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SEÇÃO IV - FERTILIDADE DO SOLO E NUTRIÇÃO DE PLANTAS

AVAILABILITY OF A SOLUBLE PHOSPHORUS SOURCE APPLIED TO SOIL SAMPLES WITH DIFFERENT ACIDICITY LEVELS⁽¹⁾

Ricardo Almeida Viégas⁽²⁾, Roberto Ferreira Novais⁽³⁾ & Fernanda Schulthais⁽⁴⁾

SUMMARY

Considerations on the interactions of P in the soil-plant system have a long history, but are still topical and not yet satisfactorily understood. One concern is the effect of liming before or after application of soluble sources on the crop yield and efficiency of available P under these conditions. The aim of this study was to evaluate the effect of soil acidity on availability of P from a soluble source, based on plant growth and chemical extractants. Nine soil samples were incubated with a dose of 200 mg kg-1 P in soil with different levels of previously adjusted acidity $(pH_{H2O} 4.5; 5.0; 5.5; 6.0)$ and 6.5) and compared to soils without P application. After 40 days of soil incubation with a P source, each treatment was limed again so that all pH values were adjusted to 6.5 and then sorghum was planted. After the first and second liming the P levels were determined by the extractants Mehlich-1, Bray-1 and Resin, and the fractionated inorganic P forms. In general, the different acidity levels did not influence the P availability measured by plant growth and P uptake at the studied P dose. For some soils however these values increased or decreased according to the initial soil pH (from 4.5 to 6.5). Plant growth, P uptake and P extractable by Mehlich-1 and Bray-1 were significantly correlated, unlike resin-extractable P, at pH values raised to 6.5. These latter correlations were however significant before the second liming. The P contents extracted by Mehlich-1 and Bray-1 were significantly correlated with each other in the entire test range of soil acidity, even after adjusting pH to 6.5, besides depending on the soil buffering capacity for P. Resin was also sensitive to the properties that express the soil

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buffering capacity for P, but less clearly than Mehlich-1 and Bray-1. The application of triple superphosphate tended to increase the levels of P-Al, P-Fe and P-Ca and the highest P levels extracted by Bray-1 were due to a higher occurrence of P-Al and P-Fe in the soils.

Index terms: tropical soils, Mehlich-1, Bray-1, Resin.

RESUMO: DISPONIBILIDADE DE FÓSFORO DE UMA FONTE SOLÚVEL APLICADA EM AMOSTRAS DE SOLOS COM DIFERENTES NÍVEIS DE ACIDEZ

Considerações históricas sobre a interação do P no sistema solo-planta são ainda atuais e não satisfatoriamente resolvidas. Uma delas diz respeito ao efeito da calagem antes ou após a aplicação de fontes solúveis de P no rendimento das culturas e na eficiência do P disponível nessas condições. O objetivo desse trabalho foi avaliar o efeito da acidez do solo sobre a disponibilidade de P de uma fonte solúvel, por meio do crescimento de plantas e extratores químicos. Amostras de nove solos foram incubadas com uma dose de P (200 mg kg·1) em diferentes níveis de acidez previamente ajustados (p H_{H2O} 4,5; 5,0; 5,5; 6,0 e 6,5), comparativamente à não-adicão de P nos solos. Após 40 dias de incubação do solo com a fonte de P, cada tratamento recebeu uma nova calagem de maneira que todos os valores de pH fossem elevados igualmente para 6,5 e, após essa etapa, foi cultivado sorgo. Após a primeira e a segunda calagem foram determinados os teores de P pelos extratores Mehlich-1, Bray-1 e Resina e, realizado o fracionamento das formas inorgânicas de P. De modo geral, para a dose de Paplicada, os diferentes níveis de acidez não alteraram a disponibilidade deste nutriente, medida pelo crescimento de plantas e pelo Pabsorvido, porém para alguns solos houve aumentos ou decréscimos dessas medidas com o aumento inicial do pH do solo (de 4,5 a 6,5). Correlações significativas foram encontradas entre crescimento de planta, Pabsorvido e o P-extraível pelo Mehlich-1 e pelo Bray-1, mas não para a Resina quando todos os valores de pH foram elevados para 6,5. Todavia, essas mesmas correlações foram significativas antes da realização da segunda calagem. Os teores de P pelos extratores Mehlich-1 e Bray-1 correlacionam-se significativamente entre si para toda a faixa de acidez do solo testada, inclusive após o ajuste do pH para 6,5, além de terem se mostrado dependentes do poder tampão de P do solo. A Resina também se mostrou sensível à propriedades que refletem o poder tampão de P no solo, porém de maneira menos expressiva que o Mehlich-1 e o Bray-1. Com a aplicação do superfosfato triplo ocorreu uma tendência de aumentos nos teores de P-Al, P-Fe e P-Ca e, os maiores teores de P recuperados pelo Bray-1 deve-se à maior ocorrência de P-Al e P-Fe nos solos.

Termos de indexação: solos tropicais, Mehlich-1, Bray-1, Resina.

INTRODUCTION

In view of the growing global fertilizer demand for agricultural production, the understanding and enhancement of the efficiency of fertilizer use in different soils and crops has increasingly been sought. Among the nutrients, P is one of the most limiting to growth and development of plants (Taiz & Zeiger, 2004), especially in tropical environments, given the great power of these more electropositive soils to retain P in forms not available to plants (Novais et al., 2007, Fernandez R. et al., 2008a, b).

Long-standing questions about the interaction of P in soil-plant system are still pertinent and mostly

inadequately investigated. One issue is the time to apply soluble P sources to soils with high drainage/adsorption potential (Novais & Smyth, 1999), whether before or after liming would be most ideal (Kaminski & Mello, 1984), to minimize precipitation of P by Al³+ under acidic conditions, fixing the nutrient (Neto Rolim et al. 2004). On the other hand, hydrolysis of Al³+ with liming, with recent formation of hydroxides would cause, similarly, P fixation by adsorption with ligand exchange (OH \leftrightarrow H2PO4 or HPO4²-) with practical consequences similar to the previous precipitation due to Al³+ (Haynes, 1984).

