crop season, the P content of soybean shoot biomass was determined. Soil P fractions and P content of soybean shoots were subjected to path analysis. The addition BRP in the low-P soil resulted in a winter cereal yield of 2.0 Mg ha-1 lower than TSP. In the scenario of high P, it is possible to maintain high crop yields even without phosphate fertilization for three consecutive years. Path analyses demonstrated the addition of P using either TSP or BRP boosted the contribution of the more labile inorganic P fractions. The addition of BRP should be avoided in P-deficient soils. The addition TSP or BRP reduces the pressure of plants to use soil P reserves. Therefore, the soil P legacy should be considered in fertilization recommendations for high-P soils in NT.

Keywords: phosphate fertilization, P legacy, P chemical fractionation.

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INTRODUCTION

Strongly weathered tropical and subtropical Oxisols adsorb large amounts of P due to the high Fe and Al oxide content. In the first years of cultivation in these soils, high rates of phosphate fertilizers are necessary because the P adsorption sites are still avid by phosphate, and much of the applied P is immobilized by the soil, adsorbed to Fe and Al oxides with high energy. This initial stage is called soil correction fertilization management. Over time, as the amount of fertilizer added increases, these sites tend to become saturated; P is increasingly weakly retained and, hence more readily available to plants (Rodrigues et al., 2016; Soltangheisi et al., 2018). Then, the soil available P content reaches a critical level, and the amount needed decreases to a minimum value equal to the amount exported by the crops. This step is called maintenance fertilization management.

The best choice of P source to be used in correction or maintenance fertilization management is not yet unanimous (Gatiboni et al., 2013). Triple superphosphate (TSP), a concentrate soluble phosphate fertilizer (20 % of P), has been used as a reference in some studies evaluating phosphate fertilization efficiency (Moreira et al., 2014; Santos et al., 2016; Barreto et al., 2018). Generally, in such studies, less soluble P sources such as thermophosphates and rock phosphates are less agronomically efficient because they cannot release P at the speed crops demand in the short term, especially in P-deficient soils. However, after soil fertilizer such as rock phosphates may be interesting for replacing P exported by crops. In this scenario, crops do not need immediate release of the P added via fertilizer because the soil available P stock is sufficient (Gatiboni et al., 2007).

Soluble phosphate accumulates in moderately labile inorganic fractions (P_i) in the soil (Gatiboni et al., 2013; Soltangheisi et al., 2018), which can be assessed by NaOH extraction and is associated with P binding to Fe and Al oxides (Gatiboni et al., 2013). On the other hand, natural phosphates favor Ca-bound P fractions (Soltangheisi et al., 2018), which can be assessed by HCl extraction. Phosphorus dynamics in the soil become more complex with conservative soil management. In no-tillage (NT) systems, organic matter accumulation on the soil surface reduces P adsorption by Fe and Al oxides (Fink et al., 2016). Reduced soil disturbance and accumulation of plant residues on the soil surface led to increased organic P content (Po) (Rodrigues et al., 2016). Moreover, the high soil pH and high soluble P and Ca content in the soil solution of the first centimeters of NT soil creates favorable conditions for the neoformation of Ca phosphates, transforming soluble P applied via fertilizers into forms unavailable to plants (Gatiboni et al., 2007; Tiecher et al., 2018). Although studies have shown these routes of P forms accumulation in the soil, the extent to which these P form contribute to P uptake by plants remains poorly known in the NT system.

Effects of P sources on soil P reserves can be examined using a sequential chemical fraction. The fractionation scheme proposed by Hedley et al. (1982) involves sequential extraction of P with an anion-exchange resin (AER) and chemical extractors for inorganic (P_i) and organic forms (P_o) of increasing stability or decreasing availability to plants. Phosphorus fractionation results are generally used to investigate how individual P-fractions correlate with available P (Gatiboni et al., 2007; Guardini et al., 2012; Schmitt et al., 2013; Teles et al., 2017). However, the fact that a soil P fraction correlates with the available P does not necessarily mean the two variables are directly or indirectly related. The causal relationship between soil P forms and the way they are supplied to plants can be established by path analysis, which allows the direct contribution of a predictor to a response variable to be estimated using a suitable model (Shipley, 2016). In addition, path analysis allows the indirect contributions of other variables in the model to be assessed and the direction of a causal path to be identified (Shipley, 2016). Path analysis



has been successfully used in combination with chemical fractionation of soil P to assess the contribution of several organic and inorganic P fractions to available P (Ciampitti et al., 2011; Hashimoto et al., 2012; Gama-Rodrigues et al., 2014; Sales et al., 2015; Tiecher et al., 2018; Soltangheisi et al., 2019).

