Soil Fertility & Plant Nutrition Note

Soil Characteristics Involved in Phosphorus Sorption in Mollisols

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The role of different soil properties on defining the P sorption capacity was investigated in a group of Mollisols of the Pampean Region (Argentina). Two-single point and three-multiple point P sorption indices were evaluated. Both simple and multiple regression models indicated that ammonium oxalate extractable Al (Al_{ox}) and ammonium oxalate extractable Fe (Fe_{ox}) were the main properties defining P sorption. Ammonium oxalate extractable Al prevailed as the best predictor of short-term P sorption indices and Fe_{ox} as the best predictor for those indices that involves longer interaction periods. After Al_{ox} and Fe_{ox}, the best correlations were obtained for the sum of Ca and Mg. The higher P retention of soils located in the Southern part of the Region was associated with the parental material rather than with anthropogenic effects. Obtained information can strengthen P fertilization programs by providing a methodology to estimate fertilizer P requirements to optimize crop yields while reducing environmental risks.

Abbreviations: b_{45}, slope of the function of P increase vs. P level; k, constant of the adsorption isotherm; subscript [ox], ammonium oxalate extractable; PRI, phosphorus retention index; S_{max}, P sorption maximum; VIF, variance inflation factor.

Core ideas

- **Predictive models of phosphorus sorption were developed for a group of Mollisols.**
- **Al_{ox} was the best predictor of short-term phosphorus sorption indices.**
- **Fe_{ox} was the best predictor for those indices that involves longer interaction periods.**
- **Phosphorus needs to maximize yield avoiding environmental risks can be estimated with our data.**

The ability to estimate the P sorption capacity of the soils is critical to define the optimum amount of fertilizer P to use and to assess the soil capacity to retain P against leaching or runoff (Ciampitti et al., 2011; Wang et al., 2015). Soil P sorption has been characterized by single- and multiple-point indices. Single-point indices are obtained by exposing the soil to a P solution with known concentration, whereas multiple-point indices involve the exposition of the soil to solutions containing a range of P concentrations (e.g., Sims, 2000). Other multiple-point methods evaluate the proportion of added P recovered by a soil test P (i.e., Bray-P; Cox, 1994; Rubio et al., 2008a). These indices have been successfully used to estimate the fertilizer P requirements to raise soil available P to a target value, especially when incubation periods of 6 to 8 wk were employed (Quintero et al., 1999; Rubio et al., 2008b).

Sorption of P is related to ligand exchange reactions between the soil matrix and soluble phosphates. Most works aiming to estimate P sorption have been developed using a range of soils with ample variation in soil properties (Herlihy and McCarthy, 2006; Cox, 1994; Quintero et al., 1999; Daly et al., 2015). Soil properties frequently associated with P sorption are Fe and Al oxides, extractable Ca and Mg, pH, soil texture, and C content (Maguire et al., 2001; Ige et al., 2007; Daly et al., 2015).

Many of the most productive agricultural areas of the world occupy large surfaces of land with soils that belongs to only one or two soil orders, like the US Corn Belt or the Pampean Region in Argentina (Salazar Lea Plaza and Moscatelli, 1989; Soil Survey Staff, 1999). In previous works, we studied the P sorption

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features of Pampean Mollisols (Rubio et al., 2008a; Gutiérrez Boem et al., 2008) and found that soils located in the southern part of the region had higher P retention than soils located in the northern area. The basic soil properties were not enough to explain this strong effect of the geographic position, suggesting that other soil features would be intervening. Local results (Zarate, 2003) suggest some differences between both Pampean zones in the parent material which could affect the adsorptive matrix of the soil.

The objectives of this study were (i) to investigate the role of different soil properties on defining the P sorption indices in a range of soils belonging to the Mollisol order, (ii) to identify the soil properties responsible for determining why soils located in the southern area of the Pampean Region retain more P than soils located in the northern area.