Studies conducted to evaluate P uptake or plant growth in response to the application of soluble P

sources to the soil, before or after liming, suggest that soil acidity reduces plant growth and P uptake (Bataglia et al. 1984; Kaminski & Mello, 1984). The interpretation of this result, which would indicate decreased P concentration in a solution of acid soils and a likely increase after liming, seems to be misleading. Indeed, the toxicity caused by Al under acidic conditions (Masion & Bertsch, 1997) creates unfavorable condition for the efficiency of plant P uptake, even if a high concentration of the nutrient in the solution is ensured, due to the toxicity caused by Al (Foy, 1984; Silva et al., 2002).

Therefore, the efficiency of soluble P sources in acidic soils is governed particularly by the greater or lesser plant tolerance to Al and not necessarily by the characteristics of soil adsorption for P, modified by varying degrees of acidity (Foy, 1984). In fact, studies that measured P availability under these acidic conditions, in chemical determinations such as maximum P adsorption (Vasconcellos et al., 1974, Gonçalves et al., 1985), Padsorption energy (Ernani et al. 1996), and extractants (Novais et al., 2007), etc., are consistent when addressing the minimal or little influence of soil acidity on the chemical changes in soil P, caused by reactions of precipitation/adsorption. The high value of the point of zero charge (PZC) of oxyhydroxides in tropical soils, highly affected by weathering (Mello & Novais, 2007), is the main reason for this fact.

Another question concerns inorganic P forms in soil and P availability for plants. It could be more convenient for plants to have more P-Ca in soils with high P adsorption capacity than P-Al and P-Fe, which are theoretically more stable forms than the first (P-Ca), generated from the dissolution of applied P-Ca (rock phosphates). It can be concluded that low levels of P-Al and P-Fe are more limiting to plant growth than high levels of P-Ca (Novais & Smyth, 1999; R. Fernández et al, 2008a, b).

The extractant Mehlich-1, used nation-wide in laboratory routine analyses, is composed of strong diluted acids and may overestimate the available P levels of soils treated with rock phosphate or in which the levels of inorganic P-Ca are higher due to low weathering (Novelino et al., 1985). On the other hand, it can underestimate the values of available P in soils with high clay content, as a consequence of the exhaustion of the extractant under such conditions (Novais & Kamprath, 1979a; Muniz et al., 1987). However, the Resin method is also questioned with regard to the probable underestimation of labile P, especially in soils with high P adsorption capacity (Campello et al., 1994). A recent study confirms this fact (Schlindwein & Gianello, 2008).

The purpose of this paper was to evaluate the effect of soil acidity on the availability of P from a soluble source, measured by plant growth and by chemical extractants.

MATERIAL AND METHODS

Samples were collected from the 0–20 cm layer of nine soil types, in the state of Minas Gerais, for chemical and physical analyses (Table 1). The maximum P adsorption capacity (MPAC) and the constant related to P adsorption energy (PAE) were estimated using the Langmuir isotherm (Olsen & Watanabe, 1957), adjusted with the points of region II (Novais & Smyth, 1999).

The samples were air-dried, sieved through 2 mm mesh, homogenized and treated with increasing doses of a mixture of CaCO₃ and MgCO₃ (molar ratio 4:1), defined by an incubation curve, required to raise the pH (H_2O) of these subsamples to 4.5; 5.0; 5.5, 6.0 and 6.5 and then packed in plastic bags. After 30 days of incubation at moisture adjusted to field capacity the samples were air-dried, sieved through 2 mm mesh and homogenized. Each sample was treated with 200 mg kg⁻¹ P as triple superphosphate, sieved through 0.25 mm mesh, and homogenized with the whole soil mass. Soil samples under natural conditions, without P addition, were used as control. The treated samples were incubated for 40 days (moisture at field capacity). After this period, the samples were air-dried and sieved again. Then the pH_{H2O} of each sample was determined by adding corrective lime to initially raise all pH values to 6.5. The samples were incubated again for 30 days. After this period they were dried, sieved and separated into portions of 1.7 kg of soil and filled in plastic pots, with four replications. At this stage, standard fertilization was applied according to Alvarez V. (1974), minus P, and sorghum (Sorghum bicolor L. Moench) hybrid "Br 300" was sown, thinned to 10 plants per pot after emergence. Five days after thinning K was topdressed in KCl solution to increase the nutrient content of each soil sample to 150 mg kg⁻¹ K.

During crop growth, daily irrigations maintained soil moisture near field capacity, and weekly N topdressings of 75 mg/pot were applied in solution, in the form of NH_4NO_3 .

Thirty-five days after emergence, the plant shoots were cut at the ground and dried to constant weight in a forced-air oven at 70 °C. After determining the shoot dry weight, the plant material was ground and homogenized. These samples were then subjected to nitroperchloric digestion (Sarruge & Haag, 1974), analyzed, and the P levels in this extract, as well as in the others obtained in this study, were determined using a colorimetric method of ascorbic acid, proposed by Braga & Defelipo (1974).

