



## Phosphorus adsorption after drainage in two soil classes<sup>1</sup>

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### ABSTRACT

Lowland soils, seasonally flooded for rice cultivation, feature alternate oxidation and reduction conditions, which determine intense modifications in the soil mineral solid phase and in the dynamics of highly reactive elements, such as phosphorus. This study aimed to evaluate the effect of drainage of two lowland soils (Albaqualf and Argiaquoll) after a flooding period on the maximum phosphorus adsorption capacity (MPAC). The experiment was conducted in a greenhouse, and the system factor was composed of two levels: 1) flooded soil for 63 days, followed by drainage, and then humidity remained at 16% for 184 days; 2) soil moisture maintained at 16% throughout the trial period. After drainage, soil samples were collected at 0, 36, 96 and, 184 days for MPAC determination, which was performed by the adjustment of adsorption isotherms according to the Langmuir model. The behavior of MPAC after soil drainage was different for both soil classes evaluated. An immediate reduction of maximum phosphorus adsorption capacity was seen after drainage in the case of Albaqualf, while for Argiaquoll, there was a tendency to maintain higher values of MPAC after drainage, with subsequent reduction. Soil drainage after a flooding period increases de maximum phosphorus adsorption capacity, and this effect remains for approximately 163 days in Argiaquoll and 121 days in Albaqualf soils.

**Keywords:** flooding; reduction; Langmuir isotherm.

### RESUMO

#### Adsorção de fósforo após a drenagem de dois solos alagados

Os solos de várzea, sazonalmente alagados para o cultivo do arroz, apresentam alternância nas condições de oxidação e redução, que determinam modificações intensas na fase sólida mineral do solo e na dinâmica de elementos reativos, como o fósforo. Este estudo teve como objetivo avaliar o efeito da drenagem de dois solos de várzea, (Planossolo Háptico e Chernossolo Ebânico), após período de alagamento sobre a capacidade máxima de adsorção de fósforo (CMAP). O experimento foi conduzido em casa de vegetação, o fator sistema foi composto por dois níveis: 1) solos alagados por 63 dias seguido de drenagem e após manteve-se a umidade em 16% Ug por 184 dias; 2) solos mantidos com umidade de 16% Ug durante todo o período do experimento. Após a drenagem foram feitas coletas de solo nos tempos zero, 36, 66, 96 e 184 dias para determinação da CMAP. A determinação da CMAP foi feita por meio do ajuste de isotermas de adsorção segundo o modelo de Langmuir. O comportamento da CMAP após a drenagem do solo foi diferente para as duas classes de solo avaliadas. O Planossolo demonstrou tendência de redução imediata da CMAP após a drenagem do solo, no caso do Chernossolo, houve tendência de manutenção de valores elevados da CMAP logo após a drenagem, com posterior início da redução. A drenagem dos solos após período de alagamento aumenta a capacidade máxima de adsorção de fósforo, sendo que este efeito perdura por 163 dias para o Chernossolo e 121 dias para o Planossolo.

**Palavras-chave:** alagamento; redução; isoterma de Langmuir.

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## INTRODUCTION

A high soil use efficiency is one of the most important factors to maximize the yield potential of agricultural areas. One of the major strategies used to achieve this goal is crop rotation. In lowland areas, however, soil aptitude to rice cultivation under flooding can make it difficult to establish such systems.

The long period of anaerobiosis observed in soils cultivated with rice under flooding promotes a series of changes that can negatively affect the agricultural activities that follow. Such changes result from soil microorganism metabolic adaptation to low oxygen conditions, and among nutrients, phosphorus (P) is the most unstable during this process. Although P is not directly involved in the soil redox reactions, it is affected by flooding because it is chemically linked to oxidized substances, such as iron and manganese oxides (Shahandeh *et al.*, 2003).

Frequent changes in redox conditions in lowland soils result in changes in the stability of different soil minerals, such as those poorly crystallized Fe oxides and hydroxides that become predominant after some time (Churchman & Lowe, 2012).

