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Phosphorus availability in the central area of the Argentine Pampean region. 1: Relationship between soil parameters, adsorption processes and wheat, soybean and corn yields in different soil and management environments

Disponibilidad de fósforo en el área central de la Región Pampeana Argentina. 1: Relación entre los parámetros edáficos, los procesos de adsorción y los rendimientos de trigo, soja y maíz en diferentes ambientes de suelo y de manejo del cultivo

Disponibilidade de fósforo na área central da Pampa Argentina. 1: Relação entre parâmetros do solo, processos de adsorção e rendimentos de trigo, soja e milho em diferentes ambientes de solo e manejo da cultura

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ABSTRACT

Retention of phosphorus in the soil solid phase is a complex process, caused by a combination of physical and chemical mechanisms that determine pools of compounds with different degrees of solubility. The amount of P available in a given pool can be associated with the adsorption maximum proposed by the Langmuir isotherm model, and with the energy with which it is retained. The aims of this work were: *i)* to evaluate the impact of the fertilization history and soil type on phosphorus adsorption parameters, and *ii)* to analyze the effect of soil properties, mainly the phosphorus adsorption parameters, on the yield of wheat, soybean and corn crops. In this study we established that the Bray & Kurtz 1 extractant is insufficiently sensitive for assessing changes in the nutrient availability when phosphorous concentrations are relatively low. The amount of phosphorus retained in the labile pool and its retention energy, however, are sensitive indicators of the availability of this nutrient. These indexes explain most of the variations in crop yields, and are determined more by P fertilization management than by soil type.

RESUMEN

La retención de fósforo en la fase sólida del suelo es un proceso complejo que es causada por una combinación de varios mecanismos físicos y químicos, que determinarán reservorios de compuestos con diferente grado de solubilidad. La cantidad de P disponible en un reservorio dado se puede asociar al máximo de adsorción propuesto por el modelo de isoterma de Langmuir y a la energía con la que está retenida en la fase sólida. Los objetivos de este trabajo fueron: i) evaluar el impacto de la historia de fertilización y el tipo de suelo en los parámetros de adsorción de fósforo, y ii) analizar el efecto de las propiedades del suelo, principalmente los parámetros de adsorción de fósforo, en el rendimiento de los cultivos de trigo, soja y maíz. En este estudio se estableció la baja sensibilidad del extractante Bray y Kurtz 1 para evaluar los cambios en la disponibilidad de fósforo cuando las concentraciones son relativamente bajas, mientras que la cantidad del nutriente retenido en el reservorio lábil y su energía de adsorción son indicadores sensibles de su disponibilidad. Estos índices explican la mayor parte de las variaciones en los rendimientos de los cultivos y están determinados más por las condiciones de manejo que por el tipo de suelo.

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RESUMO

A retenção de fósforo na fase sólida do solo é um processo complexo, que é causada por uma combinação de vários mecanismos físicos e químicos que determinam reservatórios de compostos com diferentes graus de solubilidade. A quantidade de P disponível em um determinado reservatório pode ser associada com a adsorção máxima proposta pelo modelo de isotérmica de Langmuir e pela energia que é retida na fase sólida. Os objetivos deste estudo foram: i) avaliar o impacto do historial do tipo de fertilização e de solo sobre os parâmetros de sorção de fósforo, e ii) analisar o efeito das propriedades dos solos, principalmente os parâmetros de adsorção de fósforo, nas produções de trigo, soja e milho. Este estudo permitiu verificar a baixa sensibilidade do extractante de Bray e Kurtz 1 para avaliar mudanças na disponibilidade de fósforo, quando as concentrações são relativamente baixas, enquanto a quantidade de nutrientes retida no reservatório lábil e na energia de adsorção são indicadores sensíveis à disponibilidade deste nutriente. Estes índices explicam a maior parte da variação que ocorre na produção das culturas, e são determinados essencialmente pela gestão da fertilização fosfatada mais do que pelo tipo de solo.