For analysis of the P content and inorganic P forms, soil samples were taken from each treatment before and after the second liming. Phosphorus levels were determined by the extractants Mehlich-1, Bray-1 and Resin. For Mehlich-1 and Bray-1, the soil: solution ratio was 1:10, with a shaking time of 5 min. For resin, the method proposed by Raij et al. (1987) was used,

Table 1. Chemical and physical properties of the surface samples (0-20 cm) of the studied soils

Duranton					Soil				
Property	SL	Tb	Ac.	Vi1	Vi2	It.	Ci.	Di1	Di2
pH in H ₂ O (1:2.5)	4.62	4.09	4.14	4.30	4.28	4.52	4.05	4.60	4.49
Al (cmol _c dm ⁻³) (1)	1.6	1.8	0.6	1.4	1.4	0.2	1.1	1.4	0.6
Ca (cmol _c dm ⁻³) (1)	0.70	0.16	0.07	0.60	0.40	0.10	0.02	0.30	0.30
$ m Mg~(cmol_c~dm^{-3})^{~(1)}$	0.10	0.07	0.06	0.40	0.20	0.05	0.20	0.10	0.10
K mg dm ⁻³ (2)	49	54	21	48	52	6	32	80	48
Saturation by Al (%)	63.3	83.0	76.5	55.5	65.6	54.7	78.5	69.8	53.4
Saturation by bases (%)	36.7	17.0	23.5	44.5	34.4	45.3	21.5	30.2	46.6
H+Al (cmol _c dm ⁻³)	1.60	1.80	0.60	1.40	1.40	0.20	1.10	1.40	0.60
effective CTC (cmol _c dm ⁻³)	2.5	2.2	0.8	2.5	2.1	0.4	1.4	2.0	1.1
P Mehlich-1 (mg dm ⁻³) ⁽³⁾	4.8	4.4	1.2	2.1	2.7	0.2	0.2	8.8	1.6
P Bray-1 (mg dm ⁻³) ⁽⁴⁾	5.8	8.4	2.1	4.2	5.1	1.2	1.0	11.5	1.2
P Resin (mg dm ⁻³) ⁽⁵⁾	4.3	5.2	0.7	2.6	6.1	1.1	0.4	6.2	1.4
P remnant (mg L-1) ⁽⁶⁾	5.9	16.8	15.5	13.1	22.6	5.2	10.4	23.5	12.4
MPAC (mg cm ⁻³) (7)	1.464	1.029	1.044	1.136	0.680	1.400	1.060	0.630	1.253
PAE (L mg ⁻¹) ⁽⁸⁾	0.523	0.348	0.490	0.472	0.430	0.567	0.749	0.380	1.128
Organic Carbon (g kg-1)(9)	40.9	24.9	15.6	35.8	28.8	17.5	12.1	25.3	10.9
Coarse sand (g kg ⁻¹) ⁽¹⁰⁾	90	420	230	170	190	80	80	330	170
Fine sand (g kg ⁻¹) ⁽¹⁰⁾	180	90	140	140	230	230	390	330	200
Silt (g kg ⁻¹) ⁽¹⁰⁾	150	40	40	70	80	60	80	60	140
Clay (g kg ⁻¹) ⁽¹⁰⁾	580	450	590	620	500	630	450	280	490
Moisture Equiv. (%)(11)	32	17	24	31	26	25	22	27	23
Field capacity (%) (11)	35	25	28	34	31	34	25	31	28
Total Al ₂ O ₃ (%) (12)	25.5	6.1	6.1	20.9	16.1	5.9	4.6	12.2	7.9
Total Fe ₂ O ₃ (%) $^{(12)}$	10.9	0.0	4.0	9.2	6.2	2.1	1.2	3.3	7.2

^{(1983). (1983). (1983). (1983). (1984). (1984). (1984). (1984). (1984). (1985)}

with a soil: solution ratio of 1:1, and 16 h of shaking. Then the inorganic P forms were subdivided, as proposed by Chang & Jackson (1957) and adapted by Braga (1980).

The treatments were arranged in a randomized block design with four replications. The experiment had a 9 x 6 factorial design, corresponding, respectively, to the soil and pH levels, including the control.

Correlations between variables were calculated and regressions fitted to the data of dry matter production as the dependent variable of different acidity levels at which the different soil samples were incubated with soluble P source and, on this basis, the pH $_{\rm H2O}$ values related to the lowest production estimated. Regression equations were selected by testing the coefficients of the components of each model to a level of 5 %.

RESULTS AND DISCUSSION

Plant growth and phosphorus uptake

Incubation of soil samples with triple superphosphate, not considering the control (no P application), at

different pH values, appears to influence plant growth and P absorption in most soils significantly (Table 2). For some soils, these two variables increased or decreased with rising pH during the initial incubation period of the P source in the soils at increasing pH levels. Thus, the different regression models adjusted for dry matter production as dependent variable of the pH in soil incubated with superphosphate, suggest a differentiated behavior of P applied in relation to the chemical particularities of some soils (Table 3). Estimation of the soil pH, corresponding to the lower dry matter production (Table 3) indicated accentuated variation, ranging from 4.5 to 6.5. This fact, coupled with the occurrence of non-significant differences in dry matter production in most soils, indicates that increased P availability for plants is not always verified by applying a soluble source of this nutrient to limed soils, since the transformation of labile into a nonlabile P happens in very short time intervals and is apparently little related to the initial soil pH (Novais et al., 2007).

In literature, it appears that application of lime prior to the soluble P source promotes increases, decreases or no change in plant P availability (Mendez

Table 2. Effect of incubation of soil samples fertilized with triple superphosphate, at varying acidity levels, on sorghum growth and phosphorus uptake