MATERIALS AND METHODS

The sampling methods and the selected soils employed in the present research can be found in Rubio et al. (2008a). Seventy-one soils belonging to the Mollisol order were selected from 20 representative agricultural areas of the Pampean Region. In each one, the 0- to 20-cm layer was sampled and analyzed for pH, particle-size distribution, organic C, total P, and Bray-1 P (Rubio et al., 2008a) and Mehlich-3 P (Gutiérrez Boem et al., 2011). For the present study, we determined the Al_{ox}, Fe_{ox}, extractable Ca and Mg content, clay specific surface area, and clay pore area. The forms Al_{ox} and Fe_{ox} were obtained after stirring the soil in a solution of 0.175 M ammonium oxalate and 0.1 M oxalic acid at pH 3 for 2 h in complete darkness (Loeppert and Inskeep, 1996). The extractable Ca and Mg were obtained with 1 M KCl (Donagema et al., 2011). The content of Fe, Al, Ca, and Mg in the extracts was determined with an atomic absorption spectrophotometer. Specific surface area ($Clay_{SSA\text{-}BET}$) and pore area of the clay fraction were estimated using the multi-point Brunauer–Emmett–Teller (BET) method (Brunauer et al., 1938; Carter et al., 1986).

Five P retention or sorption indices were compared: Phosphorus Retention Index I and II (PRI I, PRI II), slope of the function of P increase vs. P level (b_{45}), P sorption maximum (S_{max}) and constant of the adsorption isotherm (k). The indices PRI I, PRI II, and b_{45} coefficient were reported previously (Rubio et al., 2008a). The PRI-I evaluates the P retained by the soil through the difference between the P content in the added solution (60 mg P L^{-1} at 25°C) and the P content in the solution after 1 h of equilibrium. For PRI II, the same procedure was employed, including the same soil/solution ratio, but with an equilibration time of 18 h and a P solution of 75 mg P L^{-1} (Sims, 2000). For b_{45}, 5 levels of P (as KH_2PO_4: 0, 8, 16, 32, and 64 mg P kg^{-1}) were added to polyvinyl chloride (PVC) pots containing 150 g of soil. The difference between Bray-P from fertilized and non-fertilized pots was calculated for each P level after the incubation period of 45 d. Simple linear regressions of available P increase vs. P level were evaluated for each soil. The function used was $y = bx$ where y is the increase in Bray-P, b is the slope, and x the P level. A b value of 0.46, for example, indicates that about 46% of the P added appeared as Bray-P, which means that the remaining 54% was retained by the soil.

The P indices P sorption maximum (S_{max}) and k (binding energy constant) were calculated from the Langmuir equation:

$$S = \frac{k \times S_{max} \times C}{1 + k \times C}$$

where S is the P adsorbed (mg kg^{-1}), C is the P in the remaining solution (mg L^{-1}), S_{max} is the maximum sorption capacity of the soil P (mg kg^{-1}), and k is a constant related to the binding energy of the particles. For S_{max} and k, a representative subset of 33 units was selected from the whole set of 71 soils. Two grams of air-dried soil were weighed and put into a 50-mL centrifuge tube and 20 mL of 0.01 M KCl containing different concentrations of P (0, 5, 19, 15, 20, 40, 70, 100, 140, and 200 mg P L^{-1}) were added. The mixtures were shaken on an end-to-end shaker for 24 h at 25 ± 1°C, after which the samples were centrifuged, filtered, and the P concentration in the equilibrium solution was determined colorimetrically by the molybdate blue method. Considering the limitations of the linearized versions of the Langmuir adsorption model (Bolster and Hornberger, 2007), the untransformed data were fitted to the nonlinear form of that model. Other adsorption models (e.g., the two-surface Langmuir model) were tested, but they did not significantly improve the relationships obtained with simpler models as Langmuir (with only two parameters), while adding complexity to the equation (i.e., more parameters).

To develop predictive models, simple and multiple regression analysis were used, relating obtained P indices to different soil parameters (Neter et al., 1990). Northern and southern soils were compared by t tests. Stepwise procedure was employed for multiple regression analysis. The stepwise process was stopped when no variables not already in the model meet the selection criterion and no variables in the model meet the elimination criterion. For both criterions, the p-value threshold was 0.05. Collinearity was checked using the variance inflation factor (VIF), which showed low values (from 1.0 to 2.0), with a mean VIF of 1.16.