KEY WORDS
Soil fertility, Mollisols, Langmuir isotherm

PALABRAS CLAVE
Fertilidad de suelo, Molisoles, Isoterma de Langmuir

PALAVRAS-CHAVE
Fertilidade do solo, Mollisols, Isotérmica de Langmuir

1. Introduction

Retention of phosphorus in the soil solid phase is a complex process that is caused by a combination of various physical and chemical mechanisms. The solubility of the product resulting from this interaction will depend, among other factors, on the soil-solution contact time (Amacher 1991). Almost instantaneous reactions take place on the surface of the particles, whereas others are slower as the phosphorus needs to be transported to the interior (McGechan and Lewis 2002). These physical processes are often accompanied by chemical precipitation reactions, known as chemisorption (Álvarez et al. 2004). According to the reaction and the type of resulting product, the phosphorus will be part of different compartments or *"pools"*, depending on its solubility. The amount of phosphorus in each *pool* at any given time depends on the history of phosphate fertilization and on the time passed since the application of the fertilizer (Hartikainen 1991).

Similar to other chemical compounds, non-linear relationships are observed between the quantities retained and those present in solution as the phosphorus is adsorbed. This is because the bonds that occur with solid surfaces have different levels of energy, which decrease as the different adsorption sites become occupied (McGechan and Lewis 2002).

The amount of P available in a given *pool* can be associated with the adsorption maximum proposed by the Langmuir isotherm model (*Qmax*). In this case it represents the maximum amount of P adsorbed in rapid adsorption processes that are, in general, reversible by different means (Sparks 1995). Situations in which there are two or more pools of available P have been observed. These pools are identified by different adsorption maxima *Qmax* ($Qmax_1...Qmax_n$), each with different adsorption energy ($k_1...k_n$), and are represented by double-site Langmuir isotherms (Sparks 1995), where the first components represent the chemical adsorption, and the subsequent components represent the physical adsorption that occurs over longer periods of time.

The extent of adsorption depends on soil type, thus it tends to be high in soils with a high proportion of fine particles, such as oxides and clay minerals. In different soils of the Argentinean Pampa region, Giuffré (1989) found that, in general, phosphorus adsorption increases with the amount of clay, cation exchange capacity, the content in exchangeable calcium, and the percentage of iron oxides; whereas it is negatively correlated with soil pH and extractable phosphorus. In other Argentinean soils, Mendoza (1986) observed that the soil capacity of phosphorus adsorption increases with extractable aluminum, mainly in the form of amorphous oxides, and with clay content. Colloidal organic compounds also provide sites for adsorption of P, although the effect of the organic matter is variable (De Willigen et al. 1982; Eghball et al. 1996). Giuffré et al. (1986) observed that organic compounds could retain significant amounts of phosphorus when they were associated with Fe^{3+}, Al^{3+} and Ca^{2+} cations.

These studies only refer to variations in the amounts of P adsorbed, and not to changes in the retention energy, which determines the availability of the phosphate compound. Bachmeier (2011) and Silva Rossi (2012a and 2012b) observed an inverse relationship between the amount of P adsorbed and the adsorption energy in different soils of the Pampa region, which would indicate the labile nature of the phosphorus adsorbed in fast reactions that are adequately described by Langmuir models.

Our hypothesis was that the history of phosphate fertilization and the soil properties affect P availability and its sorption energy, as well as impacting on the crop yields of wheat, second-crop soybean and corn in different environmental conditions. In order to corroborate this, the following objectives were set using three soils of the central pampas region or Argentina: *i)* to evaluate the impact of the fertilization history and soil type on phosphorus adsorption parameters, and *ii)* to analyze the effect of soil properties, mainly the phosphorus adsorption parameters, on the yield of wheat, soybean and corn crops.