Ca:1						pН	$H_2O^{(1)}$					
Soil	4.5	5.0	5.5	6.0	6.5	T ⁽²⁾	4.5	5.0	5.5	6.0	6.5	T ⁽²⁾
		Dry mat	erial pro	duction (g	g/pot)			P accu	mulated i	n the sho	ots (mg/po	t)
S.L	11.08	9.97	12.49	10.85	11.85	1.16	12.63	11.27	14.11	11.94	13.04	1.20
Tb.	14.65	12.77	12.02	11.93	11.36	1.14	19.34	15.71	15.39	14.91	15.68	0.71
Ac.	10.84	10.97	11.47	12.70	12.23	1.00	10.80	9.98	10.32	11.81	11.76	0.77
Vi1	8.00	9.51	8.44	8.71	9.15	1.13	6.64	9.03	9.54	9.93	9.97	0.59
Vi2	12.63	13.40	11.71	12.02	12.73	2.11	17.18	16.88	15.93	16.71	16.68	1.11
It.	10.45	11.15	10.71	9.20	9.67	1.90	9.19	9.70	9.21	8.19	8.90	0.53
Ci.	12.74	10.10	11.73	11.30	11.91	1.87	11.59	9.19	10.04	11.75	10.36	0.52
Di1	22.12	21.78	18.43	22.41	24.66	2.11	28.98	29.19	25.80	31.15	32.30	1.18
Di2	11.02	8.66	10.48	10.88	9.76	1.28	9.04	7.71	8.59	9.14	8.00	0.59
Mean	12.61	12.03	11.94	12.22	12.59	1.52	13.85	13.18	13.21	13.95	14.08	0.8
		P conte	nt in sho	ots (g kg	1)		P extracted by the plant (%)					
S.L	1.14	1.13	1.13	1.10	1.10	1.03	3.36	2.96	3.79	3.15	3.19	
Tb.	1.32	1.23	1.28	1.25	1.38	0.62	5.48	4.41	4.32	4.18	4.40	
Ac.	0.93	0.91	0.90	0.93	0.91	0.77	2.74	2.71	2.81	3.25	3.23	
Vi1	0.83	0.95	1.13	1.14	1.09	0.52	1.78	2.48	2.63	2.75	2.76	
Vi2	1.36	1.26	1.36	1.39	1.31	0.53	4.73	4.64	4.36	4.59	4.64	
It.	0.88	0.87	0.86	0.89	0.92	0.28	2.54	2.70	2.55	2.25	2.46	
Ci.	0.91	0.91	0.89	1.04	0.87	0.28	3.26	2.55	2.80	3.30	2.89	
Di1	1.31	1.34	1.40	1.39	1.31	0.56	8.18	8.24	7.24	8.81	9.15	
Di2	0.82	0.89	0.82	0.84	0.82	0.46	2.49	2.09	2.35	2.51	2.18	
Mean	1.06	1.05	1.09	1.11	1.08	0.56	3.84	3.64	3.65	3.87	3.88	

⁽¹⁾ pH values corresponding to the incubation environment of the triple superphosphate. (2) Soils without P application. SL: Sete Lagoas (clayey LV); Tb.: Taobeiras (clayey LVA); Ac.: Acesita (clayey LVA); Vi1: Viçosa Tiro de Guerra (very clayey LVA); Vi2: Viçosa Sítio da Economia (clayey LVA); It.: Itamarandiba (very clayey LV); Ci.: Cimetal (clayey LVA); Di1: Dionísio 1 (loamy LVA) and Di2: Dionísio 2 (clayey LVA). P extracted was obtained by the ratio between P accumulated in the shoots minus P in control and the amount of P appllied to each soil sample, multiplied by 100.

Table 3. Regression equations adjusted for dry matter production (g/pot) of the sorghum shoots as a variable of the pH $_2$ O of soil incubated with triple superphosphate incubation

Soil	Equation	R ²	$pH_{\rm H_2O}{}^{(1)}$
SL	$\hat{y} = \overline{y} = 11.25$		
Tb	$\hat{y} = 20.207 - 1.4865** \text{ pH}$	0.843	$6.5^{(2)}$
Ac Vi1	$\hat{\mathcal{Y}} = 6.56274 + 0.9255** \text{ pH}$ $\hat{\mathcal{V}} = \overline{\mathcal{V}} = 8.76$	0.803	$4.5^{(2)}$
Vi2	$\hat{y} = \overline{y} = 12.50$		
It	$\hat{y} = \overline{y} = 10.24$		
Ci	$\hat{\mathcal{Y}} = \overline{\mathcal{Y}} = 11.56$		
Di1	$\hat{y} = 121.929 - 38.1748** \text{ pH } + 3.57436** \text{ pH}^2$	0.723	5.3
Di2	$\hat{\mathcal{Y}} = 696.072 - 379.477^{\text{ns}} \text{ pH} + 64.3136 \text{ pH}^2 - 4.18144** \text{ pH}^3$	0.971	5.0

⁽¹⁾ Estimated pH corresponding to the lowest production. (2) Observed pH corresponding to the lowest production. SL: Sete Lagoas (clayey LV); Tb.: Taobeiras (clayey LVA); Ac.: Acesita (clayey LVA); Vi1: Viçosa Tiro de Guerra (very clayey LVA); Vi2: Viçosa Sítio da Economia (clayey LVA); It.: Itamarandiba (very clayey LV); Ci.: Cimetal (clayey LVA); Di1: Dionísio 1 (LVA loam) and Di2: Dionísio 2 (clayey LVA). ^{ns} and **: non-significant and significant at 1 %, respectively.

& Kamprath, 1978; Haynes & Ludecke, 1981; Kunich, 1982). Results show that dry matter production and plant recovery of applied P are highest in the soils with lowest clay content and lowest MPAC and highest remnant P values (Tables 1, 2 and 4). These results are similar to those obtained by other

researchers (Bahia Filho, 1982; Fabres, 1987; Moura Filho, 1990), which can be explained by the lower P adsorption in soils less buffered (Novais & Smyth, 1999; Fernández et al., 2008a, b) and consequently by the increased diffusion under this condition (Villani et al., 1993).

Table 4. Simple linear correlation coefficients between some soil properties and the mean values of recovery of phosphorus applied to sorghum

Property	P extracted
P-remman (mg L ⁻¹)	0.740*
MPAC (mg cm ³ of P in soil)	-0.757**
PAE (L mg ⁻¹)	$-0.514^{ m ns}$
Clay (%)	-0.840**

ns, *, **: non-significant and significant at the level of 5 and 1 %, respectively, MPAC: maximum P adsorption capacity; PAE: P Adsorption Energy.

