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Agronomic potential and agronomic effectiveness of three phosphate rocks with different mineralogical composition

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Abstract

The objectives of this study were: (a) to compare the agronomic potential (AP) of three phosphate rocks (PRs) of different mineralogical composition, measured in neutral ammonium citrate (NAC), 2% formic acid (FA), and 2% citric acid (CA) and (b) to estimate the relative agronomic effectiveness (RAE) of these PRs in a P-and Ca deficient Ultisol The experiment was conducted in a growth chamber at 30/26ºC day/night temperature, 12/12 hours light/dark period and 30% relative humidity. The experiment consisted of a factorial combination of two forage species (*Brachiaria decumbens* and *Stylosanthes guianensis*), two pH levels (original pH 4.9 and limed to pH 5.8 with $MgCO_3$), and five P treatments, arranged in a split plot design with three replications. Phosphorus treatments consisted of 50 $mg.kg^{-1}$ of soluble P in NAC from Monte Fresco (MFPR), Riecito (RPR) and North Carolina (NCPR) phosphate rocks, monocalcium phosphate $[Ca(H_2PO_4)_2]$ reactive grade (TSP) as a P soluble source, and a control without P. Shoot dry weight and P content in plant were determined, as well as pH, Olsen-P and exchangeable Ca in soil. Values of percentage soluble P in CA and FA placed the NCPR, RPR and MFPR as PRs of high (7.1% in CA and 8.7 in FA), medium-high (5.0% in CA and 5.2% in FA) and very low AP (0.71% in CA and 1.0% in FA) respectively. While, the percentage of soluble P in NAC place the NCPR and RPR as PRs of high AP (3.8 and 3.7% respectively) and MFPR as low AP (0.68%). The RAE for NCPR and RPR were

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higher with the legume (*Stylosanthes*) than with the grass (*Brachiaria*). There was nota significant difference in RAE between RPR (83.5% with *Brachiaria* and 95.2 % with *Stylosanthes*) and NCPR (79.2% with *Brachiaria* and 91.7% with *Stylosanthes*) in unlimed soil. In the limed soil, the RAE for RPR decreased in 29.2% (from 83.5 to 59.1%) with *Brachiaria* and (from 95.2 to 82.3%) with *Stylosanthes*, while NCPR's RAE was not significantly affected by liming. These results indicate the need of considering the PRs's AP to calculate the P dose, as well as soil acidity and crop efficiency to use P from PRs.
Key words: Agronomic potential, agronomic efficiency, phosphate rock, forage species, available P.

Introduction

The quality of phosphoric rocks (RFs) as a P source not only depends on the total P content but also on its reactivity or inherent capacity to supply the available P for the plant in specific established conditions, this is mainly determined by the chemical solubility of RF, which will be referred in this research as an agronomic potential (PA) of RF. PA of RFs mostly depends on the isomorphic substitutions of carbonates by phosphate in the crystal of the apatite. An increased in the isomorphic substitution of carbonates increases the dissolution of carbonato-fluorapatite when reduces the size of the crystal and increases the superficial area of the mineral (1). Conventionally, the PA of RFs is estimated by the quantity of released P in the solution using different extracting solutions, because the determination of isomorphic substitutions of carbonates in RFs is difficult to handle in routine analysis. Among the most used chemical extracts to determine the PA of RFs are: citrate of neutral ammonium, formic acid at 2% and citric acid at 2% (2).

On the other hand, the relative agronomic efficiency (EAR) refer to the real behavior of a determine RF under the influenced of its PA and the external conditions to which this is used, that is, it depends on its chemical and mineralogical characteristics as well as the factors of soil, crop, weather and handle (3). In base of the obtained results in the IFDC/CIAT project of the agronomic evaluation of RFs of different countries in the world (1, 4) Hammond *et al.* (1) proposed a classification system of RFs by their corresponding PAR in different chemical extracts and EAR (1). The system to classify the PA of RFs was used in this research.