2. Materials and Methods

The work was carried out in three soils that belong to long term trials from CREA South Santa Fe and IPNI Southern Cone, under crop rotation (wheat, soybean and corn) and zero tillage. The soils are classified as Typic Argiudoll (La Chispa, Santa Fe, Argentina, 33°32'28" S, 61°59'45" W), Typic Hapludoll (Teodelina, Santa Fe, Argentina, 34°14'13" S, 61°29'58" W) and Entic Haplustoll (Canals, Córdoba, Argentina, 33°31'18" S, 62°33'3" W) according to Soil Taxonomy (Soil Survey Staff 2010). The experimental design was in blocks with completely randomized parcels, with three replicates for treatment in each site. We studied annually fertilized parcels during seven agricultural seasons (38 kg P/ha/year, which exceeds the crop requirements by 10%). We also used control parcels of each site, which were under zero tillage and the same crop rotation but without phosphorus application. Composite soil samples (n = 30 subsamples) from the A horizon were taken from each of the three replications and control plots of each site at the end of the crop season of wheat (December 2008), soybean and corn (April 2009). We thus obtained the following composite samples: ((3 crops + 1 control plot) × 3 replicates) × 3 sites (soils). In each of these samples, the following analyses were performed: particle size analysis through the pipette method (Day 1986), soil pH with glass electrode in a 1:1 (v/v) soil-water suspension, soil organic matter (SOM) through the Walkley and Black procedure (Nelson and Sommers 1996) and labile and stable SOM by physical fractionation (Andriulo et al. 1991), cation exchange capacity (CEC) by displacement of adsorbed cations and saturation of the exchange complex with NH_4^+, using NH_4OAc 1 M, pH 7 (Sumner and Miller 1996), and extractable phosphorus using the Bray & Kurtz 1 (PBray1) method (Kuo 1996).

The phosphorus adsorption capacity was determined by means of adsorption isotherms. For this, solutions with increasing concentrations of phosphorus (0, 3, 6, 10, 15, 20, 25, 30 and 50 mg P/L) were added to soil samples. We allowed 96 h of equilibration time; after that, the soil solution was extracted by centrifugation at 6000 rpm and the remaining P in solution was analyzed. The results were modeled with the

Langmuir double-site equation, which is used to describe sorption data in adsorbents in which it is possible to distinguish between different groups of sites with different affinities for the adsorbate:

$$Q = \frac{Q_{\max 1} \times k_1 \times C}{(1 + k_1 \times C)} + \frac{Q_{\max 2} \times k_2 \times C}{(1 + k_2 \times C)}$$

where the variable C is the concentration of P in solution in equilibrium with the P adsorbed (Q). The subscripts ($_{1,\ 2}$) identify the maximum adsorption (*Qmax*) and the energy constant (*k*) for high and low affinity sites, respectively (Sparks 1995).

With the parameters obtained from the isotherm, the maximum buffer capacity (MBC) was estimated calculating MBC = *Qmax* × *k* (Kuo 1991).

The results were analyzed by fitting the isotherm data to non-linear regression models; analysis of variance was used to identify differences among means of Langmuir parameters (LSD Fisher at $p<0.05$); Multivariate analysis of principal components was used to describe the variables behavior and their associations with the values of the various parameters evaluated. The degree of association between the variables was evaluated through Pearson´s partial correlations. These analyses were conducted with the InfoStat statistic software (Di Rienzo et al. 2011).

3. Results and Discussion

3.1. Soil Properties

In **Table 1**, soil pH, extractable phosphorus by PBray1, total, labile and stable SOM, cation exchange capacity (CEC), and sand, loam and clay content for each of the soil and management environments are shown.