It is observed that in certain situations and more clearly in Tb soil (clayey LVA), both dry matter production and P uptake by sorghum decreased with increasing pH (Table 2). This fact is possibly associated to changes caused by liming on soil constituents associated to P adsorption. The new P adsorption sites formed (Al-OH and Fe-OH) as a result of liming, become less active over time (Sims & Ellis, 1983). Considering some methodological aspects used in this study and, in particular, those associated to the time factor, the hypothesis that this effect was more pronounced in an acidity level corresponding to pH 6.5, compared to pH 4.5, seems reasonable.

Chemical extractants

The correlations between the mean dry matter production and P uptake by sorghum with the P levels recovered by extractants for Mehlich-1 and Bray-1, unlike for resin, were significant (Table 5). This is possibly due to the higher sensitivity of Mehlich-1 and Bray-1 to the buffering capacity of soil P, similarly to the plant Plant buffering capacity or plant P uptake (Novais & Smyth, 1999). However, when regressions

of plant P uptake are adjusted as related to P extracted by Mehlich-1, Bray-1 or resin, and are included in the regression properties that reflect the P buffering capacity in soil (clay content, remnant P or MPAC), particularly those related to Resin-extracted P, the entry of these properties in the model is significant (Table 6). This fact is in agreement with data found by Campello et al. (1994) and Schlindwein & Gianello (2008), indicating that resin is sensitive to the P adsorption capacity factor, however less expressive than Mehlich-1 and Bray-1.

According to Holford & Mattingly (1979) and Holdorf (1980), an extractant is considered sensitive to the P buffering capacity in soil if P is extracted in direct relation to the P-labile content, but inverse to the P buffering capacity in soil. Thus, a comparison of the estimated percentage of P-triple superphosphate, extracted by the plant, with P contents evaluated by Mehlich-1 and Bray-1, indicated highest P contents in soils with lowest clay levels and presumably the lowest buffering capacity of P (Table 1, 2 and 4). Thus, in soil Di1 (loamy LVA), with the lowest MPAC value, dry matter production and P accumulated and

Table 5. Simple linear correlation coefficients between the mean values of dry matter and phosphorus accumulated in sorghum shoots and phosphorus extracted by Mehlich-1, Bray-1 and Resin, after adjusting the different values of pH_{H^2O} soil to 6.5

Extractant	Dry matter	Accumulated P
Mehlich-1	0.881**	0.935**
Bray-1	0.784**	0.858**
Resin	$0.255^{\rm ns}$	$0.270^{ m ns}$

ns and **: non-significant and significant at 1 %, respectively.

Table 6. Regression equations adjusted to plant P uptake as related to P extracted by Mehlich-1, Bray-1 or resin and properties that reflect the buffering capacity of P in soil

Equation	${f R}^z$ adjusted	
$\hat{y} = 3.57654 + 0.2171^{**} P_{\text{Mehlich-1}}$ $\hat{y} = 3.51180 + 0.172492^{**} P_{\text{Bray-1}}$	0.641 0.594	
$\hat{y} = 0.427860 + 0.513880^{**} P_{\text{Resina}}$ $\hat{y} = 26.0175 + 0.116923^{\circ} P_{\text{Mehlich-1}} - 0.3463238^{*} \text{ Clay}$	0.624 0.798	
$\hat{y} = 1.04520 + 0.162946^* + P_{\text{Mehlich-1}} + 0.367070^{\text{ns}} \text{ P-remman}$ $\hat{y} = 16.7199 + 0.161603^* P_{\text{Mehlich-1}} - 9.724267^{\text{ns}} \text{ MPAC}$ Bray-1	$0.681 \\ 0.736$	
$\begin{array}{l} \hat{y} = 27.376 + 0.0871145^{ns} \ P_{\text{Bray-1}} - 0.366796 ^{**} \ \text{Clay} \\ \hat{y} = 0919686 + 0.125040 ^{**} \ P_{\text{Bray-1}} + 0.391775^{ns} \ P\text{-remman} \\ \hat{y} = 17.2457 + 0.124615 ^{**} \ P_{\text{Bray-1}} - 10.0633^{ns} \ \text{MPAC} \end{array}$	0.777 0.640 0.690	
$\begin{array}{ll} \mathbf{Resin} \\ \hat{y} = \ 24.6124 + 0.261866^{\mathrm{ns}} \ P_{\mathrm{Resina}} - 0.352899^{\mathrm{o}} \ \mathrm{Clay} \\ \hat{y} = \ -2.98411 + 0.385389^{\mathrm{e}} \ P_{\mathrm{Resina}} + 0.441162^{\mathrm{o}} \ P_{\mathrm{remman}} \\ \hat{y} = 13.8994 + 0.378238^{\mathrm{e}} \ P_{\mathrm{Resina}} - 9.78046^{\mathrm{a}} \ \mathrm{MPAC} \end{array}$	0.773 0.732 0.716	

ns, a, o, * and **: non-significant, significant at 12;10;5 and 1 %, respectively.

extracted by sorghum were highest (Tables 1 and 2) showing, particularly in this soil, the greater efficiency of the plant drain compared to the soil drain.

Fractionation of inorganic P forms

Applying triple superphosphate to the soil similarly increased the values for P-Al, P-Fe and P-Ca (Table 7).

For the same P dose applied, the levels of this nutrient extracted by Mehlich-1, Bray-1 and resin were variable among soils (Table 8), due to the difference in chemical composition between extractants, resulting in an unequal extraction of P from inorganic forms in soils. The acidity of Bray-1 and especially Mehlich-1 causes a specific unequal action for P-Ca solubilization. However, the presence of fluoride in Bray-1 leads to Al complexation and a more efficient solubilizing action for the P-Al form, although with

lower efficiency for the P-Fe form (Thomas & Peasle, 1973; Novais & Kamprath, 1979b). Thus, increased P levels extracted by Bray-1 reflect a higher incidence of P-Al and P-Fe forms in soils (Table 9). Furthermore, the significant (p < 0.01) correlation of P-Al with the P content extracted by Melhich-1 indicates, as theoretically expected, the extraction of P in this form by the sulfate of Mehlich-1.