In Venezuela there are some reserves of RFs that might be used directly in the agriculture or in the fertilizer production of soluble P. In this sense, several research of PA and EAR have been done in different soil and crop conditions (8, 9, 10, 11, 12, 13), however in most of these research the PA of RFs was not considered in order to calculate the P doses to be used, therefore, the quantities of soluble P in the treatments were different, being RFs in disadvantage in relation to the sources of soluble P, underestimating the EAR of the evaluated RFs. The objectives of this research were: (a) to determine and to compare the PA of three RFs of different mineralogical composition, using three chemical extracts: neutral ammonium citrate, formic acid (2%) and citric acid (2%) and (b) to estimate the EAR of these three RFs in an Ultisol deficient in P and Ca, using two different species of pastures and two pH levels of the soil.

Materials and methods

Characterization of phosphoric rocks

Three phosphoric rocks (RF) with different mineralogical composition were used: Monte fresco (RFMF) and Riecito (RFR) located at the north-west of Venezuela (14) and North Carolina (RFCN) located at the East of the United States, this last is known as a RF of high reactivity (15). RFs samples with commercial purpose were used, which more of the 80% of the material had a particle size from 0.075 to 0.5 mm of diameter. The extraction of P and total Ca in RFs was done by incineration of 1g of Rf at 500ºC for more than 8 hours then, ashes were diluted in 5mL of concentrated HC1 and diluted in distilled water. The soluble P in neutral ammonium citrate of Rfs was extracted following the protocol of AOAC (16). The extraction of soluble P in formic acid (2%) and in citric acid (2%) was done extracting 500 mg of RF with 50 mL of each on the solutions shaking it for one hour. The total and soluble P in RFs was determined by spectrophotometry using the complex method of molibdate blue (17) and Ca was determined by atomic absorption. The mineralogical characteristics of RFs (table 1) were taken from the literature (5, 18). The PA classification of the studied RFs was done considering the ranks in percentages of soluble P in CAN, AF (2%) and AC (2%) and EAR, proposed by Hammond *et al*. (1).

Treatments and Experimental Design

The experiment was carried out in a growth chamber controlled at 30/26ºC day/night, 12/12 hours light/darkness and 30% of relative humidity. The trial consisted on a factorial combination of P treatments, limed and forage species, organized on a split-plot design with three replications. The forage species of B*rachiaria decumbens* (gramineae) and *Stylosanthes guianensis* (legume) represented the main plots and the combination of five P treatments and two pH levels of the soil (pH 4.9 and pH 5.8) represented the secondary plots. P treatments consisted on applying 50 mg kg^{-1} of soluble P in neutral ammonium citrate of RFMF, RFR y RFCN, mono-calcium phosphate [$Ca(H_2PO_4)_2$] reactive (SFT) as a reference of a source of completely soluble P, plus a control without P. The two pH levels of the soil were: the original pH of the soil,

Cuadro 1. Composición química y mineralógica de las rocas fosfóricas (RF) usadas.

	Roca Fosfórica		
	Monte Fresco	Riecito	Carolina del Norte
P total (%)	9.3	12.8	13.2
Ca total (%)	29.1	24.8	30.1
% P Soluble en la roca fosfórica:			
Citrato de Amonio Neutro	0.68	3.7	3.8
Ácido cítrico (2%)	0.71	5.0	7.1
Ácido fórmico (2%)	1.0	5.2	8.7
Composición Mineralógica:			
Apatito (%)	64¶	75¶	91§
$CaCO_3$ (%)	29¶	1¶	3§

¶Fayard and Truong (1990)
§McClellan and Gremillion (1980)