Table 1. Soil pH, PBray1, SOM, CEC, sand, loam and clay values in each of the soils and treatments. Different letters indicate the minimum significant difference in PBray1, LSD Fisher Test ($p<0.05$)

Soil:	Typic Hapludoll		Entic Haplustoll		Typic Argiudoll	
Treatment	Without P	With P	Without P	With P	Without P	With P
Soil pH	6.2	6.0	6.1	5.8	5.6	5.3
PBray1 (mg kg^{-1})	8.1b	14.5b	10.7b	25.9a	12.2b	28.3a
Total SOM (mg kg^{-1})	29.9	25.6	20.6	26.1	29.6	27.2
Stable SOM (mg kg^{-1})	26.3	24.1	19.9	23.7	25.3	26.4
Labile SOM (mg kg^{-1})	3.6	1.5	0.7	2.4	4.3	0.8
CEC (cmol$_c$ kg^{-1})	14.1		13.2		17.2	
Sand (g kg^{-1})	502.0		648.0		318.0	
Loam (g kg^{-1})	326.0		224.0		454.0	
Clay (g kg^{-1})	172.0		128.0		228.0	

As shown in **Table 1**, the different history of fertilization in the Typic Hapludoll (with and without P) did not produce significant differences in the amount of extractable P, and non-fertilizing treatments do not differ in the three soils. The reason why no differences are observed in extractable P is explained by the studies carried out in these soils by Ciampitti (2009), who evaluated the evolution of PBray1 after 7 years of phosphate fertilization and noted that, on average, a positive cumulative balance between 147 and 180 kg P ha^{-1} had to be exceeded in order to increment PBray1 by 1 mg kg^{-1}, depending on the soil type. This is because the PBray1 extractant is insufficiently sensitive to changes in P availability when the nutrient levels are low (Silva Rossi 2012b).

3.2. P Adsorption

In **Table 2**, double-site Langmuir model parameters and maximum buffer capacity (MBC) are shown in detail (an example of the isotherms is presented in **Figure 1**). Variations in the extractable P do not correspond with variations in the parameters of the double-site Langmuir isotherms. In the Typic Argiudoll, the different history of fertilization did not affect the adsorption parameters of the first segments of the isotherm; however, the PBray1 value did, where increases of this parameter did not modify the nutrient availability, since k and MBC values did not differ. In situations without history of fertilization, with equal PBray1 values, the availability of the nutrient was markedly affected by soil type; those with greatest amount of labile organic matter and clay had less retention energy in the first pool of available P. In the Entic Haplustoll, the history of fertilization positively affected the values of PBray1 and the nutrient availability. In contrast, in the Typic Hapludoll, fertilization only affected the phosphate availability. These relationships between the values of extractable P and the isotherms parameters indicate that the PBray1 extractant is insufficiently sensitive to assess changes in the nutrient availability under these conditions. In this table, a high negative association is observed between $Qmax_1$ and the adsorption energy (k_1), which indicates that when the amount of phosphorus adsorbed increases in the first site of adsorption the energy of adsorption decreases. The maximum capacity of adsorption on the first site has a positive correlation with the maximum capacity of adsorption on the second segment, so the size of the two pools is directly correlated. When the total adsorbed amounts are high ($Qmax_2$), the MBC_2 will also be high. These results coincide with those determined by Bachmeier (2011) in Typic Haplustoll soils located in the centre of Córdoba (Argentina) with a different agricultural history, and indicate the labile nature of the adsorbed phosphorus in these Mollisols of Argentina.

Table 2. Double-site Langmuir model parameters ($Qmax_1$, $Qmax_2$, k_1 y k_2), maximum buffer capacity (MBC_1 and MBC_2), extractable phosphorus (PBray1), in each site and treatment. Different letters indicate the minimum significant difference. LSD Fisher Test (p<0.05)

		PBray1	Double-site Langmuir parameters					
Soil	Treatment	(mg kg^{-1})	$Qmax_1$	k_1	MBC_1	$Qmax_2$	k_2	MBC_2
Typic Argiudoll	Without P	12.2*b*	36.2*a*	11.3*c*	409.1	185.5*a*	0.04*c*	7.4
	With P	28.3*a*	36.5*a*	13.5*c*	492.8	180.2*a*	0.06*b*	10.8
Entic Haplustoll	Without P	10.7*b*	22.8*b*	43.5*a*	991.8	144.8*b*	0.06*b*	8.7
	With P	25.9*a*	31.4*a*	21.6*b*	678.2	142.0*b*	0.07*ab*	9.7
Typic Hapludoll	Without P	8.1*b*	32.7*a*	10.6*c*	346.6	210.8*a*	0.09*a*	19.2
	With P	14.5*b*	26.1*b*	58.8*a*	1534.7	180.1*a*	0.09*a*	16.2