In lowland soils, poorly crystallized Fe oxides (ferrihydrite and poorly crystallized lepidocrocite) present low-order structures, larger specific surface, and higher chemical reactivity than better crystallized fractions (Cornell & Schwertmann, 2003). These are positively charged and could be the most important components in phosphorus adsorption during the drained period of the soil (Novais *et al.*, 1991; Ranno *et al.*, 2007). This soil adsorption occurs in the acid sites of Lewis, where the OH and  $\text{OH}_2^+$  groups linked to metal (Fe or Al) are exchanged by phosphate, forming a new surface complex, characterizing the phenomenon of ligand exchange (Sharpley, 2003). The different mechanisms as well as the degree of energy in which this occurs are responsible for the degree of reversibility of its reactions (Camargo *et al.*, 2001).

These forms of oxides will control the release of phosphorus provoked by the flooding that follows to the rice crop, since low redox potential (Eh) values (lower than 300 mV) found in these conditions favor the reduction of iron phosphates and decrease the bond energy. Thus, phosphorus is released to the soil solution as the major factor contributing phosphorus dynamics to seasonally flooded soils, affecting the supply of this nutrient to the rice crop (Fink *et al.*, 2016). On the other hand, soil drainage increases oxygen levels, enabling oxidation reactions, turning the soil into a P reservoir, and working in an opposite way for subsequent crops (Reddy *et al.*, 2005). Consequently, P dosages in the fertilization of

upland crops that succeed rice must be higher than normally recommended (Vahl, 2004).

One way to study adsorption phenomena is through the use of isotherms, which quantitatively describe the adsorption of solutes to solid surfaces, under constant conditions of temperature and pressure, showing the amount of ion adsorption as a function of an equilibrium concentration (Bohn *et al.*, 1985). Since the P adsorption in the soil depends on the mineralogy, specific surface area, and crystallization of soil mineral components, characterized by the selectivity of adsorption surfaces, pH, and electrolyte concentration, one can say that high pH values, low specific surface of clay minerals, and low phosphate concentration in the soil solution lead to a lower adsorption (Horta & Torrent, 2010).

Therefore, the major questions related to soil P dynamics is to evaluate the recovering time of oxidized iron forms in the soil to establish the dynamics of P adsorption and to define the best management to have a supply of this nutrient at adequate amounts for crop plants following a rice crop cultivated under flooding. The understanding of this phenomenon improves the efficiency of the rice crop and allows the widespread use of these areas with upland crops such as pastures, soybean, and maize, a key factor for the profitability of farming activity.

Thus, the hypothesis is that soil drainage, after a flooding period due to rice cultivation, increases phosphorus adsorption, being this increase proportional to the soil maximum phosphorus adsorption capacity (MPAC) before flooding. This study aimed to evaluate the drainage effect of two lowland soils after flooding on the MPAC.

## MATERIAL AND METHODS

The experiment was conducted in a greenhouse belonging to the Department of Soils, Eliseu Maciel School of Agronomy (FAEM), Federal University of Pelotas (UFPEL), Rio Grande do Sul State, Brazil. The treatments consisted of the combination of soil classification and system factors, according to a  $2 \times 2$  factorial scheme with four replications. The factor soil classification was formed by two levels: 1) Albaqualf; 2) Argiaquoll. The factor system was composed of two levels: 1) soil flooded for 63 days followed by drainage, in which the humidity was kept at 16% for 184 days; and 2) soil at 16% humidity for the whole period of the experiment (247 days).

The two soil classes were chosen because they represent a significant area of lowland areas in Rio Grande do Suland because they show different MPAC (Table 1). Soil samples were collected in non-flooded and non-fertilized areas, coming from a section containing a 20-cm-

deep layer sample. Later, the samples were grinded and passed through a 2.0-mm mesh.

The experimental units were arranged in a completely randomized scheme with four replications, making a total of 16 units. These units were composed of 2.0 kg dry soil in plastic pots. When the samples were placed in the pots, soil collection apparatus were placed (Sousa *et al.*, 2002) at a depth of 7.0 cm. These apparatuses consisted of polyethylene tubes with two rows of holes covered with a nylon net, built in a spiral shape, and coupled to a glass syphon projected to the outer part of the pot and allowing the collection of soil solution samples (Figure 1).