4.9 and limed until pH 5.8 using 0.15 $cmol.kg^{-1}$ of Mg as $MgCO_3$. A sandy soil was used classified as *Arenic Paleudults*, which is deficient in P and Ca (4 $mg.kg^{-1}$ of P-Olsen and 0.14 $cmol.kg^{-1}$ of changeable Ca). Stylosanthes seeds were inoculated using 4mL/pot of a specific inoculum suspension for Stylosanthes (15g of inoculum for Stylosanthes/150 mL of distilled water). A basic fertilization was applied through nutritive solutions three times a week. In pots with Brachiaria, the total quantity of applied macronutrients by pot during the essay expressed in mg kg^{-1} of soil were the followings: 160 of N, 330 of K, 88 of Mg and 150 of S as $Mg(NO_3)_2$, KNO_3, $MgSO_4$ and K_2SO_4; and the total quantity of applied micronutrients expressed as ug kg^{-1} of the soil were the followings: 54 of Mn as $MnSO_4.H_2O$, 4.0 of Cu as $CuSO_4.5H_2O$, 6.7 of B as H_3BO_3, 2.1 of Mo as $NaMoO_4.2H_2O$, 0.36 of Co as $CoCl_2.6H_2O$, 364 of Fe as $FeCl_3.6H_2O$, 197 of Na as Na_2H_2 EDTA and NaCl. Meanwhile in Stylosanthes were applied: 250 of K, 52 of Mg and 170 of S as $MgSO_4$ and K_2SO_4, and the total quantity of applied micronutrients expressed as µg kg^{-1} of soil were the followings: 55.6 of Mn as $MnSO_4.H_2O$, 3.8 of Cu as $CuSO_4.5H_2O$, 6.9 of B as H_3BO_3, 2.2 of Mo as $NaMoO_4.2H_2O$, 0.37 of Co as $CoCl_2.6H_2O$, 374.8 of Fe as $FeCl_3.6H_2O$ and 216 of Na as Na_2H_2 EDTA and NaCl. Plants were harvested eight weeks after the sow, and the aerial dry matter and the P and Ca content in tissue were determined, these were determined after had incinerated 1g of ground and dry vegetal matter at 500ºC for more of eight hours, ashes were diluted in a solution of concentrated HNO_3, 33% H_2O_2 and HCL 6N diluted in distilled water for determining P by spectrophotometry and Ca by inductively coupled plasma (ICP). It was determined pH in soil in a 1:2.5 soil-water relation, available P extracted with $NaHCO_3$ 0.5M (Olsen method) in a 1:20 soil-solution relation extracted and determined by spectrophotometry using the molibdate blue method (17), and changeable Ca extracted with KC1 1M in a 1:10 soil-extracted solution relation, with a shaking period of 10 minutes and determined by atomic absorption. The relative agronomical effectiveness (EAR) for each RF was determined as the yield percentage (aerial dry weight) and absorbed P by the plant in treatments with RF in relation to yield or absorbed P by the plant in treatments with soluble P (SFT) under the same growth conditions, for the measurement the following formula was used:

EAR= (Yield RF–Control Yield)/(SFT Yield – Control, Yield) x 100

The variance analysis of the information was done using the program for split-plot design of the Statistical Analysis Package (19) and means tests were done by the minimal significant difference (MDS) when F values were significant.

Results and discussion

Characteristics and agronomic potential of phosphoric rocks

In table 1 are shown the main chemical and mineralogical characteristics and chemical solubility of the used RFs in the experiment. In order to classify the studied RFs by their PA were considered ranks in percentage of soluble P in CAN, AF (2%) and AC (2%) and EAR proposed by Hammond *et al.* (1). Values in percentage of soluble P (weight % of RF) in AC and AF allowed to classify RFCn as high PA (7.1% in AC and 8.7 in AF), partly high PA (5.0% in AC and 5.2% in AF) and the RFMF of very low PA (0.71% in AC and 1.0% in AF). Meanwhile, when the percentage of soluble P in CAN was determined, RFCN and RFR classified as phosphoric rocks of high PA (3.8 and 3.7% respectively), and the RFMF with low PA (0.68%). In this sense, Fayard and Truong (5) reported for RFMF a content of 10.3% of total P and 0.91% of soluble P in AF, and for RFR 12.7% of total P and 4.5% of soluble P in AF. While Truong and Zapata (2) reported for RFR 12.9% of total P, 1.6 of soluble P in CAN and 4.2% of soluble P in AC and in AF, where values of soluble P in CAN, AC and AF resulted to be lower than the reported in this research (table 1).