In order to determine the relations between soil parameters and P adsorption, a correlation analysis was performed (**Table 3**). PBray1 variation did not affect the isotherm parameters, but was related to the amount of labile organic matter, which, according to the observations of Tiessen (1991), is consistent with the fact that a higher content of low molecular weight organic compounds can increase the availability of phosphorus and its supply to crops.

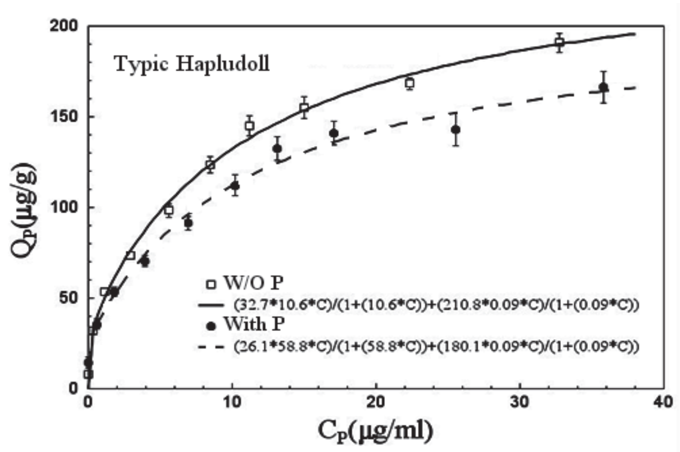

Figure 1. Phosphorus adsorption isotherms for the Typic Hapludoll, relating adsorbed soil P (Q_P) to soil solution P (C_P). Lines correspond to the fit to double-site Langmuir models, whose parameters are detailed for plots without P fertilization (W/O P) and fertilized with P (With P).

Table 3. Pearson´s correlation coefficients and its probability level among double-site Langmuir equation and soil properties. Significance level: *** p<0.001, ** p<0.05, * p<0.10

Variable	$PBray_1$	$Qmax_1$	k_1	MBC_1	$Qmax_2$	k_2	MBC_2
PBray1 (Bray1)	1	0.58	-0.49	-0.54	0.37	-0.26	0.03
pH	-0.26	0.05	0.45	0.32	-0.01	-0.09	-0.40
Total SOM	0.78	0.34	-0.37	-0.40	0.20	-0.18	0.10
Stable SOM	0.54	0.05	-0.25	-0.21	-0.04	0.09	0.38
Labile SOM	**0.85*****	0.53	-0.41	-0.49	0.37	-0.39	-0.17
Sand	0.12	-0.28	0.56	0.53	-0.48	0.49	0.31
Clay	0.06	0.46	-0.68*	-0.67*	0.63*	-0.62*	-0.40

3.3. Crop Yield

The crop yields used here are those of the crop season analyzed in this study. Yields of the corn crop in different soil and management environments are presented in **Figure 2**, which shows the effect of interaction between the soil environment and the continuous management of phosphate fertilization. **Figure 3** shows the wheat crop yields as general averages, since there was a P×site null interaction. This indicates that the wheat yield responded to the continuous management of fertilization and soil environment in a different way to corn. This effect may be due to the variable water availability for the wheat crop, since it grows in the dry season of the Argentinean pampas.