In the unflooded treatments, distilled water was added to each experimental unit to reach 16% of gravimetric humidity; then, pots were covered with transparent plastic film to maintain the humidity. The pots were weighed weekly to maintain this humidity. In the flooded treatments, a 5.0-cm water layer was applied and kept through periodic irrigations with distilled water.

Soil sampling was performed once a week for nine weeks while the soil was kept flooded. pH and Eh soil solution analyses were performed using a platinum combined electrode (Digimed model DMR-CP1), with reference system of Ag/AgCl linked to a potentiometer and previously installed in an electrometric cell, built in glass as described previously (Sousa *et al.*, 2002). Since the cell remained full of solution during the readings, it was possible to minimize the contact with molecular oxygen, decreasing the risk of electrochemical property changes. After pH and Eh readings, the samples were filtered in a millipore mesh (0.45  $\mu\text{m}$ ), transferring 30 mL of solution to glass flasks, containing 1.0 mL of HCl 3.0 mol  $\text{L}^{-1}$  to reach a final concentration of 0.1 mol  $\text{L}^{-1}$ . This

enabled the later analysis of sample chemical components in the lab. Contents of Fe and P were measured in these acidified samples, as described by Sousa *et al.*, 2002.

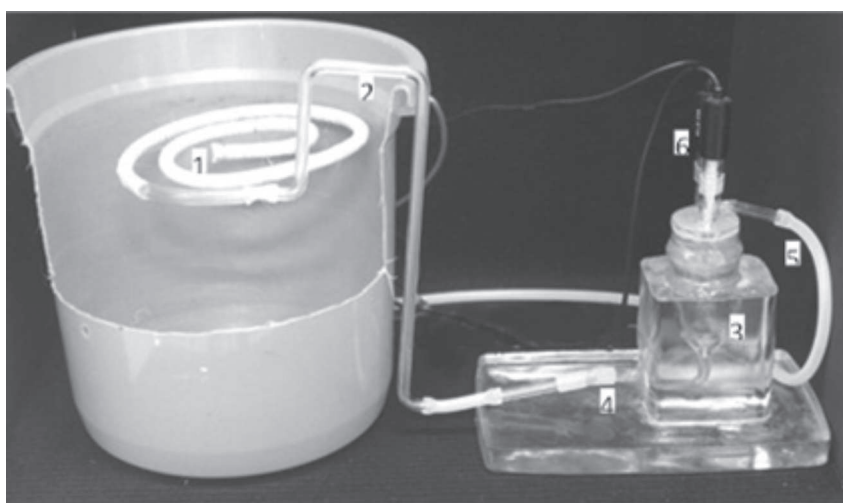
Response profiles of MPAC after soil drainage were compared between the soil classes by analysing curve identities, according to Regazzi (1993). Soil samples were collected immediately after drainage and in other four occasions, i.e., at 36, 66, 96, and 184 days after drainage in each experimental unit. Maximum phosphorus adsorption capacity was determined for all collected samples.

Analysis of MPAC was performed according to Braga (1980), in which to evaluate P adsorption, soil samples were placed in contact with 0.01 mol  $\text{L}^{-1}$   $\text{CaCl}_2$  with increasing P doses (1, 2, 4, 5, 10, 20, 30, 40, 50, 60, 70, 80, 100, and 125 mg  $\text{kg}^{-1}$  in the soil). After 16 h, the remaining P in the solution was determined. The difference between the initial and final content in the solution is attributed to adsorption by the soil solid phase.

Therefore, the effect of variations in the levels of the factor soil class on the linear, angular, and curvature coefficients of a quadratic model of linear regression were estimated (Equation 1). The variable D (*Dummy*) was introduced in the model as an independent term, aiming to explain the effect of soil class on the coefficient fitness. Also,  $\beta_0$ ,  $\beta_1$  and  $\beta_2$  are the linear, angular, and curvature coefficients, respectively, associated to the interaction DAD:D.

The hypothesis of equality of response profiles was tested using the Student's t test, through the measurement of differences between the fitted coefficients for each soil class.

The average time needed for MPAC to recover to the same levels observed for the unflooded soil condition



<sup>1</sup> Polyethylene tube perforated and recovered with a nylon mesh; <sup>2</sup> Siphon-shaped glass tube; <sup>3</sup> Electronic chamber; <sup>4</sup> Exchange solution tube; <sup>5</sup> Solution excess discharge tube; <sup>6</sup> Electrodes for Eh and pH measurements.