Since the dose of P used in the experiment was measured in base of the percentage of soluble P in CAN of each RF (table 1), and due to there were not significant differences in the average values of aerial dry weight and absorbed P between treatments with RFR and RFCN (table 2), it can be said that RFR and RFCN have a similar PA under the conditions of this research.

Values in percentage of the

apatite weight and $CaCO_3$ in the studied RFs (table 1) have been reported as: 64.0 and 29.0 respectively for RFMF, 75.0 and 1.0 for RFR (5) and 90.7 and 2.9 for RFCN 818). It can be observed that RFMF has the highest values of $CaCO_3$ and the lowest values of soluble P in any of the used chemical extrants, which indicates that at the same time that increases the $CaCO_3$ content in RFs, reduces its solubility. This is explained by the fact that $CaCO_3$ is more soluble than the apatite and its dissolution increases the concentration of Ca and pH in the surface of the apatite (20), reducing the dissolution of RN (21).

Production of dry matter and absorption of P

There were significant differences ($P<0.05$) in aerial dry matter between forage species, P treatments and the forage species and P treatments interaction. The average values of aerial dry matter of Brachiaria were the double of Stylosanthes. In both species, the averaged aerial dry weight by limed treatment increased with the solubility of the P source, especially in Brachiaria, where the highest yields were obtained with SFT. There were not significant differences in the aerial dry weight of Stylosanthes between the treatments with RFR, RFCN and SFT, while the treatment with RFMF had lower values of aerial dry weight than the control treatment without P in both forage species.

The limed had not any effect on the aerial dry weight of species (table 2). However, there was a significant reduction (30%) in the aerial dry weight of Brachiaria (gramineae) with the limed treatment and RFR (table 2), while the same treatment only reduced in 6.5% the aerial dry weight of Stylosanthes (legume).

These results do not agree to those reported in the literature (1, 3, 22), when saying that limed reduces the efficiency of RFs as a direct fertilizer. In table 2, it can be observed that there were not significant differences in the aerial dry weight of Brachiaria between treatments with RFR and RFCN in soil without lime (0.9 g/pot), while in the limed soil the difference between these two RFs was highly significant (4.8 g/pot). With Stylosanthes, there were not significant differences in aerial dry weight between RFR and RFCN in soil with or without lime, which is related to the lowest values of the pH of the soil with Stylosanthes compare to Brachiaria, independently of the limed treatment (table 2). This indicates that RFR depends even more on the soils acidity than RFCN, and that the acidification of the soil by effect of Stylosanthes (legume) significantly contributed with the dissolution and efficiency of these two RFs.

The P absorbed by crops was significantly affected by P treatments (table 2). The absorbed P by both species in the treatments with RFMF (the RF of lower PA) was similar to the control treatment without phosphorus, and inferior to the other sources of P. There were not significant differences in the P absorbed by Stylosanthes in treatments

Table 2. Effect of P treatments and limed on average values of dry aerial matter and absorbed P in Brachiaria and Stylosanthes and on pH, available P and interchangeable Ca in soil.