Our initial hypothesis is that plants absorb P from different extractable fractions, including low lability fractions, and the level of P availability in the soil and the solubility of the used phosphate fertilizer influence this. In this study, we used P budget, path analysis, and chemical fractionation of soil P to elucidate the way soluble phosphate (TSP) and Bayovar rock phosphate (BRP) supply P reserves in the soil and how they influence P uptake by plants in NT subtropical Oxisols with low and high initial soil available P content.

MATERIALS AND METHODS

Study site and experimental design

The experiments were conducted in two Oxisols (Soil Survey Staff, 2014), which correspond to *Latossolos*, according to Brazilian Soil Classification System (Santos et al., 2013), in the South-Center region of Paraná State, Southern Brazil (Table 1). In this region, nutrient calibration studies have found the threshold of soil available P for grain crops in the 0.00-0.20 m soil layer is 8.0 mg dm⁻³ extracted with Mehlich-1 solution (Vieira et al., 2015). Therefore, to evaluate our hypothesis, one experiment had the initial soil available P content considered "low" (<4.0 mg dm⁻³, low-P soil), and the other had the initial soil available P content considered "high" (8.0–16.0 mg dm⁻³, high-P soil). The high-P soil experiment started in 2014, and the low-P soil experiment began in 2015.

The experimental design was a factorial block design with one additional treatment $[(2 \times 2) + 1]$ and three replications. The main factor was P sources, one soluble (triple superphosphate - TSP) and another moderately soluble (Bayovar rock phosphate - BRP). The second factor was two fertilization strategies: in the crop-based fertilization strategy, the annual P rate was split and applied before each crop season (summer and winter), and in the system-based fertilization strategy, the annual P rate was applied once a year before the winter crop. The additional treatment received no P.

The P rates used were 50 kg ha⁻¹ yr⁻¹ for the high-P soil and 153 kg ha⁻¹ yr⁻¹ for the low-P soil, following the recommendations of Vieira et al. (2015). Fertilizer rate used for each treatment in each experiment is shown in table 2. Both fertilizers were applied along the sowing line. Soils were cultivated and fertilized for three consecutive years before soil and plant sampling.

Property	High-P soil	Low-P soil
Site	Guarapuava	Campina do Simão
Clay (g kg ⁻¹)	503	600
Total organic carbon (g kg ⁻¹)	27.3	29.6
pH(H ₂ O)	5.4	5.4
Available P extracted by Mehlich-1 (mg dm ⁻³)	11.2	3.3
Available K extracted by Mehlich-1 (cmol _c dm ⁻³)	0.3	0.2
Exchangeable AI (cmol _c dm ⁻³)	0.2	0.1
Exchangeable Ca (cmol _c dm ⁻³)	6.9	4.3
Exchangeable Mg (cmol _c dm ⁻³)	2.4	4.0
Base saturation (%)	65	48
Al saturation (%)	2	4

Table 1. Initial chemical and physical properties of the 0.00–0.20 m soil layer in the low- and high-P studied Oxisols

Table 2. Properties and rates of the used phosphate fertilizers

Property	TSP	BRP
Solubility	Total	Moderate
Total P content (%)	20	13
Soluble P content (%) ⁽¹⁾	20	6
Phosphate rate applied to high-P soil (kg ha ⁻¹ yr ⁻¹)	256	821
Phosphate rate applied to low-P soil (kg ha-1 yr-1)	778	2500

TST: triple superphosphate. BRP Bayovar rock phosphate. ⁽¹⁾ As estimated by extraction with neutral ammonium citrate in water (TSP) or citric acid (BRP).

Grain yield

Grain yield was determined over three years in both experiments. In the high-P site, soybean yield was accessed in 2014/2015, 2015/2016 and 2016/2017, and in the winter, grain yield was accessed for wheat (2014), barley (2015), and oat (2016).