Source: Sousa *et al.* (2002).

**Figure 1:** Soil solution extraction system coupled to an electrometric cell for determination of redox potential and pH.

was obtained by solving the fitted quadratic model. Bhaskara's formula was used, transposing the models to have the objective MPAC values coinciding with the ordinate axis. All procedures of data analyses were performed with the R software (R Core Team, 2012).

## RESULTS AND DISCUSSION

In Figure 2a, the evolution of Eh with flooding is observed. A sharp decrease in Eh can be seen, for both soils, due to microorganism anaerobic metabolism. However, for Albaqualf, the stabilization of Eh values were observed at eight days, while for Argiaquoll, the stabilization was observed at 29 days of flooding with the smallest Eh values. The stable Eh values at 110 mV and 20 mV for Albaqualf and Argiaquoll, respectively, characterize an anoxic environment (Tian-Yen, 1985). The lower the Eh value, the higher will be the concentration of reduced compounds, i.e., the higher the reduction state of the soil (Pezeshki & DeLaune, 2012). It is possible that the lowest Eh value in Argiaquoll was due to a higher concentration of organic matter (Figure 2). Organic matter content affects the oxidation-reduction of flooded soils, since its increase favors soil reduction due to a higher electron supply (Camargo *et al.*, 1993).

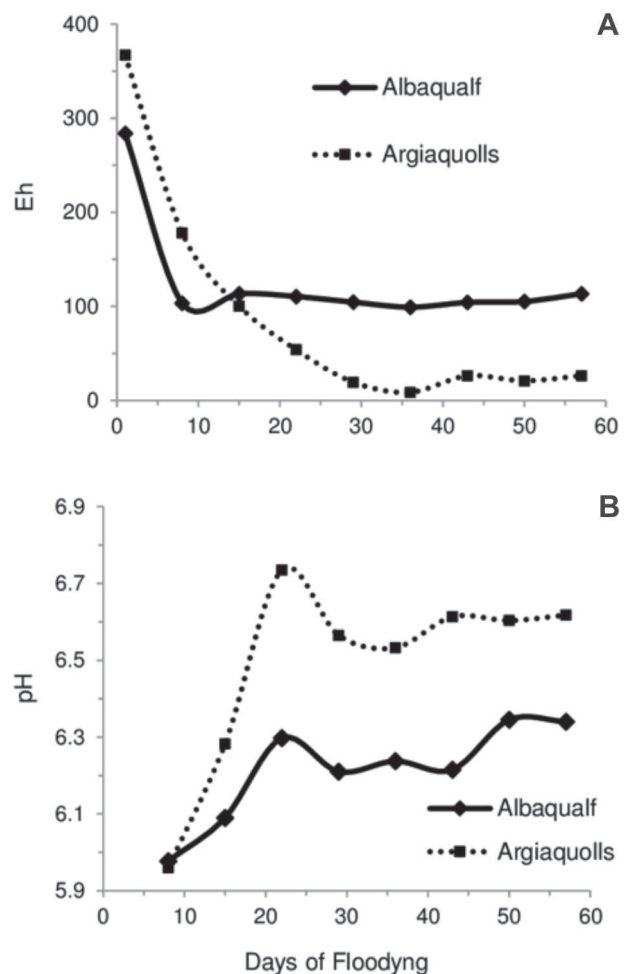
Redox potential constitutes an intensity measure, essentially expressing the availability, instead of the effective number of electrons involved in redox reactions. Redox potential represents the most important physical chemistry parameter in the characterization of the degree of oxidation-reduction of a flooded soil (Oliveira *et al.*, 1993). It is the major factor differentiating flooded and drained soils, being the low redox potential of flooded soils an indicative of its reduction state, while the high Eh of well drained soils, is an indicative of its oxydative state (Ponnamperuma, 1972). For pH values higher than 6.0 (observed in this work, according to Figure 2), Eh values below 150 mV already characterize an anoxic environment (Tian-Yen, 1985).