RESULTS AND DISCUSSION

Association between Phosphorus Sorption Indices and Soil Properties

Five P sorption indices were regressed against soil properties to identify those properties most relevant for P sorption (Tables 1 and 2). Between these indices, k was the only one that did not show any significant association with the evaluated soil properties (Table 2), suggesting that the binding agents of our soils offered rather similar energy. These results are in line with those reported by Herlihy and McCarthy (2006). However, other studies with a wider range of variation in the soil properties (e.g., Daly et al., 2015) found a significant role of k in discriminating soils of varying P sorption.

Table 1. Mean and coefficient of variation (CV) and number of sampled soils (*N*) for the analyzed soil properties and P sorption indices for the soils of the Argentinean Pampas selected for this study. Soils samples were taken from the top 20 cm. Values are shown for the whole set of soils and grouped according to the geographical location (northern and southern Pampas). The *p* value for the comparison between locations is shown.

	All soils			Northern soils			Southern soils			
Soil properties‡	**Mean**	**CV**	***N***	**Mean**	**CV**	***N***	**Mean**	**CV**	***N***	***p***
Clay, %	23.11	28.0	71	21.01	30.4	4	26.34	19.9	28	***
silt, %	38.97	34.9	71	42.21	34.6	43	34.00	30.1	28	*
clay + silt, %	62.27	27.8	71	63.21	31.7	43	60.75	19.7	28	ns †
Al_{ox}, mmol, kg^{-1}	36.69	28.4	68	31.21	17.6	41	45.01	23.9	27	***
Fe_{ox}, mmol, kg^{-1}	28.15	40.1	68	23.91	28.9	41	34.96	39.2	27	***
Ca, $cmol_c$ kg^{-1}	4.17	31.13	69	3.72	27.6	42	4.87	28.33	27	***
Ca + Mg, $cmol_c$ kg^{-1}	5.14	20.54	69	4.54	13.69	42	6.06	15.3	27	***
$Clay_{SSA\text{-}BET}$, m^2 g $soil^{-1}$	16.02	52.8	66	13.35	46.1	40	20.14	49.2	26	**
Clay pore area, m^2 g^{-1}	2.298	82.9	66	1.86	101.3	40	2.976	59.4	26	*
pH	6.18	6.2	70	6.04	4.8	43	6.40	6.4	27	***
total carbon, g kg^{-1}	21.86	32.9	71	18.32	22.7	43	27.29	27.6	28	***
P_{Bray1}, µg P g^{-1}	12.18	64.8	71	11.19	65.2	43	13.71	63.0	28	ns
$P_{Mehlich3}$, µg P g^{-1}	18.01	55.1	71	17.9	48.6	43	18.19	64.6	28	ns
total P, µg P g^{-1}	324.3	19.7	70	299.1	12.8	42	362.0	21.0	28	***
P sorption indices										
PRI-I	251.5	6.85	71	245.9	5.2	43	260.2	7.6	28	*
PRI-II	310.2	12.59	71	289.1	7.1	43	342.7	11.3	28	***
S_{max}	466.29	52.15	33	306.3	28.7	20	725.6	26.7	13	***
k	0.06	61.55	33	0.07	51.2	20	0.04	36.7	13	**
b_{45}	0.52	22.46	71	0.58	13.6	43	0.41	20.0	28	***

* Significant at $p < 0.05$.

** Significant at $p < 0.01$.

*** significant at $p < 0.001$.

† ns: not significant for the *t* test comparing northern and southern soils.

‡ Alox, ammonium oxalate extractable Al; Feox, ammonium oxalate extrable Fe; PRI I, Phosphorus Retention Index I; PRI II, Phosphorus Retention Index II; S_{max}, P sorption maximum; b_{45}, slope of the function of P increase vs. P level.