Treatment							
Specie	pH	P	Aerial dry weight g/pot	Absorbed P mg/pot	pH in H_2O 1:2,5	Available P $mg.kg^{-1}$	Interch. Ca $cmol.kg^{-1}$
Brachiaria	4.9	Control	2.4	1.4	5.5	3.0	0.26
		RFMF	1.7	0.8	7.4	2.3	1.47
		RFR	21.0	20.7	5.5	10.2	0.64
		RFCN	20.1	18.9	5.8	8.3	0.50
		SFT	24.7	29.5	5.3	25.4	0.48
	5.8	Control	1.6	0.8	6.1	2.1	0.27
		RFMF	1.6	0.7	7.6	2.1	1.47
		RFR	14.7	11.5	6.6	5.0	0.39
		RFCN	19.5	15.5	6.3	4.6	0.62
		SFT	23.7	31.7	5.7	24.2	0.51
		Average	13.1	13.1	6.2	8.7	0.66
Stylosanthes	4.9	Control	2.3	2.0	4.7	3.5	0.31
		RFMF	1.0	0.8	7.3	2.4	1.32
		RFR	9.2	19.7	4.4	17.2	0.90
		RFCN	8.9	19.3	4.8	15.8	0.98
		SFT	9.5	18.6	4.0	29.1	0.36
	5.8	Control	3.1	2.8	4.7	3.3	0.25
		RFMF	1.7	1.4	7.3	2.4	1.32
		RFR	8.6	17.1	4.6	11.8	0.73
		RFCN	9.4	20.3	4.7	14.8	0.78
		SFT	9.8	20.7	4.1	32.7	0.49
		Average	6.4	12.3	5.1	13.3	0.74
			Averages for pH				
	4.9		10.1	13.2	5.5	11.7	0.72
	5.8		9.4	12.3	5.8	10.3	0.68
			Average for P treatments				
Control	2.3	1.8	5.3	2.9	0.27		
		RFMF	1.5	0.9	7.4	2.3	1.40
		RFR	13.4	17.2	5.3	11.1	0.66
		RFCN	14.5	18.5	5.4	10.9	0.72
		SFT	16.9	25.1	4.8	27.8	0.46
MDS 0.05:							
Species			0.8	NS[¶]	0.1	0.97	NS
pH			NS	NS	0.1	0.97	NS
Species x pH			NS	NS	0.1	NS	NS
P			1.3	2.8	0.1	1.53	0.14
P x Specie			1.9	4.0	0.2	2.30	0.19
P x pH			1.9	NS	0.2	2.30	NS
Specie x pH x P			NS	NS	NS	NS	NS

[¶]NS= Non significant F values at $P \leq 0,05$

with RFR, RFCN and SFt, while in Brachiaria, the absorption of P was higher in treatments with SFT than with RFs. This indicates that Stylosanthes is more efficient when using P of Rfs than Brachiaria, which corresponds to the results reported by Van diest *et al.* (23) and Khasawneh and Sample (24) who say that legumes have a higher capacity of using P of RFs than gramineae. In this sense, Marschner (25) says that legumes have a higher capacity for using RFs than the dependent species of mineral N, due to the firsts have a higher cation/anion relation, which can provoke that the plant releases H^+ through the roots toward the rhizosphere, and consequently, the dissolution of RFs.

Relative agronomic efficiency of phosphoric rocks

The relative agronomic efficiency (EAR) provides a yield index or the P absorption of the crop with the evaluated RFs in relation to SFT. The EAR values measured on the yield or in the absorption of P, incremented with the solubility of RFs for both crops (figures 1 and 2). The negative values of EAR in treatments with RFMF show that yields and the P absorption with this RF were lower than the obtained with the control treatment without P.