The pH values in the solution increased during the early weeks of flooding up to 23 days (Figure 2b), stabilizing at values close to 6.6 in Argiaquoll and 6.3 in Albaqualf. Soil solution pH is due to H ion consumption as a function of redox reactions that occur during flooding. Reactions of soil oxidized compounds as N-NO<sub>3</sub>, Mn, and Fe oxides and hydroxides as well as S-sulphate are used as electron acceptors in the absence of oxygen, being transformed into their reduced forms. This leads to a great consumption of H ions and decreases the number of H<sup>+</sup> protons in the soil solution, causing an increase in pH (Bartlett & James, 1993). In flooded soils, pH tends to neutrality after a few weeks of flooding (Ponnamperuma, 1972).

Electrochemical changes serve as a starting point for unchaining reduction processes resulting from the decrease in oxygen, leading to significant changes in the Eh and pH (Kögel-Knabner *et al.*, 2010).

Iron content in the solution (Figure 3a), for both soils, presented a behavior typical of a flooded soil, showing increased values during the early weeks after flooding due to the ferric (Fe<sup>3+</sup>) to ferrous (Fe<sup>2+</sup>) reduction processes with a consequent increase of iron solubility (Ponnamperuma, 1972).

The highest peak of iron content in Albaqualf did occur at 15 days after flooding with 150 mg kg<sup>-1</sup>. In Argiaquoll, the iron release peak into soil solution occurred later, 93 mg kg<sup>-1</sup> at 30 days. This behavior can be associated to the presence of other reducible compounds following a preferential sequence of redox reactions, such as nitrate and manganese oxides (Sousa *et al.*, 2002) as a function of their affinity for electron acceptance, delaying the iron release process into the soil solution. Argiaquoll presented higher Mn<sub>0</sub> levels (extracted with ammonium oxalate at pH 3.0), when compared with Albaqualf (Table

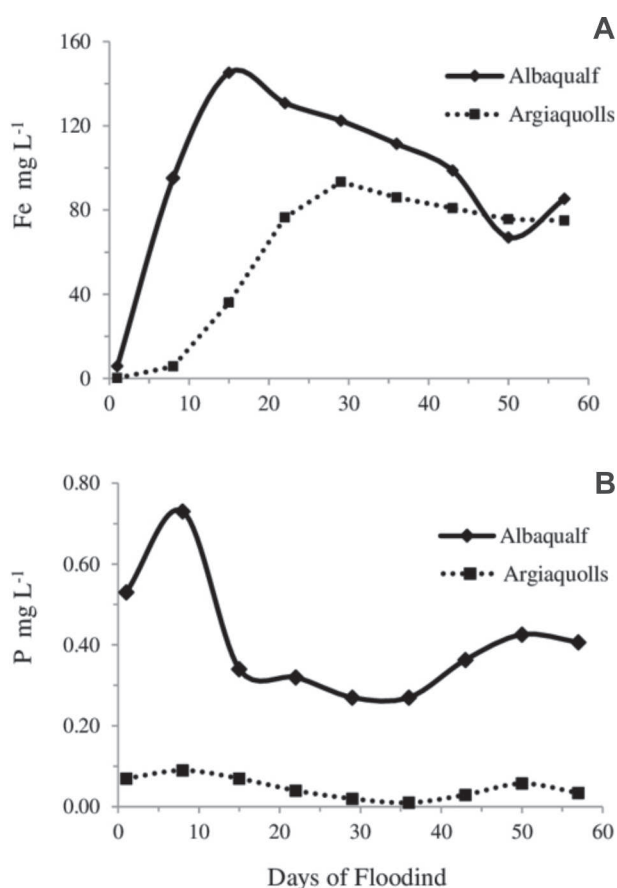


**Figure 2:** Eh (a) and pH (b) evolution in soil solution for the two studied soils: Albaqualf and Argiaquoll.

1). Also, we must consider that, after iron reduction,  $\text{Fe}^{2+}$  starts to be part of soil cation exchangeable portion and that  $\text{Fe}^{2+}$  in the solution represents only part of the iron that has been reduced. Thus, the amount of  $\text{Fe}^{2+}$  present in Argiaquoll must be higher than the one observed in Albaqualf due to a higher CEC (Table 1).