In the low-P site, soybean yield was accessed in 2015/2016, 2016/2017, and 2017/2018, and in the winter, grain yield was accessed for wheat (2016) and barley (2017). Oat grain yield in 2015 was used only for soil cover, and no grain yield was obtained.

Phosphorus content in soybean tissue

Phosphorus content in soybean shoots during the last crop season at each experiment site was used as a proxy for soil available P. For this purpose, the above-ground biomass of soybean was collected at the flowering stage, dried at 60 °C, ground, and digested with a nitric-perchloric acid mixture according to Tedesco et al. (1995). The volume was completed to 50 mL with distilled water, and the P concentration was determined according to Murphy and Riley (1962) method.

Soil sampling

At the end of the third cropping year, soil samples were collected from the 0.00–0.10 and 0.10–0.20 m layers, dried at 50 °C, ground, passed through a 2 mm sieve, and stored for subsequent analysis. One aliquot of the sample was used to determine the soil available P content using the spherical exchange resin method, and another aliquot was used for the sequential chemical fractionation of Hedley et al. (1982).

Available P analysis and P-budget

Soil samples from 0.00–0.10 and 0.10–0.20 m soil layers were analyzed for available P with a Sinth Amberlite IRA-400 anion-exchange resin according to van Raij et al. (2001). Soil P budget was calculated from the initial and final P contents of the 0.00–0.20 m layer (average of the two soil layers), according to equation 1.

$$SB = FS - IS$$

Eq. 1

in which: SB denotes the soil budget, and FS and IS are the final and initial soil available P content, respectively, which were calculated with provision for the average density of the two soils in each experiment.

Effective P budget (Equation 2) was calculated by considering the SB and all P inputs (fertilization) and outputs (grain export). To estimate P grain export, we used an average P content of 4.4 kg Mg⁻¹ of P for the winter crops and 6.1 kg Mg⁻¹ of P for soybean (Vieira et al., 2015).

$$EB = SB - (IF - OG)$$

Eq. 2

4



in which: EB denotes the effective balance of P; SB is the soil budget; IF is the amount of P added via fertilizers; and OG is the amount of exported P via grain crops.

Finally, P recovery was calculated for fertilized treatments as the ratio between EB and the amount of P applied via fertilizers (Equation 3).

P recovery (%) = $EB/IF \times 100$

Eq. 3

Sequential chemical fractionation of soil P

Samples from the 0.00–0.10 m soil layer were subjected to sequential chemical fractionation of P using the method of Hedley et al. (1982). Briefly, 1.0 g of soil samples were treated sequentially with the following extractants: 2.5 cm² plates of AR 103 QDP 434 anion-exchange resin (AER) (inorganic P); NaHCO₃ 0.5 mol L⁻¹ at pH 8.5 (inorganic and organic P); NaOH 0.1 mol L⁻¹ (inorganic and organic P); HCl 1.0 mol L⁻¹ (inorganic P) and NaOH 0.5 mol L⁻¹ (inorganic and organic P). All extractants were allowed to stand in contact with the samples in an endless stirrer at 33 rpm for 16 h and then centrifuged at 3500 rpm for 15 min.

Total P in alkaline extracts in NaHCO₃ and NaOH was estimated by digestion with sodium persulfate and sulfuric acid in an autoclave at 121 °C and subsequent determination of P according to Murphy and Riley (1962) method. Inorganic P (P_i) in the alkaline extracts (NaHCO₃ and NaOH) was determined according to Dick and Tabatabai (1977) method, and P_i in the acid extracts (AER and HCl) according to Murphy and Riley (1962) method. Organic phosphorus (P_o) was calculated as the difference between total and inorganic P in the alkaline extracts. Total residual P (P_{RES}) was determined by digestion with H₂SO₄ and H₂O₂ in the presence of saturated MgCl₂ (Olsen and Sommers, 1982). Phosphorus extracted by the resin and NaHCO₃ was deemed labile; P extracted by NaOH (0.1 and 0.5 mol L⁻¹) and HCl was moderately labile; and residual P was non-labile (Hedley et al., 1982; Tiecher et al., 2018).