The other P sorption indices were associated either with different soil characteristics or, more often, with the same characteristic but to a different extent. It should be taken into account that the indices PRI I, PRI II, and S_{max} reflect how much of the added P is retained by the soil, whereas b_{45} reflects how much of the added P remains as Bray-P (i.e., the opposite of P retention). Therefore, and as expected, those soil properties that had a positive influence on PRI I, PRI II, and S_{max} generally showed a negative influence on b_{45} (Fig. 1).

The PRI I and PRI II indices reflects the interaction between P in solution and the soil matrix in the short (1 h) and longer term (18 h), respectively. For the PRI I index, clay and Al_{ox} showed the highest correlation coefficients (Table 2; Fig. 1) whereas the best multiple regression model included clay content, Al_{ox}, and Fe_{ox} as predictor variables (Table 3). Linear regression between the PRI II index and soil properties followed a similar pattern than for PRI I, although the correlation coefficients were slightly higher (Table 2; Fig. 1). For this index, the variables Al_{ox}, and total C showed the highest r coefficients (Fig. 1; Table 2), whereas Ca + Mg, Fe_{ox} and Al_{ox} were those selected in the best multiple regression model (Table 3). The parameter S_{max} has been identified as a key constituent of environmental indices (Mallarino, 1997; Zhang et al., 2005). In our set of soils, S_{max} was significantly correlated with most analyzed soil properties, especially Fe_{ox} (Table 2; Fig. 1). In the multiple regression analysis, S_{max} was best predicted by Fe_{ox} and Ca + Mg (Table 3).

Table 2. Correlation coefficients (*r* values) of P sorption indices and soil properties. ns = nonsignificant r values ($p > 0.05$).†

Soil properties	All soils				Northern soils				Southern soils			
	PRI I	**PRI II**	**S_{max}**	**b_{45}**	**PRI I**	**PRI II**	**S_{max}**	**b_{45}**	**PRI I**	**PRI II**	**S_{max}**	**b_{45}**
Clay, %	0.71	0.64	0.44	−0.46	0.59	0.55	ns	−0.40	0.78	0.63	ns	ns
clay + silt, %	0.46	0.31	ns	ns	0.56	0.50	ns	ns	0.65	0.66	ns	ns
Silt, %	0.29	ns	ns	ns	0.51	0.44	ns	ns	0.54	0.61	ns	−0.38
Al_{ox}, mmol kg^{-1}	0.63	0.76	0.60	−0.49	0.40	0.36	ns	ns	0.61	0.65	ns	ns
Fe_{ox}, mmol kg^{-1}	0.48	0.63	0.83	−0.63	0.39	0.40	ns	−0.49	ns	0.51	0.65	−0.51
Ca, $cmol_c$ kg^{-1}	0.58	0.60	0.61	−0.35	0.37	0.34	ns	ns	0.58	0.55	ns	ns
Ca + Mg, $cmol_c$ kg^{-1}	0.54	0.69	0.67	−0.54	0.31	0.38	ns	−0.32	0.48	0.46	ns	ns
$Clay_{SSA\text{-}BET}$, m^2 g $soil^{-1}$	0.57	0.53	0.47	−0.36	0.51	0.32	ns	−0.32	0.48	0.42	ns	ns
clay pore area, m^2 g^{-1}	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
pH	NS	0.24	0.38	−0.34	ns	ns	ns	ns	ns	ns	ns	ns
total carbon, g kg^{-1}	0.62	0.74	0.54	−0.56	0.49	0.56	ns	ns	0.53	0.57	ns	ns
P_{Bray1}, µg P g^{-1}	ns	ns	ns	ns	ns	ns	ns	0.37	ns	ns	ns	ns
$P_{Mehlich3}$, µg P g^{-1}	ns	ns	ns	ns	ns	ns	ns	0.38	ns	0.38	ns	ns
total P, µg P g^{-1}	0.54	0.62	0.53	−0.42	ns	ns	ns	NS	0.61	0.70	ns	ns

† Alox, ammonium oxalate extractable Al; Feox, ammonium oxalate extrable Fe; PRI I, Phosphorus Retention Index I; PRI II, Phosphorus Retention Index II; S_{max}, P sorption maximum; b_{45}, slope of the function of P increase vs. P level.