The later decrease in Fe content in the soil solution of both soils occurred as a function of the equilibrium between the iron forms as well as the stabilization of Eh and increase in pH values (Figure 2), decreasing the solubility of iron compounds during the reduction.

Regarding Argiaquoll (Figure 3b), the P contents in the solution did not present a defined behavior, ranging from low values, not exceeding  $0.10 \text{ mg L}^{-1}$ . Albaqualf presented high P values during the first week of flooding,



**Figure 3:** Fe (a) and P (b) concentrations in soil solution for the two studied soils: Albaqualf and Argiaquoll.

**Table 1:** Chemical features and clay content of the studied soils

	pH ( $\text{H}_2\text{O}$ )	OM	Clay	$\text{Fe}_{\text{ox}}^1$	$\text{Fe}_{\text{dit}}^2$	$\text{P}_{\text{Melich}}^3$	$\text{Mn}_{\text{ox}}^1$	MPAC	Ca	Mg	$\text{CEC}_{\text{efetiva}}$	Al	H+Al
		(%)		(g $\text{dm}^{-3}$ )			(mg $\text{kg}^{-1}$ )		(cmol $\text{c dm}^{-3}$ )				
Albaqualf	5.3	1.2	15.3	1.1	3.1	9.4	0.04	243	2.4	0.5	5.1	0.4	1.9
Argiaquoll	5.1	1.6	28.7	4.4	17.9	3.9	2.78	769	12.2	1.5	16.9	0.02	2.6

OM - organic matter; MPAC - maximum phosphorus adsorption capacity - Langmuir's isotherm.

<sup>1</sup>Ammonium oxalate extraction at pH 6.0; <sup>2</sup>Ditionyrocitrate-bicarbonate <sup>3</sup>Mehlich-1 method.

with values of approximately  $0.74 \text{ mg kg}^{-1}$ , which decreased in the second week up to  $0.32 \text{ mg L}^{-1}$ , remaining high until the end of the flooding period and ranging from 0.28 to  $0.41 \text{ mg L}^{-1}$ .

Soils with different mineral origin also presented higher P content in the solution for Albaqualf when compared with Argiaquoll (Gonçalves & Meurer, 2010). According to these authors, this difference could be based on the fact that basalt soils have a predominance of manganic to manganous reductions, leading to little P increase in the soil solution. Also, an absence or minimal reduction of ferric to ferrous oxides with a release of adsorption P and readsorption of P desorption by reduction.

Phosphorus contents in flooded soil solutions result from two processes: reduction of  $\text{Fe}^{3+}$  oxides with a release of associated P and its readsorption after being released into the soil solution. Argiaquoll, despite the highest contents of  $\text{Fe}_0$  (Table 1), which contribute to a higher reduction of Fe and a higher degree of P release, also presented higher MPAC (Table 1), increasing P readsorption when compared with Albaqualf, therefore decreasing the P content in the soil solution.

The MPAC observed in the Argiaquoll is attributed to the higher iron oxide values ( $\text{Fe}_{\text{dit}}$  and  $\text{Fe}_{\text{ox}}$ ) when compared with Albaqualf (Table 1). The high ability of iron extracted by ammonium oxalate at pH 3.0 to react with phosphorus has been proven (Börling, 2003), in which reduced levels of P adsorption were found in soil samples from Rio Grande do Sul, Brazil.

As a soil mineral attribute,  $\text{Fe}_{\text{dit}}$  was found to be the best parameter correlating with MPAC in five soil samples from different regions of Brazil (Fink *et al.*, 2014), while high correlations between MPAC and  $\text{Fe}_{\text{ox}}$  ( $R=0.98$ ) and  $\text{Fe}_{\text{dit}}$  ( $R=0.95$ ) were also found (Gonçalves *et al.*, 2011). These results agree with those from Abolfazli *et al.* (2012), in which P adsorption in acid soils occurred preferentially in the iron fractions.

According to Gonçalves *et al.* (2011), as well as to the results presented here, Albaqualfs have lower values of Mn oxides and poorly crystallized Fe (Table 1), which promote a low P adsorption ability.

Model coefficient estimate values, their differences, associated probabilities to Student t distribution, and model fitting parameters are shown in Table 2.