Statistical analysis

Grain yield, P balance, and P fractions results were subjected to analysis of variance (ANOVA), and, when significant, the means were compared with the Tukey test at the 5 % probability level.

Contribution of different P fractions to P supply to the plants was assessed using path analysis along if causal testing (Tiecher et al., 2018). Phosphorus in soybean plant biomass (P_{Abs}) was used as a proxy for P availability to plants instead of P extracted by the anion-exchange resin (AER). Although the P content extracted by AER is a good indicator of the amount of P available to the plant, the direct use of the P content absorbed by soybean plants represents a much more realistic and true value of P amount readily bioavailable in the soil. Once it has been demonstrated that residual P contributed inappreciably to P supply to plants (Tiecher et al., 2018) and that the treatments did not influence residual P in our study, we did not use this P fraction in path analysis to simplify the mathematical model.

Path analysis was performed for five situations: without phosphate fertilizers, combining data from the two experimental sites (i), in the low-P soil with the application of TSP (ii) and BRP (iii), and in the high-P soil with the application of TSP (iv) and BRP (v). Briefly, the procedure involved following the d-separation approach to define a set of independent relations between the variables for the proposed causal model to connect P fractions with P uptake by soybean plants (P_{Abs}) and their mutual combinations. Each independent connection involved partial and total correlations, which were evaluated by permutation (Manly, 2007). Each causal model provided a probability value for the composite statistic Fisher's C (Shipley, 2016) that was tested via the χ^2 probability distribution. For the

causal model to be valid, its *p*-value should exceed an acceptable level (p>0.05). For each valid model, regression methodology was used to calculate the corresponding path coefficients and probabilities by permutation (Manly, 2007) in addition to a coefficient of no determination *U*. Variables (factors and responses) were centered and standardized on the variance unit to compare path coefficients (β) between models.

RESULTS

Cumulative grain yield — and hence the amount of P exported — was greater in the high-P soil than in the low-P soils (Table 3). The sum of the harvests of the three years evaluated with fertilization of both P sources resulted in an average grain yield of 15 and 32 Mg ha⁻¹ in the low-P and high-P soil. In the low-P soil, a cumulative rate of 458 kg ha⁻¹ of P increased total grain yield by 375 % (average for the two phosphate fertilizer sources). Each kilogram of P added resulted in an average yield of 33 kg of grain, which is much less than the figure obtained in the high-P soil (212 kg of grain per kilogram of P). In fact, even without P fertilization, over six harvests in the high-P soil reached 94 % of the total grain yield found in the fertilized treatments (Table 3).

Soluble P source (TSP) increased the labile inorganic ($P_{_{IBIC}}$) and moderately labile fractions ($P_{_{OHID-0.1}}$) in both soils (Table 4) and led to more efficient use of P by crops. On the other hand, the increase in $P_{_{IHCI}}$, which extracts Ca-phosphate compounds, was more marked with BRP than with TSP, especially in the low-P soil, where higher rates of phosphate were used. The BRP contains a large amount of apatites (Ca-phosphate minerals) that tend to accumulate in the soil due to their low solubility.

In the absence of fertilizer, most of the P fractions examined directly contributed to the available P absorbed by the plants (P_{Abs}). Path analysis revealed that P_{Abs} were directly supplied (p>0.10) by all the inorganic fractions evaluated. Based on these results, the plants absorbed available P from labile (P_{iBIC}) and moderately labile P fractions ($P_{iHID-0.5}$, P_{iHID-0.5} and P_{iHCI}), which constitute the P reserves of soil (Figure 1). Without P fertilization, the organic moderately labile P fraction ($P_{oHID-0.1}$) showed a direct relationship with P uptake by soybean plants (Figure 1), with a high path coefficient ($\beta = 0.92$).