The adjustment of correlations between dry matter yield and P accumulated in the plant shoots with the levels of P-Al, P-Fe and P-Ca (Table 10) shows that these correlations tend to be significant (p < 0.1) and positive for P-Al, thus highlighting the importance of this P form for plant growth and development (Novais et al., 2007). In the case of P forms P-Fe and P-Ca, these correlations tend to be negative and not significant.

Table 7. Fractionation $^{(1)}$ of the inorganic P forms in soil as related to the pH (4.5; 5.5 and 6.5) and the application of 200 mg kg $^{-1}$ of triple superphosphate in the samples studied before and after the second liming, to raise the pH of samples to 6.5

~		Bef	ore pH adju	stment	After	pH adjustm	ent	T (3)
Soil	P form	4.5	5.5	6.5	6.5	6.5	6.5(2)	T
				mg	dm ⁻³ —			
	P-Al	132.9	130.7	132.9	102.9	98.9	89.0	12.0
SL	P-Fe	169.1	156.5	169.1	130.7	132.9	144.5	13.1
	P-Ca	35.1	29.8	27.2	36.9	35.1	29.8	2.1
	P-Al	137.5	121.8	139.3	124.0	109.1	113.3	4.9
Tb.	P-Fe	52.7	49.3	64.9	73.9	70.3	64.9	52.4
	P-Ca	16.4	16.7	20.5	16.4	16.4	15.6	4.3
	P-Al	52.7	54.4	49.3	32.9	32.9	26.6	13.1
Ac.	P-Fe	169.1	174.3	164.0	132.9	137.5	126.2	92.5
	P-Ca	24.6	24.6	25.5	27.2	34.4	29.8	4.3
	P-Al	81.4	83.2	77.6	51.0	49.3	44.3	7.8
Vi1	P-Fe	154.1	151.7	159.0	149.8	146.9	159.0	46.4
	P-Ca	40.7	42.6	36.9	18.0	29.8	24.6	6.6
	P-Al	77.6	64.9	63.1	44.3	37.7	39.4	8.9
Vi2	P-Fe	146.9	149.2	154.1	156.5	149.2	164.0	46.4
	P-Ca	29.8	23.8	29.8	28.0	22.9	31.5	6.2
	P-Al	56.1	59.6	54.4	42.6	41.0	36.1	9.9
It.	P-Fe	87.1	96.9	87.1	119.7	126.2	117.5	49.4
	P-Ca	12.5	16.4	14.9	17.2	17.2	18.8	5.5
	P-Al	57.8	56.1	51.0	47.6	37.7	37.7	3.8
Ci.	P-Fe	85.2	90.9	100.9	100.9	109.1	109.1	21.0
	P-Ca	22.9	22.1	36.9	19.7	19.7	20.5	3.6
	P-Al	119.7	117.5	98.9	102.9	100.9	94.9	15.3
Di1	P-Fe	87.1	85.2	87.1	100.9	100.9	100.9	29.8
	P-Ca	22.1	28.9	27.2	24.6	29.9	26.3	5.1
	P-Al	77.6	81.4	50.1	42.6	42.6	41.0	1.9
Di2	P-Fe	161.5	164.0	144.5	144.5	151.6	159.0	15.3
	P-Ca	33.3	35.1	24.5	33.3	38.8	34.2	2.1
Overall	P-Al	88.1	85.5	79.6	65.6	61.1	58.0	8.6
Mean	P-Fe	123.6	124.2	125.6	123.3	125.0	127.2	40.7
	P-Ca	26.4	26.7	27.0	24.6	27.1	25.7	4.7

⁽¹⁾ Only in soils with pH incubation values 4.5; 5.5 and 6.5. (2) Soils with pH value adjusted to 6.5 in the first liming were incubated for 30 days, then fertilized with P and incubated again for 40 days, without a second liming, since their pH values had been adjusted previously to 6.5 in the first liming. (3) T: Soils without addition of P. SL: Sete Lagoas (clayey LV); Tb.: Taobeiras (clayey LVA); Ac.: Acesita (clayey LVA); Vi1: Viçosa Tiro de Guerra (very clayey LVA); Vi2: Viçosa Sítio da Economia (very clayey LVA); It.: Itamarandiba (very clayey LV); Ci.: Cimetal (very clayey LVA); Di1: Dionísio 1 (loamy LVA) and Di2: Dionísio 2 (clayey LVA).

Table 8. Phosphorus content in soil as determined by the extractants Mehlich-1, Bray-1 and Resin, before and after the adjustment of different pH values to 6.5