**Table 2:** Coefficient estimates ( $\beta_0$ -linear,  $\beta_1$ -angular, and  $\beta_2$ -curvature), their differences, associated probabilities to the t statistics, determination coefficient ( $R^2$ ), and standard error of model residues

Coefficient	Estimates	p   t
$\beta_0$ Albaqualf	669.1424	< 0.001**
$\beta_0$ Argiaquoll	742.7541	< 0.001**
$\beta_0$ Albaqualf - $\beta_0$ Argiaquoll	-73.6117	0.02863*
$\beta_1$ Albaqualf	-5.4201	< 0.001**
$\beta_1$ Argiaquoll	0.2794	0.6531
$\beta_1$ Albaqualf - $\beta_1$ Argiaquoll	-5.6995	< 0.001**
$\beta_2$ Albaqualf	0.0177	< 0.001**
$\beta_2$ Argiaquoll	-0.0108	0.002*
$\beta_2$ Albaqualf - $\beta_2$ Argiaquoll	0.0177	< 0.001**
$R^2$	0.9286	
Standard error of residues	49.29	

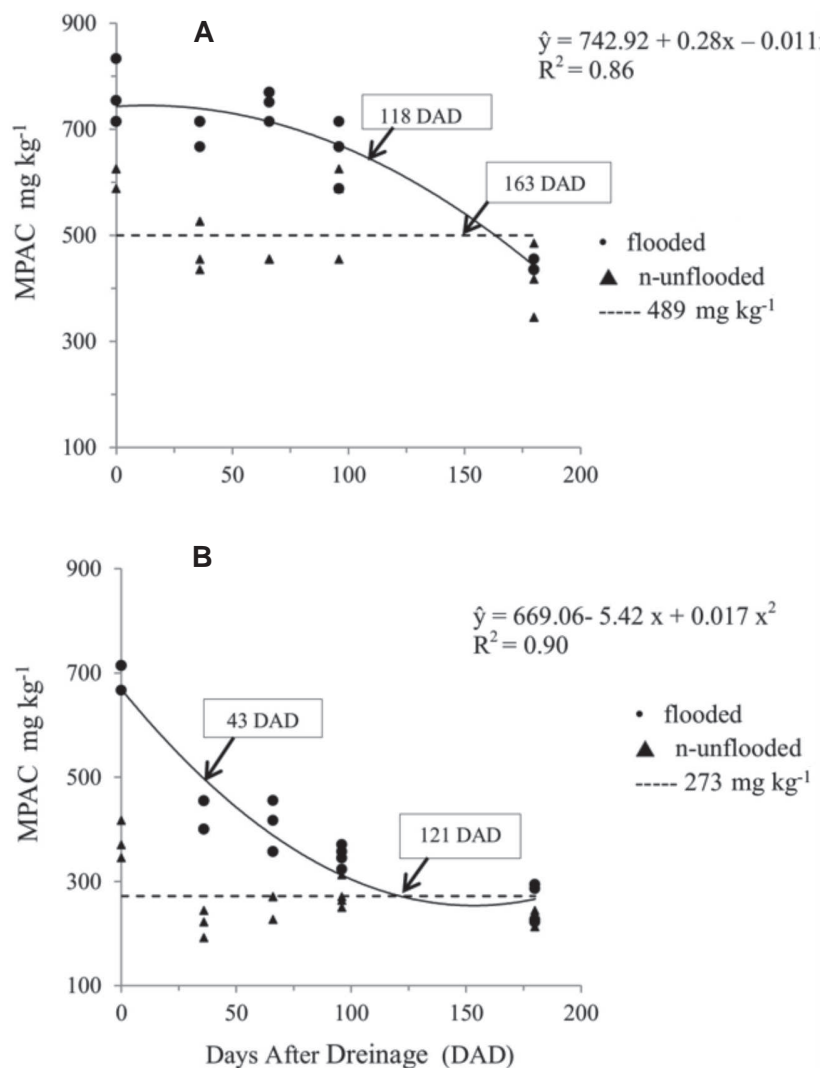
\* Significant at  $p \leq 0.05$ .