Even though the average of the total value of aerial dry matter by treatments of P and limed (table 2) in Brachiaria was the double (13.1 g/pot) of the obtained in Stylosanthes (6.4 g/pot), there was not a significant difference in the total of P absorbed between species (13.1 and 12.3 g/pot in Brachiaria and Stylosanthes respectively). The measured EAR in base of the aerial dry weight (figure 1a and 1b) reduced in 29.2% with the limed for RFR with Brachiaria and 13.6% with Stylosanthes, while the limed did not affect the EAR of RFFCN. The EAR measured in base of the absorbed P reduced in 49.6% with the limed for the RFR with Brachiaria and 25% with Stylosanthes (figures 2a and 2b) and 23.6 and 6.2% with Brachiaria and Stylosanthes respectively for RFCN. This indicates that EAR of RFR and RFCN is higher with legume than with gramineae, also that increases of the pH of the soil drastically reduces the effectiveness of RFR. It is important to prove that the measured EAR in base of the absorbed P by the plant seems to detect in higher quantity the differences in EAR of the RFs, than when this is measured in base of the aerial dry weight.

Treatments effect on pH, available P and interchangeable CA in the soil

There were significant differences ($P<0.05$ in the pH of the soil by effect of the forage specie, limed and P treatment and its interactions (table 2). With the RFMF, pH values of the soil increased at 7.4 and 7.3 for Brachiaria and Stylosanthes respectively, in treatments with limed and 7.6 – 7.3 respectively, in treatments without limed. The pH values of the soil in the controlled treatments without P for both species with and without being limed indicate that Stylosanthes acidified the soil, while Brachiaria increased it. The