a		Before	e pH adju	stment		M		After	pH adju	stment		Mean
Soil	4.5	5.0	5.5	6.0	6.5	Mean	6.5	6.5	6.5	6.5	6.5 (1)	Mea
					P-N	Лehlich-1 (1	ng dm ⁻³)					
SL	53.5	53.5	49.0	48.1	51.7	51.2	36.4	34.1	38.0	36.6	32.6	35.
Tb.	82.7	90.1	87.6	86.4	83.9	86.2	73.6	61.1	72.5	67.2	64.1	67.
Ac.	30.3	32.6	31.0	34.1	29.5	31.5	23.7	24.4	22.3	24.4	22.3	23.4
Vi1	49.9	34.1	37.2	34.9	35.7	38.3	29.5	28.8	28.1	23.7	28.8	27.8
Vi2	43.8	43.0	33.3	35.7	37.2	38.6	37.2	34.1	31.0	34.1	37.7	34.8
It.	15.5	13.6	18.2	16.9	18.9	16.6	11.7	12.3	14.2	14.2	16.9	13.9
Ci.	28.8	24.4	22.3	26.6	34.1	27.2	19.6	17.5	18.2	16.9	20.2	18.5
Di1	95.3	91.4	87.6	87.6	86.4	89.7	106.5	99.9	99.4	96.7	102.2	100.9
Di2	29.5	27.3	30.3	27.3	31.8	29.3	19.6	23.7	22.3	20.9	24.4	22.5
Mean	47.7	45.6	44.1	44.2	45.5	45.4	39.8	37.3	38.4	37.2	38.8	38.3
					P-1	Bray-1 (mg						
SL	52.6	51.7	52.6	48.1	44.7	49.9	44.7	40.5	41.3	38.0	39.7	40.
Tb.	124.0	117.3	117.3	108.0	100.8	113.5	98.0	90.1	87.6	95.3	91.4	92.
Ac.	32.7	34.6	30.1	28.5	24.5	30.1	25.5	28.9	26.2	27.3	25.5	26.
Vi1	51.7	40.5	44.7	43.8	37.2	43.6	37.2	34.1	34.9	34.1	36.6	35.4
Vi2	66.1	65.1	46.4	48.1	46.4	54.4	45.5	46.4	38.8	40.5	42.1	42.
It.	31.0	31.8	28.9	27.7	24.5	28.8	21.6	22.9	22.8	20.7	22.2	22.0
Ci.	43.8	37.2	43.1	35.1	34.6	38.7	36.1	36.1	36.1	34.1	37.4	36.0
Di1	102.2	102.2	98.0	100.8	99.4	100.5	103.6	103.6	98.0	98.0	96.7	100.
Di2	39.6	41.9	44.4	43.8	36.2	41.2	24.5	24.5	25.8	24.0	23.6	24.5
Mean	60.4	58.0	56.2	53.8	49.8	55.6	48.5	47.5	45.7	45.8	46.1	46.7
					P-	Resin (mg	dm ⁻³)					
SL	23.5	21.1	21.1	21.6	33.7	24.2	27.6	26.9	29.8	27.1	31.4	28.0
Tb.	44.9	37.2	33.1	33.1	36.0	36.9	31.4	33.1	34.2	38.4	37.4	34.
Ac.	19.2	22.1	21.1	21.6	21.1	21.0	25.5	24.5	24.0	26.1	27.1	25.
Vi1	26.1	23.5	16.9	24.5	30.6	24.3	17.3	16.5	21.1	17.3	16.5	17.
Vi2	24.5	22.2	18.3	22.1	26.1	22.6	24.0	27.1	22.5	24.0	28.7	25.
It.	23.0	25.0	28.2	26.1	26.1	25.7	28.7	29.2	30.3	29.0	32.5	29.
Ci.	29.2	27.6	26.6	32.0	37.2	30.5	31.4	30.3	31.4	29.8	30.9	30.
Di1	46.9	42.2	41.5	38.4	43.5	42.5	26.6	24.0	27.1	27.6	28.7	26.
Di2	14.2	12.9	15.1	13.4	15.6	14.2	19.7	15.5	16.0	17.3	18.8	17.
Mean	27.9	26.0	24.7	25.9	30.0	26.9	25.8	25.2	26.3	26.3	28.0	26.

⁽¹⁾ Soils with pH value adjusted to 6.5 in the first liming were incubated for 30 days, then fertilized with P and incubated again for 40 days, with out a second liming, since their pH values had been adjusted previously to 6.5 in the first liming. SL: Sete Lagoas (clayey LV); Tb.: Taobeiras (clayey LVA); Ac.: Acesita (clayey LVA); Vi1: Viçosa Tiro de Guerra (very clayey LVA); Vi2: Viçosa Sítio da Economia (clayey LVA); It.: Itamarandiba (very clayey LV); Ci.: Cimetal (clayey LVA); Di1: Dionísio 1 (loamy LVA) and Di2: Dionísio 2 (clayey LVA).

Table 9. Simple linear correlation coefficients between the forms P-Al, P-Fe and P-Ca, and the P content determined by Mehlich-1, Bray-1 and Resin extractants before and after the adjustments of different pH values to 6.5

					pН								
T	4.5				5.5		6.5						
Extractant	P-Al	P-Fe	P-Ca	P-Al	P-Fe	P-Ca	P-Al	P-Fe	P-Ca				
		Before pH adjustment											
Mehlich-1	0.853**	0.375^{ns}	0.035^{ns}	0.821**	$0.546^{ m ns}$	0.068^{ns}	0.789**	$0.487^{\rm ns}$	$0.064^{ m ns}$				
Bray-1	0.785**	0.591*	0.262^{ns}	0.754**	0.696*	$0.186^{ m ns}$	0.715**	0.594*	$0.133^{\rm ns}$				
Resin	0.632*	0.761**	0.426^{ns}	0.596*	0.822**	0.520^{ns}	0.588*	$-0.523^{\rm ns}$	0.253^{ns}				
				After	pH adjustme	nt							
Mehlich-1	0.779**	$-0.537^{\rm ns}$	-0.093 ns	0.831**	0.661*	$-0.058^{\rm ns}$	0.758**	$-0.495^{\rm ns}$	$-0.130^{\rm ns}$				
Bray-1	0.852**	-0.668*	-0.218^{ns}	0.830**	-0.781**	$-0.226^{\rm ns}$	0.854**	-0.677*	$-0.375^{ m ns}$				
Resin	$0.430^{\rm ns}$	-0.796**	$\text{-}0.268^{\mathrm{ns}}$	$0.501^{\rm ns}$	-0.804**	-0.690*	$0.491^{\rm ns}$	-0.734*	$-0.578^{\rm ns}$				

ns, * and **: non-significant and significant at 5 and 1 %, respectively.

The correlations between the P levels obtained by Mehlich-1 and Bray-1 (Table 11) suggest similar selectivity to the P-Al form, which may be related to preferential extraction of certain forms of inorganic P (Bahia Filho and Braga, 1975a; Novais & Kamprath, 1978). It was also observed that correlation coefficients obtained among the P levels extracted by Mehlich-1 and Bray-1 increased with increasing pH, and decreased when considering the correlations between these extractants and resin (Table 11). This behavior is possibly due to the consumption of acidity and of exchange anions $\mathrm{SO_4^{2^-}}$ (Mehlich-1) and F (Bray-1) in the extractants by soil constituents, a phenomenon responsible for the exhaustion or "wear" of the extractant (Bahia Filho , 1982), as stated before.