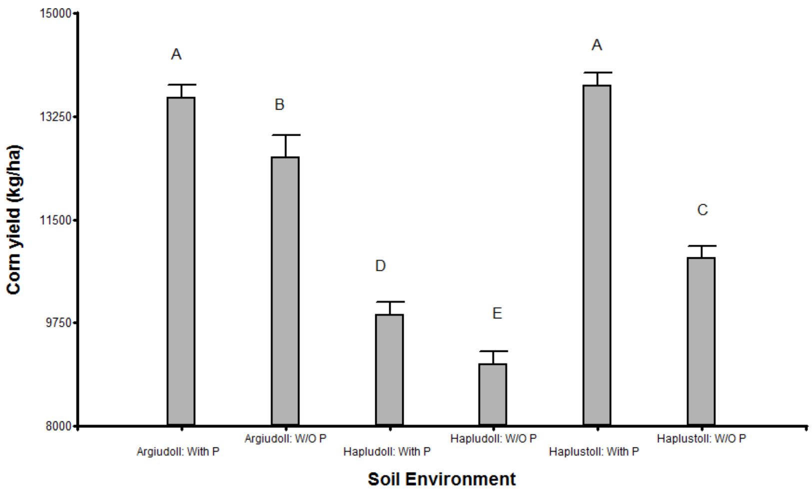

Figure 2. Average yield values of corn for each soil and management environment. Different letters indicate the LSD Fisher Test significant differences (p<0.05).

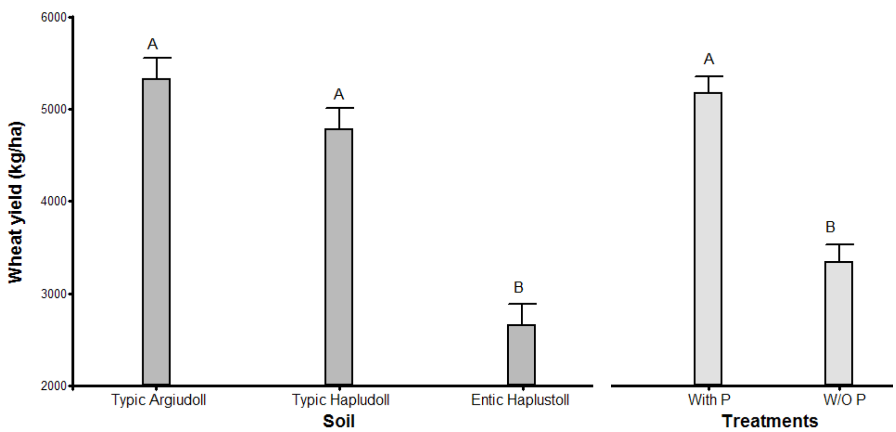

Figure 3. Average yield values of wheat for each soil and management environment. Different letters indicate the LSD Fisher Test significant differences (p<0.05).

Second-crop soybean yields are shown in Figure 4. As with corn, the second-crop soybean yields also exhibit an effect of interaction between soil environment and continuous management of phosphate fertilization. Figure 4 shows that the soybean yield of the Argiudoll with P is lower than the yield at the same site without P; this effect is explained later, using a principal components multivariate analysis.

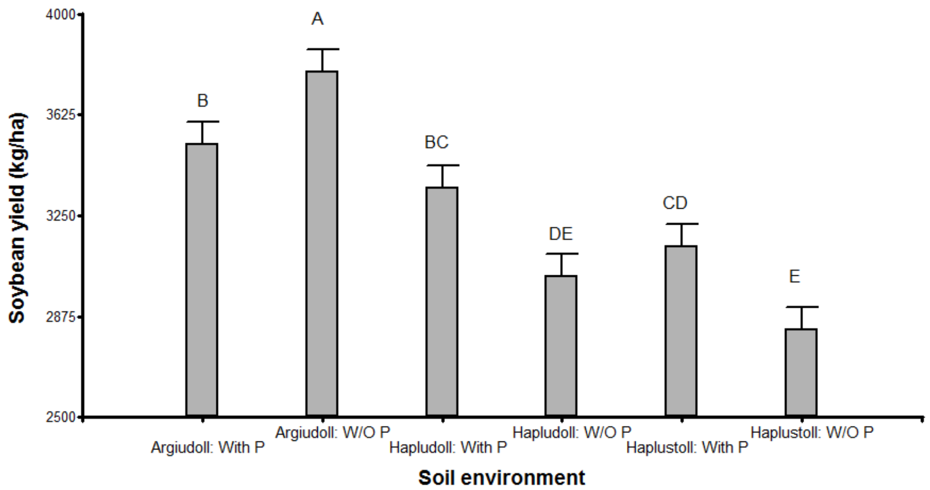

Figure 4. Average yield values of second-crop soybean (i.e. soybean crop sowed just after the wheat crop harvest) for each soil and management environment. Different letters indicate the LSD Fisher Test significant differences ($p<0.05$).