Cite (Cumul	ative grain	n yield	Initial	Accumula 2014 t	ated from o 2017	Final	Soil	Effective budget ⁽⁴⁾	P recovery ⁽⁵⁾
treatments	Winter	Summer	Sum	available P ⁽¹⁾	P input via fertilizer	P output by grain crop ⁽²⁾	available P	P budget ⁽³⁾		
		– Mg ha-1 –		kg ha-1			kg ha¹ of F)		%
				Low-P site						
No fertilizer	1.1 c	2.5 b	3.6 b	36	0	23	10 c	-26 c	-3 a	-
TSP	4.4 a	11.6 a	16.0 a	36	458.2	89	70 b	35 b	-334 c	27 b
BRP	2.9 b	11.0 a	13.9 a	36	458.2	80	120 a	85 a	-293 b	36 a
	High-P site									
No fertilizer	14.9 a	15.3 a	30.2 a	120	0	159	76 a	-44 a	115 a	-
TSP	16.5 a	15.6 a	32.1 a	120	150.6	167	102 a	-18 a	-1 b	99 a
BRP	16.1 a	15.8 a	31.9 a	120	150.6	167	100 a	-22 a	-5 b	97 a

Table 3. Available phosphorus budget for the 0.00–0.20 m soil layer, cumulative grain yield and P export by grains after three years in two Oxisols with low and high initial soil available P content subjected to no P fertilization, and supplied with triple superphosphate (TSP) and Bayovar rock phosphate (BRP)

Means followed by the same letter in each column for each experimental site were not significantly different by Tukey test at p<0.05. ⁽¹⁾ Calculated from the initial available P content (mg kg⁻¹) extracted by anion exchange resin. ⁽²⁾ P export by grains was calculated using the concentration of 4.4 kg Mg⁻¹ of P for winter cereals (oat, wheat and barley) and 6.1 kg Mg⁻¹ of P for soybean (Vieira et al. 2015). ⁽³⁾ SB = FS – IS (SB = soil budget). ⁽⁴⁾ EB = SB – (IF – OG). EB: effective budget of P; SB: soil budget; IF: inputs of P via fertilizer; OG: outputs of P via grain. ⁽⁵⁾ P recovery = EB/IF × 100.

0.00–0.10 m soil layer supplied with no P fertilization and supplied with triple superphosphate (TSP) and Bayovar rock phosphate (BPR)													
Site/	P uptake by		Soil ino	rganic frac	tions of ph	osphorus		Soil org	anic fracti	ons of phosp	horus	Residual	Tabal D
Treatments	soybean plan	AER	NaHCO ₃ 0.5 mol L ⁻¹	NaOH 0.1 mol L ^{.1}	HCI 1.0 mol L ⁻¹	NaOH 0.5 mol L ⁻¹	Total inorganic	NaHCO ₃ 0.5 mol L ⁻¹	NaOH 0.1 mol L ^{.:}	NaOH ^L 0.5 mol L ⁻¹	Total organic	P	lotal P

Table 4. Total P uptake by soybean plants and soil P fractions in two Oxisols with low and high initial soil available P content in the

	plan		0.5 mol L ⁻¹	0.1 mol L ^{.1}	1.0 mol L ⁻¹	0.5 mol L ⁻¹	inorganic	0.5 mol L [.] 1	0.1 mol L ⁻¹	0.5 mol L ⁻¹	organic		
	kg ha∙¹		mg kg ^{.1}										
						Low-P	site						
No fertilizer	1 b	3 b	4 b	17 a	2 b	24 a	50 c	18 a	255 b	159 b	432 b	825 a	1307 b
TSP	10 a	51 a	31 a	39 a	4 b	19 a	144 ab	20 a	539 a	208 b	767 a	883 a	1796 ab
BRP	6 ab	42 a	7 ab	28 a	147 a	28 a	252 a	26 a	359 b	531 a	916 a	1115 a	2283 a
						High-P	site						
No fertilizer	7 a	14 a	13 a	46 a	4 b	57 b	134 b	19 a	557 b	238 b	814	2280 a	3231 a
TSP	8 a	29 a	20 a	62 a	7 b	68 ab	186 ab	19 a	724 a	303 ab	1046	2444 a	3676 a
BRP	8 a	28 a	21 a	60 a	30 a	81 a	220 a	20 a	614 ab	415 a	1049	2384 a	3653 a

Means followed by the same letter in each column in each experimental site were not significantly different by Tukey test at p<0.05. AER: anion exchange resin.