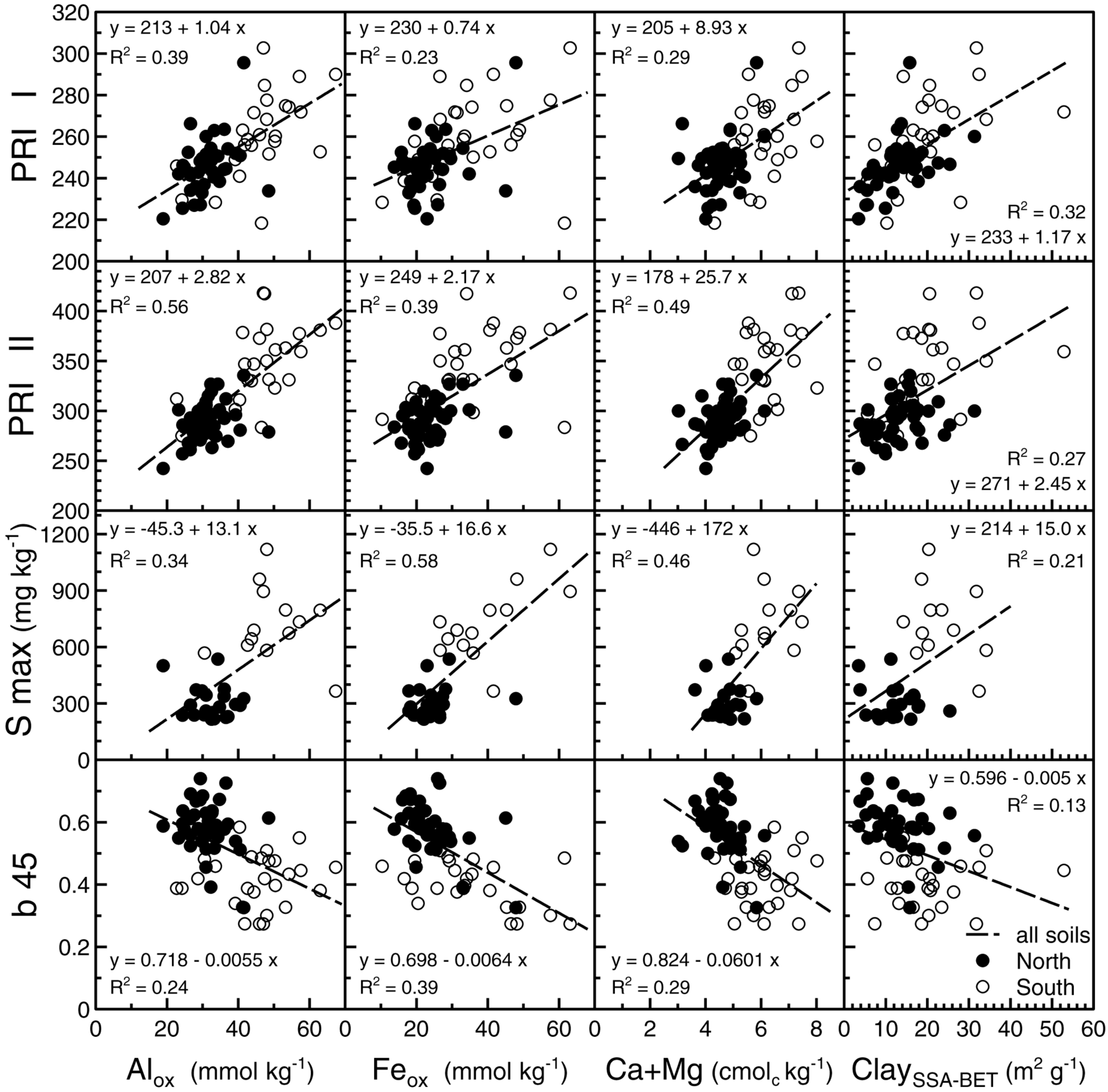

Fig. 1. Relationships between P sorption indices (Phosphorus retention index [PRI] I and II, S_{max} and b_{45}) and Al_{ox}, Fe_{ox}, the sum of extractable Ca and Mg and clay specific surface area ($Clay_{SSA\text{-}BET}$) for Pampean soils. Equations and coefficients of determinations for the linear regressions are included for the whole set of soils. All relationships were statistically significant ($p < 0.05$). Soils belonging to the northern and southern Pampa are represented by different symbols.