3.4. Relation between the adsorption parameters, soil variables and crop yield in the different soil and management environments

In order to describe these relationships, a principal component multivariate analysis was performed among all the variables evaluated in different soil and management environments. This analysis is presented in the biplot in Figure 5.

The principal component analysis explained the 80.3% of total variability: the first component is responsible for the greater variability proportion (51.5%) and in this direction the wheat and second-crop soybean yield vector increases; the corn yield vector varies according to the second component (28.8%).

Soybean and wheat yields were associated with the amount of phosphorus adsorbed on the first segments of the double-site Langmuir isotherm ($Qmax_1$) and with the amount of clay; this is explained by the acute angle between the vectors. Additionally, there was no association between the yield of these crops and the extractable phosphorus obtained by the Bray and Kurtz 1 method, the maximum buffer capacity (MBC_1, MBC_2) and the amount of organic matter, demonstrated by the right angle observed between the vectors. The amount of sand, soil pH and phosphorus retention energy in the first segment of the isotherm (k_1) showed a negative association with these crops yield, demonstrated by the straight angle between the vectors. These relationships explain, in part, why the soybean yield of the Argiudoll with P is lower than at the same site without P. Corn yield showed a positive association with P availability; and was negatively associated with soil pH and phosphorus retention energy in the second segment of the

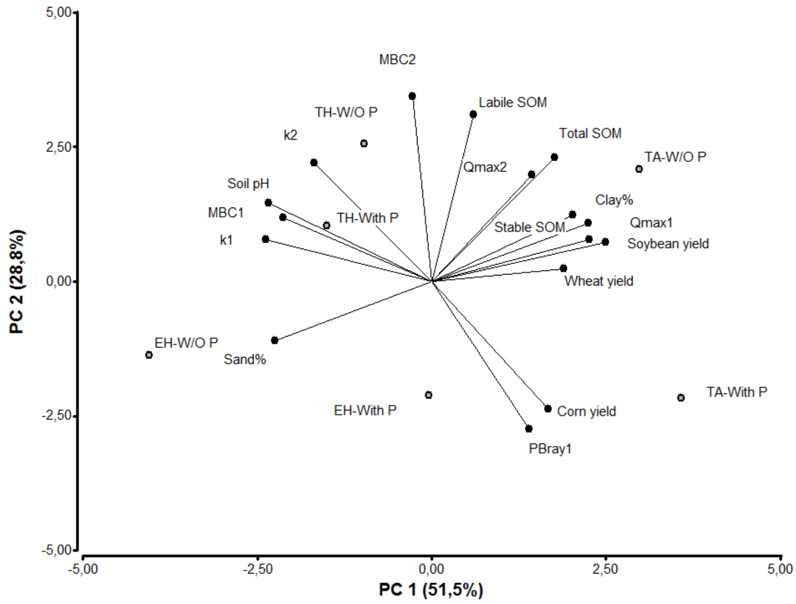

Figure 5. Biplot for the relation between the soil and management environments, crop yield, soil properties and P adsorption parameters (TH with P: Typic Hapludoll with P, TH W/O P: Typic Hapludoll without P, TA with P: Typic Argiudoll with P, TA W/O P: Typic Argiudoll without P, EH with P: Entic Haplustoll with P, EH W/O P: Entic Haplustoll without P).

isotherm. In order to establish the relative importance of each of these physical and chemical properties on the crop yield, an analysis of correlations was performed (Table 4).