Soluble P addition using TSP altered the P supply path to plants (Figure 2). In the low-P soil, there was a suppression of the direct contribution of organic P fractions and the direct and indirect contribution of inorganic P of moderate lability ($P_{iHID-0.5}$) (Figure 2a). The direct path coefficient of labile inorganic P (P_{iBIC} , $\beta = 0.74$) to the plant increased compared with the control without P (P_{iBIC} , $\beta = 0.63$). On the other hand, the contribution of inorganic P extracted by HCl (associated with Ca-phosphates) decreased with the addition of TSP ($\beta = 0.84$), compared with the treatments without P ($\beta = 0.91$).

Similar trend in low-P soil was observed in high-P soil (Figure 2b). The main differences were that the increase in the contribution of labile inorganic P was greater ($P_{_{IBIC}}$, $\beta = 0.88$) than that observed in the low-P soil ($P_{_{IBIC}}$, $\beta = 0.74$), and there was total suppression of the supply of P from Ca-phosphates ($P_{_{IHC}}$). In addition, unlike the low-P soil, the addition of TSP in the high-P soil maintained the P supply by the moderately labile organic P, but with a lower path coefficient ($P_{_{OHID-0.1}}$, $\beta = 0.83$) (Figure 2b) than that observed in the control without P ($P_{_{OHID-0.1}}$, $\beta = 0.91$) (Figure 1).

As observed in TSP treatments, the addition of BRP boosted the supply of labile inorganic P to plants. Although the P_{iBIC} path coefficient was greater than that observed in the control without P, it was lower than that observed with TSP. Moreover, the intensity at which the supply of labile inorganic P increased was higher in the soil with high-P (Figure 3b) than in the soil with low-P (Figure 1). On the other hand, in the low-P soil, the contribution of moderate lability Ca-phosphates (Pi_{HCI}) decreased with the addition of BRP ($\beta = 0.84$), compared with the treatment without P ($\beta = 0.84$), and completely suppressed the supply of Pi_{HCI} when added to the high-P soil.

DISCUSSION

We can estimate that during these three years of cultivation, crops could access about 115 kg ha⁻¹ of P from less available forms in the soil (Table 3). Similarly, several studies suggested that P legacy in NT soils can be a potential source of P for crops (Bassamba et al., 2006; Bravo et al., 2006; Zamuner et al., 2008; Gatiboni et al., 2008). Reserves in long-term NT soils lead to high grain yields for three years, thus suggesting the P legacy of soils with a long history of phosphate fertilization was be considered in establishing



the fertilizer rates to be used — if any — for future cultivation (Withers et al., 2018). Our results agree with those of Liu et al. (2017), in China. They estimated that, in some cases, the soil P legacy could maintain agricultural productivity above 90 % for up to 20 years. Thus, the P legacy can reduce the effect of a negative P budget in fertilizer management.

Effective P budget in the high-P soil with the application of both P sources was only slightly negative and very close to zero (-2.6 kg ha-1; Table 3). This means the P rate used is adequate to maintain the P availability in the soil and to restore exports by crops. In the high-P soil, almost all applied P was recovered on export by plants and in the available form in the soil (recovery rate of 98 % on average). On the other hand, the effective P budget was much more negative for both P sources in the low-P soil (Table 3). On average, for both P sources, 313 kg ha⁻¹ of P applied via fertilizer (68 % of the total) in these three years in the low-P soil were accumulated in forms unavailable to plants in the soil. That is, a recovery rate of only 32 %. These results suggest crop yields heavily relied on fertilizer P in the low-P soil (Gatiboni et al., 2007; Pavinato et al., 2009; Soltangheisi et al., 2019). This occurs because there was a greater amount of phosphate adsorption sites in the low-P soil. However, using BRP minimized phosphate adsorption in the low-P soil, thereby increasing the final availability of P with a less negative P budget compared with TSP (-293 vs -334 kg ha⁻¹). This means the amount of P applied that becomes unavailable to plants was smaller with BRP than with TSP. Consequently, the P recovery was higher for BRP (36 %) compared to TSP (27 %). As a result, more P remained in the available form after three years, probably due to the gradual release of P by BRP, which can lead to lower adsorption of high-energy phosphate compared to TSP. However, the gradual dissolution of natural phosphate failed to make P available to an adequate extent for the crops, resulting in winter cereals yields of approximately 2.0 Mg ha⁻¹ lower than the TSP (Table 3). This result indicates that some available and unavailable P fractions can be overestimated in soils treated with rock phosphate (Tiecher et al., 2021), also observed in this study.