When the different incubation pH values were raised to 6.5, it was observed that the correlations obtained between the resin and Mehlich-1 and Bray-1 extractants were not significant (Table 11). This behavior suggests a lower sensitivity of Resin, when compared to Mehlich-1 and Bray-1, to physical and chemical characteristics, which reflect the buffering capacity of P in soil (Table 12), as stated by Novais et al. (2007). When the different pH values were raised to 6.5, P levels by Mehlich-1 and Bray-1 decreased, more expressively in the latter (Table 8). Besides the consumption of acidity in the extractants, this decrease is possibly due to the reductions observed in the P-Al levels (Table 7), since this behavior was

different from P-Fe, where, in some cases, levels were higher, and from P-Ca, with similar contents to those observed at different pH values.

The trend of decreases of Resin-extracted P to a minimum value at pH 5.5 was detected in the soils with the highest initial exchangeable Al contents (Tables 1 and 8). This suggests that reactions involving Al, with increasing pH, must have caused substantial changes in the adsorption surface for P in the soil, due to the creation of new active adsorption sites. According to Haynes & Ludecke (1981), there is a very close relationship between the lime effect on Al precipitation, as amorphous Al hydroxide, and the increase of P adsorption by soil. Robarge & Corey (1979) studied P adsorption by hydroxide species of Al in Al-saturated resin and observed a similar behavior as found here.

Sims & Ellis (1983) studied P adsorption and availability, after liming of an acid soil with high $\rm Al^{3+}$ levels, and observed an increase in P adsorption in a period ranging from 30 to 240 days. For these authors, a plausible explanation for the increase observed is possibly a continuous polymerization of Al-OH precipitate with time, which would produce new surfaces capable of adsorbing more P.

The results of this study do not indicate the main factor behind the increasing trend of P-labile at pH 6.0 and higher, for most soils, detected by Resin (Table 8).

Table 10. Simple linear correlation coefficients between the forms P-Al, P-Fe and P-Ca, and P accumulated
(P-ac) and dry material (DM) at different pH values

					pН					
	4.5				5.5 6.5					
	P-Al	P-Fe	P-Ca	P-Al	P-Fe	P-Ca	P-Al	P-Fe	P-Ca	
P-ac DM	0.587* 0.475°	-0.432° -0.532°	$-0.351^{\rm ns}$ $-0.405^{\rm ns}$	0.557° 0.468°	$-0.430^{\rm ns}$ $-0.403^{\rm ns}$	$-0.150^{ m ns}$ $-0.2034^{ m ns}$	$0.3954^{\rm ns} \ 0.231^{\rm ns}$	-0.3430^{ns} -0.312^{ns}	$0.0490^{\mathrm{ns}} \\ 0.048^{\mathrm{ns}}$	

 $^{^{\}rm ns},$ ° ,* and **: non-significant and significant at 10 and 5 %, respectively.

Table 11. Simple linear correlation coefficients between the contents of phosphorus extracted from soil through extractants Mehlich-1, Bray-1 and Resin, before and after the adjustment of different pH values to 6,5

	P-Mehlich -	1 x P -Bray -1	P-Bray -1 x	P -Resina	P-Mehlich -1 x P -Resina		
pН	Before	After	Before	After	Before	After	
4.5	0.919**	0.966**	0.899**	$0.351^{ m ns}$	0.866**	0.218^{ns}	
5.0	0.956**	0.953**	0.781**	$0.326^{\rm ns}$	0.733**	$0.089^{ m ns}$	
5.5	0.960**	0.977**	0.701*	$0.429^{ m ns}$	0.697*	$0.302^{\rm ns}$	
6.0	0.967**	0.954**	0.643*	$0.570^{ m ns}$	0.656*	0.419^{ns}	
6.5	0.977**	0.939**	0.672*	$0.429^{ m ns}$	0.715*	0.253^{ns}	

^{*} and **: significant, at 5 and 1 %, respectively.

Table 12. Simple linear correlation coefficients between the mean P levels extracted by Mehlich-1, Bray-1 and resin, after adjusting different values of pH to 6.5, and properties that reflect the capacity factor of phosphorus

Property	Mehlich-1	Bray-1	Resina
P-remman (mg L^{-1})	0.664*	0.615*	-0.086^{ns}
MCAP (mg cm³ de P no solo)	-0.615*	-0.716**	$-0.022^{\rm ns}$
PAE (L mg ⁻¹)	-0.496 ns	$-0.539^{ m ns}$	$-0.481^{\rm ns}$
Clay (%)	-0.801**	-0.781**	$-0.221^{\rm ns}$

ns, * and **: non-significant and significant at 5 and 1 %, respectively.

However, this behavior may be partly due to the dissolution of crystalline phosphates of Fe and/or Al, original soil constituents, or due to competition of OH for new P adsorption sites, as suggested by Fernandez et al. (2008a).

CONCLUSIONS

- 1. For most soil types, initial values of varying pH do not alter the availability from an applied soluble P source, measured by plant growth and P uptake. For other soil types, these results increased and decreased with increasing soil pH.
- 2. The correlations between plant growth, absorbed P and P extracted by Mehlich-1 and by Bray-1 were significant, but non-significant for resin-extracted P.
- 3. P retrieved by acid extractants depended strongly on the buffering capacity of P in soil, while for resin this dependency was smaller.
- 4. The P contents obtained by the extractants Mehlich-1 and Bray-1 were significantly correlated with each other in the entire acidic range of the soil tested. However, when these contents are compared to those extracted by resin, the correlations decrease with increasing soil pH.

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