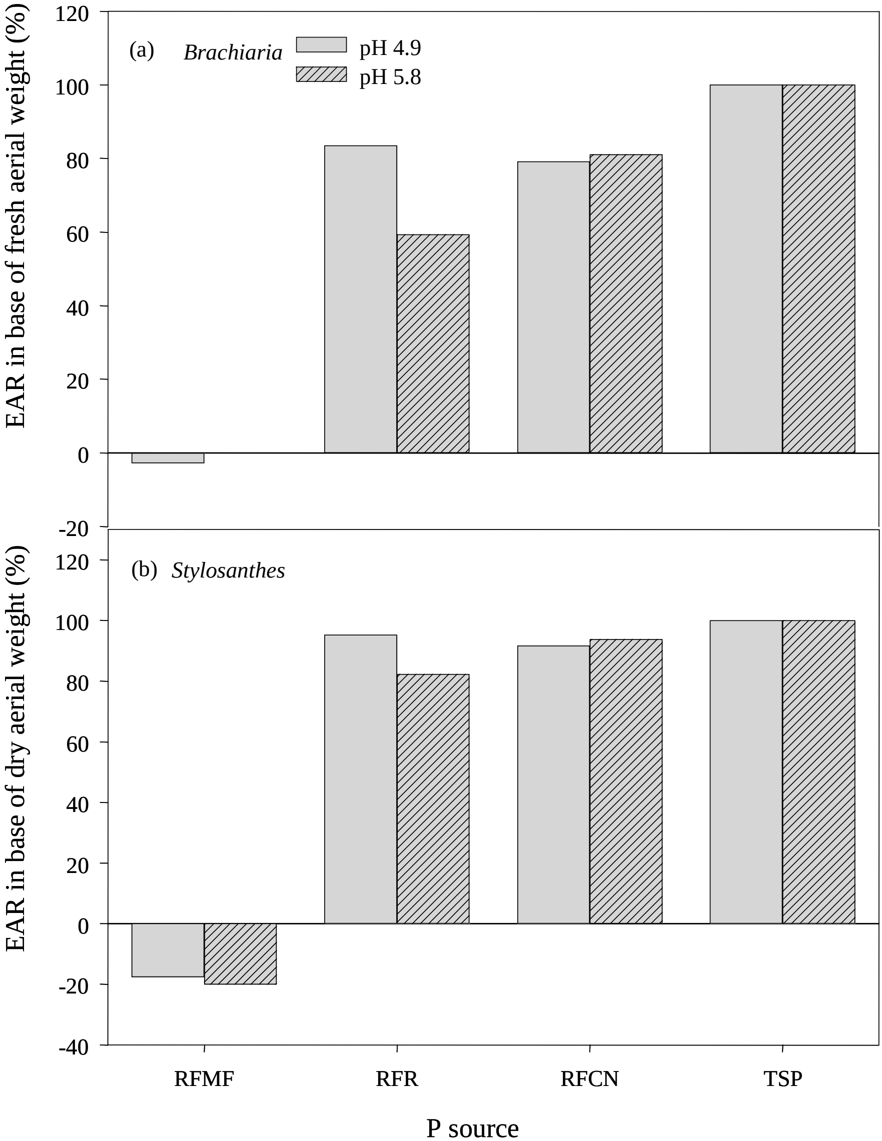

Figure 1. Relative agronomic affectivity (EAR) of the evaluated phosphoric rocks in limed and without limed soil, calculated in base of the dry aerial weight of *Brachiaria* (a) and *Stylosanthes* (b). EAR= [(RF-Control)/(SFT-Control)] x 100.