Moderately labile organic P ($P_{oHID-0.5}$) was overestimated when BRP was applied (Table 4). This occurs because organic P is not directly measured by chemical fractionation. In the Hedley fractionation procedure, as well as in other similar methods, organic P is calculated as the difference between the total P extracted with alkaline reactants (NaOH) and the molybdate-reactive P, assuming that this difference is organic P (Tiecher et al., 2021). However, several complex inorganic P compounds in these extracts may



Figure 1. Relationship between the inorganic and organic fractions of P in two no-till Oxisols and their contributions to P supply to plants (P_{Abs}) in the absence of P fertilization for three years; Black arrows indicate significant paths (p<0.10).





not react with molybdate, such as pyrophosphate, and they will be accounted for as "organic P" (Turner et al., 2005). In a recent study, Tiecher et al. (2021) found Hedley fractionation overestimate the organic P content about ten times as compared to the amount of organic P detected by ³¹P-NMR method. Even with some possibly overrated fractions, it is also important to note that, even after three years receiving three times higher rates of P, the total P content in the low-P soil fertilized is approximately half that observed in the high-P soil (Table 4). Moreover, the proportion of residual P in the fertilized high-P soil (67 %) is considerably higher than that in the low-P soil (49 %), demonstrating that to reach a level of P availability suitable for crops, it is necessary to add a large amount of P that is adsorbed with high energy in the soil, which is not available to plants.

In the absence of fertilizer, plants may exudate low molecular-weight organic acids in the rhizosphere environment that can release low-labile P_i bound to Fe and Al oxides and dissolve Ca phosphates minerals (Hedley et al., 1982; Condron et al., 1985; Linquist et al., 1997; Fink et al., 2016; Liu et al., 2017). Path analysis shows the depletion of the more available inorganic P fraction (P_{iBIC}) is supplied by the ones less available ($P_{iHID-0.1}$, $P_{iHID-0.5}$) in a ripple effect (Gatiboni et al., 2007; Pavinato et al., 2009). Similar results were reported by Tiecher et al. (2018), who found available P was buffered by inorganic fractions of low and moderate lability in NT Oxisol. These results demonstrate that poorly available fractions can directly and indirectly supply part of the P absorbed





Figure 3. Relationships between inorganic and organic pools of P in no-till Oxisols with a low (a) and a high (b) initial available P content that were supplied for three years basis with P from a source of moderate solubility (Bayovar rock phosphate, BRP) and their contribution to P supply to plants (P_{Abs}); Black arrows indicate significant paths (p < 0.1).

by plants in the absence of fertilization. In soils with high legacy P (such as the high-P site), these processes of P release are sufficient to guarantee high crop yields (94 % of the maximum obtained with P fertilization) even when fertilization is stopped for up to three years (Table 3).

Mineralization of soil organic P forms ($P_{oHID-0.1}$) can be a major source of P to plants in tropical and subtropical soils (Condron and Tiessen, 2005; Cherubin et al., 2016), especially under P-deficient conditions (Chimdi et al., 2014) or in the absence of fertilization. The $P_{oHID-0.1}$ fraction contains moderately labile organic P, particularly orthophosphate monoesters (Hedley et al.,1982; Condron et al., 1985; Linquist et al., 1997; Liu et al., 2017), but also readily mineralized compounds such as P diesters and teichoic acids (Guggenberger et al., 1996; Liu et al., 2017). The P deficiency caused by suppressing P fertilization can trigger plant exudation of acid phosphatase enzymes (Gatiboni et al., 2007) and microbial mineralization of organic P of moderate availability, especially when C and N are present at high levels for microbial proliferation (Richardson and Simpson, 2011; Mander et al., 2012). Similar results were obtained by Soltangheisi et al. (2019), who found the contribution of organic P forms to plants can reach 83 % on average in clayey Oxisols under unfertilized forest and pastureland.