\*\* Significant at  $p \leq 0.01$ .

$$\text{MPAC} = \beta_0 D + \beta_1 \text{DAD} + \beta_2 \text{DAD}^2 \quad (\text{Equation 1})$$

The significant effects for the differences between the coefficient estimates indicate that MPAC behavior after soil drainage was different for both evaluated soil classes. The linear coefficient values showed that, immediately after drainage, the MPAC for the Argiaquoll was much higher than that observed for the Albaqualf. Although this difference was observed from the beginning of the experiment, the MPAC profiles tended to be more contrasting between the soils at longer times after drainage.

In Figure 4a and 4b, the MPAC response profiles for the evaluated soils are presented. For the Argiaquoll, a negative curvature coefficient value, characterizing a convex response profile, indicated a tendency of maintaining high MPAC values soon after drainage, with later start of reduction. For Albaqualf, the concavity of the response profile, characterized by a positive curvature coefficient ( $\beta_2$ ), indicated a tendency of immediate MPAC reduction after soil drainage.



**Figure 4:** Maximum phosphorus adsorption capacity (MPAC) response profiles for (a) Argiaquoll and (b) Albaqualf during the drainage period following and unflooded conditions.

However, the highest contrasting values between the response profiles are observed for the MPAC reduction rate, evidenced by angular coefficient values ( $\beta_1$ ) of the model. For Argiaquoll, a non-significant  $\beta_1$  suggests a slow MPAC reduction, which starts approximately 30 days after drainage. For Albaqualf, the angular coefficient value shows a steep decrease of MPAC, rapidly reaching an equilibrium condition.

The difference in soil behavior is associated to content and behavior of Fe oxides in oxidation and reduction in soil environments. Argiaquoll presented higher absolute contents of poorly crystallized iron and manganese oxides (Table 1), promoting higher MPAC. The lower degree of oxide crystallization results in higher reactivity and higher P adsorption. Thus, it requires longer times for the reoxidation of reduced forms after drainage until MPAC reaches its initial condition.

In addition, in Figure 4a and 4b, the necessary times for reestablishing the original MPAC values, i.e., values of aerobic conditions (TR) for both soils, are presented. For Argiaquoll, the TR value was estimated considering only the positive root of the Bhaskara solution, since there are no possible negative values for time in a physical sense. For Albaqualf, only the smaller root value was considered, since the larger value results only from the geometric features of the fitted profile.

The TR value for Argiaquoll (163 days) was 42 days longer than the one observed for Albaqualf (121 days) (Figure 3a and 3b). Considering the TR for half of the difference between flooded and non-flooded levels, the variation between the soil classes increases to 75 days (118 and 43 days for Argiaquoll and Albaqualf, respectively).

The frequent changes in oxidation and reduction conditions in flooded soils alter the stability of different soil minerals, such that poorly crystallized Fe oxides and hydroxides become predominant with time (Reddy & DeLaune, 2008). In this environment, poorly crystallized Fe oxides, which present larger specific superficial area and higher chemical reactivity than better crystallized fractions (Schwertmann & Taylor, 1989), will be the most important components of P adsorption during the period in which the soil remains drained. Besides, these will control P release caused by the later flooding for rice cultivation. This fraction is very important in the P supply for rice crop and is also responsible for many differences between upland and flooded soils regarding response to phosphate fertilizers added to the soils.

Ranno *et al.* (2007) performed the fractioning of phosphorus in lowland soils of Rio Grande do Sul and concluded that Fe-P is the major form of inorganic P in lowland soils, increasing its proportion with soil flooding. According to Tian *et al.* (2017), Fe minerals are the major

controllers of P dynamics in seasonally flooded environments, such as lowland soils.

Considering the cultivation of rice in a crop rotation scheme, with winter pastures and upland summer grain crops, it is expected that winter pastures will show higher limitations regarding P nutrition due to an increase in MPAC after the flooding period during rice cultivation.

For summer grain crops, which are cultivated between six and seven months after rice harvest, the effects of flooding on the MPAC are no longer so strong and should not be taken into account when considering P nutrition for these crops in lowland areas.

## CONCLUSION

Soil drainage after a flooding period increases de maximum phosphorus adsorption capacity, and this effect remains for approximately 163 days in Argiaquoll and 121 days Albaqualf soils.

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