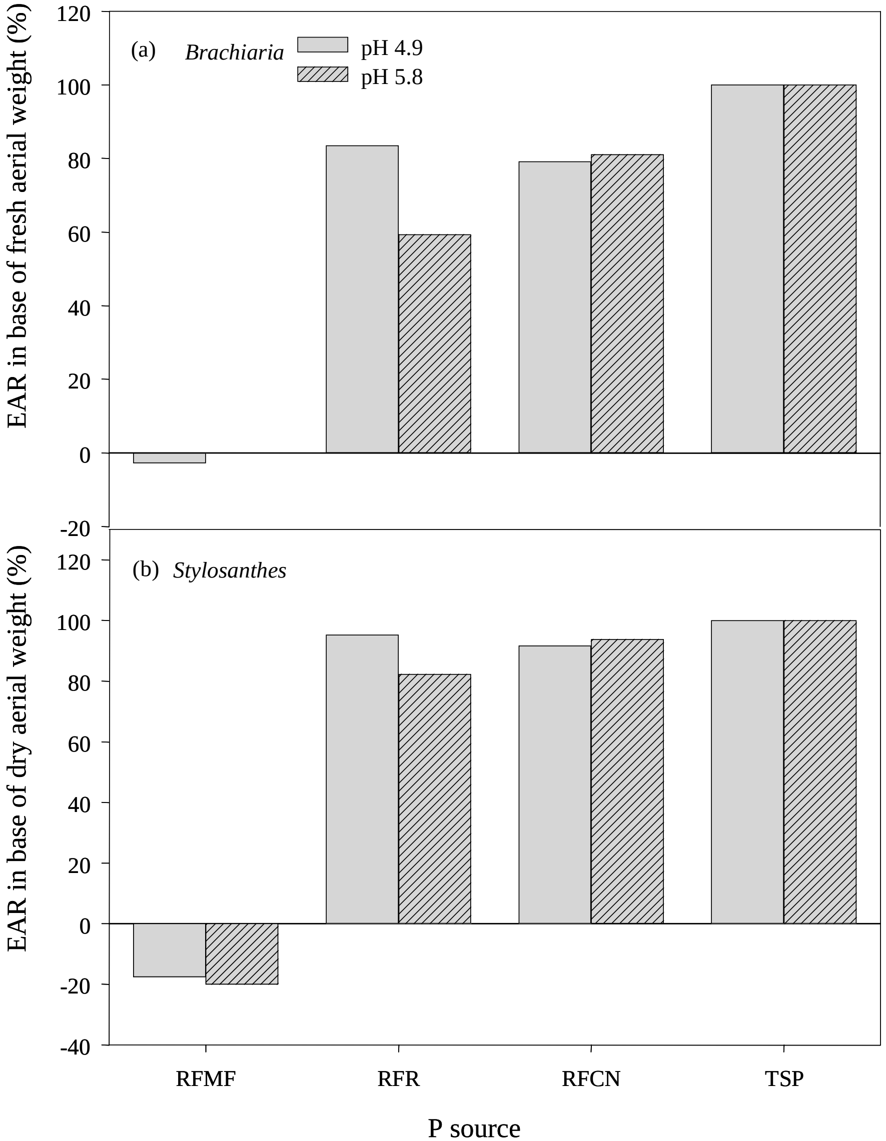

Figure 2. Relative agronomic affectivity (EAR) of the evaluated phosphoric rocks in limed and without limed soil, calculated in base of absorbed P in *Brachiaria* (a) and *Stylosanthes* (b). EAR= [(RF-Control)/(SFT-Control)] x 100.

reason of this effect of the plant on the pH of the soil will be better discussed in another publication.

The availability of O in the soil was affected by the forage specie, P treatments, limed and the interactions of P treatments with the specie and the limed (table 2). Treatments with RFMF had the lowest values of available P in soil for both species, which corresponds to the low PA and EAR of this RF, while the highest values in the available P for both species corresponded to the source of soluble P (SFT). The total approximate values of available P in the soil in function of the source of P indicate that there was not a significant difference between RFR and RFCN, however, the availability of P in the non-limed soil was higher for RFR than for RFCN with both crops. This corroborates that EAR of RFR is higher than the one of RFCN in acid soil conditions.

The interchangeable Ca in the soil was influenced by the source of P and the forage specie (table 2). It must be mentioned that it was not applied Ca to the soil, more than the provided by the used P sources. Since the used P sources have different content of Ca (table 1), the quantities of provided Ca (in $mg.kg^{-1}$) with the doses of applied P (50 $mg .kg^{-1}$of soluble P) for each source of P were the followings: 1870 with RFMF, 336 with RFR, 408 with RFCN and 32 with SFT. The relatively high values of interchangeable Ca in soil in treatments with RFMF for both crops correspond to the increment of pH (>7.0) and the low availability of P in soil in the treatments with this RF. This agrees to what Rajan *et al.* (20) and Bolan and Hedley (21) say, when indicating that at the same time that increases the content of $CaCO_{3\ in}$ RF, reduces its solubility, due to $CaCO_3$ by being more soluble than apatite, its dilution increases the concentration of Ca and pH in the surface of the apatite, thus reduces the dissolution of RF.

Considering that for lime was used $MgCO_3$ instead of $CaCO_3$, increments in available Ca in soil, in the treatments with Rfs in relation to the controlled treatments without P might be due to the dissolution of RFs. However, this difference in available Ca coming from RF, is not a good indicator of the dissolution estimate of RF, in the contrary case, RFMF would have been the most soluble in this group of RFs, which is not true. This does not agree to what Kanabo and Gilkes say (26), when reporting that the difference in interchangeable Ca in the soil, between treatments with RF and the controlled (ΔCa) is an indicator of the quantity of RF diluted in the soil.

Conclusions

Values of soluble P in citric acid (2%) and in formic acid (2%), allowed to classify the RFCN, RFR and RFMF as phosphoric rocks with high PA (7.1% in AC and 8.7 in AF), partly high PA (5.0% in AC and 4.3 in AF) and very low PA (0.71% in AC and 1.0% in AF) respectively. While the values of soluble P in CA classified RFCN and RFR as phosphoric rocks of high PA (3.8 and 3.7 respectively), and the RFMF as with low PA (0.68%). There were not significant differences in EAR between RFR and RFCN in the soil without lime. However, the EAR of RFR reduced significantly with the lime. RFR and RFCN had a higher EAR with legume (Stylosanthes) than with gramineae (Brachiaria). RFMF (RFs of low PA) increased the levels of pH (>7.0) and interchangeable Ca in soil, which corresponded to the low EAR and relatively high contents of $CaCO_3$ in this RF. These results indicate the importance of considering the PA of RFs for the measurement of the doses of P, as well as the acidity level of the soil and the crop efficiency in dissolving and using P of RFs.

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