The wheat crop yield variation was only explained by the soil texture, increasing with the amount of clay, and is a property related to the soil water holding capacity. This property, together with the amount of available water stored during the fallow period, is a determining factor in the yield of this crop in the Argentinean Pampa region, since the monsoon rainfall regime (Conti and Gianoni 1983) determines the occurrence of poor winter rainfall that occurs in spring around the anthesis of the cultivation period.

Corn yield increased with the increase in PBray1 levels. This positive relationship can be attributed to the agro-ecological conditions of the environments that displayed the larger PBray1 levels: the Typic Argiudoll is from an environment with a more recently developed agricultural history, and the Entic Haplustoll experienced meteorological conditions that allowed high yields. The production of this crop decreased with an increase in the phosphorus retention energy, in a greater proportion along the second segments of the double-site Langmuir isotherm (k_2), and also decreased with the pH of the soil reaction. It can be deduced that this species is highly sensitive to P bioavailability (Silva Rossi 2012b). Soybean yield was directly related to the maximum capacity of retention of phosphorus ($Qmax_2$), mostly by the first segment of the isotherm ($Qmax_1$, r=0.97), and to the amount of clay. This implies that this crop requires high rates of desorption of the initially adsorbed P (Silva Rossi 2012b). This is reinforced by the fact that the yield in second-crop soybeans, like corn, decreased with an increase in phosphorus retention energy in the first segment of the isotherm (k_1) and pH reaction. This positive relationship between the second-crop soybean yield and the size and low retention energy of the first phosphorus labile pool may explain the lack of response to phosphate

Table 4. Pearson´s correlation coefficients among the soil parameters and crop yield. Significance level: *** p<0.001, ** p<0.05, * p<0.10

Variable	Wheat	Corn	Second-crop Soybean
Wheat	1		
Corn	0.20	1	
Second-crop soybean	0.53	0.53	1
PBray1	0.49	**0.83****	0.26
$Qmax_1$	0.36	0.55	**0.97*****
k_1	-0.66	**-0.71***	**-0.72***
MBC_1	-0.65	-0.66	-0.58
$Qmax_2$	0.11	0.16	**0.79***
k_2	-0.15	**-0.90*****	-0.59
MBC_2	0.12	-0.73	0.07
pH	-0.61	**-0.83****	-0.78*
Total OM	0.55	-0.02	0.70
Stable OM	**0.80****	0.13	0.64
Labile OM	0.03	-0.33	0.41
Sand	**-0.72***	-0.23	**-0.88***
Clay	**0.72***	0.23	**0.88***

fertilization, or the negative response in the Typic Argiudoll, since both parameters define a high phosphorus bioavailability in these environments; a fact that is not reflected in the amount of extractable phosphorus obtained with the Bray and Kurtz 1 method.

4. Conclusions

In soils of the Argentinean Pampa region, at least two pools of available phosphorus were identified. These pools are characterized by two sites of adsorption, where the high phosphorus retention capacity in each one of them was positively associated with soybean yield. This demonstrates the labile nature of the adsorbed phosphorus. Availability is shown with the inverse relation between retention energy and adsorption capacity, therefore soils with higher *Qmax* on the two sites of the isotherm have lower energy retention (related to lower Langmuir k_1 and k_2 constants).

In the soil environments studied, corn yield, as well as the second-crop soybean yield, decreases with the increase in phosphorus retention energy and the decrease in the soil pH, since the lower pH values affect the ionic mechanisms of adsorption, increasing the positive electrical charges rising phosphates energy retention.

Within the ranges evaluated, the Bray and Kurtz 1 phosphorus extractant was not sensitive enough to changes in the nutrient availability in the different soil, fertilization management and crop production environments analyzed. Retention energy, in turn, is a reliable indicator of the availability of this soil nutrient.

The history of phosphate fertilization does not explain the variations observed in the quantity and energy of adsorbed phosphorus in all the environments studied.

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