In the consolidated NT system with high-P, phosphate fertilization with TSP may favor biological activity, microbial biomass cycling and organic P mineralization, thereby



releasing organic P to plants (Conte et al., 2003; Gatiboni et al., 2007). Addition of TSP boosted the contribution of more labile inorganic P fractions to plants at the expense of moderately and low-labile inorganic P fractions, thus reducing the pressure of plants to use soil P reserves, that is, the legacy P. The intensity at which the supply of labile inorganic P to plants increased and the supply of moderate labile inorganic P decreased was higher in the soil with high-P than in soil with low-P. In other words, when fertilizing soils rich in P with soluble phosphate, we decrease the potential for using the legacy P. The immediate release of soluble P from TSP facilitated strong phosphate binding to Fe and Al oxides (Pearse et al., 2007; Rodrigues et al., 2016). Adsorption sites saturation with phosphate blocks immobilization and renders the soil surface more negative (Barrow and Debnath, 2014), thereby leading to faster P accumulation in the more labile P fractions, as shown in table 4. Once adsorption sites are occupied, a greater proportion of P added as fertilizer is converted into more readily available fractions, thereby increasing the efficiency of phosphate fertilization (Herrera et al., 2016; Rodrigues et al., 2016).

The HCl 1.0 mol L⁻¹ solution used in the fractionation scheme extracts part of apatitebound P in addition to other poorly soluble Ca phosphates (Hedley et al., 1982). Usually, this fraction is increased by the application of natural phosphates to soil (Soltangheisi et al., 2018) because BRP is reached in apatites poorly crystalline (Barreto et al., 2018). Moreover, NT soils can lead to neoformation of Ca phosphates — particularly in the top few centimeters due to surface liming (Rheinheimer and Anghinoni, 2001; Gatiboni et al., 2007). However, little is known about the contribution of this P fraction to plant nutrition, which is deemed to be a moderately labile P fraction. Based on the path analysis results, Ca phosphates added as natural phosphates and/or precipitated in the soil may contribute directly to P supply to plants in NT soils, but only in low-P soils. Similar results were obtained by Liu et al. (2017), who found the reserves of P associated with Ca to decrease by 55 % in unfertilized Mollisols, and increase by 323 % in P-fertilized soils after 23 years. Calcium phosphates may thus constitute an important P reserve that crops can use after fertilization is suppressed.

Phosphate fertilization alters the way soil makes P available to plants. Both TSP and BRP increased the contribution of the more labile inorganic P fractions and decreased the contribution of the less available inorganic fractions. Therefore, fertilizing soil alleviates the pressure on inorganic and organic P reserves in soil whatever the source. In addition, suppressing fertilization led to plants using P legacy. Therefore, the P legacy constitutes a major source of P for NT soil as it can largely fulfil plant P requirements and reduce the need for high fertilizer rates simply by correcting P deficiency (Rowe et al., 2016; Withers et al., 2018; Soltangheisi et al., 2019). In this way, technicians and farms can use the dynamics of P legacy availability in planning phosphate fertilization in the medium and long term, building reserves through fertilization or using this legacy when necessary. In this scenario, phosphate fertilizer management becomes more flexible and ensures P supply to plants even in years without fertilization.

CONCLUSIONS

In both low- and high-P Oxisols, the P supplied by triple superphosphate and rock phosphate accumulated in the soil mainly in P fractions of low and moderate lability. Rock phosphate should be avoided on P-deficient soils because its gradual dissolution is not sufficient to meet the soil and plant needs, resulting in low crop yields. On the other hand, once reaching a high availability of P in the soil, rock phosphate can be used for replacement of P exported by crops, because crops do not need immediate release of the P added via fertilizer, since the soil available P stock is sufficient. In this scenario, it is possible to maintain high crop yields without phosphate fertilization for three consecutive years, which testifies to the importance of the P legacy accumulating in NT soils.



The proposed causal model, constructed from path analysis results, accurately accounts for differences in P uptake by plants in terms of changes in available P fractions and P reserves from low- and high-P soils. In soils with phosphate fertilization, plants access only labile and moderately labile fractions of P, do not change non-labile P reserves. The intensity at which the supply of labile inorganic P increased and the supply of low lability inorganic P to plants decreased was higher in the soil with high P than in soil with low P. That is, when fertilizing P-rich soils with phosphate fertilizers, we decrease the potential of crops to use the soil P legacy.

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