The b_{45} index also correlated significantly with most evaluated soil properties (Table 2; Fig. 1). As expected and noted above, in each case the slope had a negative sign (Fig. 1). The higher correlations were obtained with the variable Fe_{ox} (Table 2), whereas the variables selected by the best prediction model (R^2 0.60) were Ca + Mg, Fe_{ox} and initial Bray-P (Table 3). The general average for b_{45} was 0.52, indicating that approximately half of the added P was recovered as Bray-P 45 d after fertilizer application. This index is used by local farmers to estimate the fertilizer P dose to bring the soil P level above the threshold for normal crop growth (for the method see Rubio et al., 2008b).

Overall, both simple and multiple regression models indicated that Al and Fe oxides were the main soil properties defining P sorption. Similar strong correlations were found for other soils, which is a sign of the strength and versatility of Al_{ox} and Fe_{ox} to define P sorption, at least in non-calcareous soils (Maguire et al., 2001; Zhang et al., 2005; Burkitt et al., 2006). Interestingly, Al_{ox} was better predictor than Fe_{ox} in the two short-term indices (PRI-I and PRI-II), whereas Fe_{ox} was a better predictor than Al_{ox} in those indices involving longer periods of interaction (S_{max} and b_{45}). This switch from Al_{ox} to Fe_{ox} suggests that the preference of P for adsorption sites would be affected by the time of exposure of added P to the soil matrix. This is consistent with the view that, in the short term, Al oxides are more reactive than Fe oxides (Cabrera et al., 1977; Penn et al., 2005). However, it has been pointed out that this preference may be affected by the degree of P saturation of Al and Fe materials (Penn et al., 2005). After Al_{ox} and Fe_{ox}, the best correlations were obtained for the sum of Ca and Mg. Ige et al. (2008) also found that the combination of Ca, Mg, and Al_{ox} provided the best estimate of the P retention parameters. These results strongly suggest that the divalent cations, often neglected in P sorption models, can make a significant contribution to the process.

Table 3. Multiple linear models for predicting the P sorption indices for Pampean soils (all soils pooled or grouped by location: northern or southern soils) according to the stepwise method. All models were significant at the 0.001 level. A maximum of three predictor variables were allowed for each model. The coefficient of determination (R^2) is shown for each equation.

	Soils	Equation	R^2
PRI I	All	$190.686 + 0.432\ (Fe_{ox}) + 0.392\ (Al_{ox}) + 1.484$ clay	0.68
	Northern	$194.661 + 1.096\ (Fe_{ox}) + 1.206$ clay	0.62
	Southern	$141.202 + 0.573\ (Fe_{ox}) + 5.386\ (Ca+Mg) + 2.527$ clay	0.78
PRI II	All	$166.745 + 12.429\ (Ca+Mg) + (1.271 Al_{ox}) + 1.217\ (Fe_{ox})$	0.72
	Northern	$214.802 + 1.635\ (Fe_{ox}) + 1.711$ clay	0.53
	Southern	$105.939 + 1.608\ (Fe_{ox}) + 14.228\ (Ca+Mg) + 3.623$ clay	0.75
S_{max}	All	$-357.486 + 87.327\ (Ca+Mg) + 12.03\ (Fe_{ox})$	0.66
	Northern		NS
	Southern	$412.398 - 12.887\ P_{Bray1} + 12.746\ (Fe_{ox})$	0.76
b_{45}	All	$0.867 - 0.005\ (Fe_{ox}) - 0.048\ (Ca+Mg) + 0.004$ P Bray	0.61
	Northern	$0.8 - 0.007\ (Fe_{ox}) + 0.004$ P Bray $- 0.005$ clay	0.62
	Southern	$0.47 - 0.003\ (Fe_{ox}) + 0.004$ P Bray	0.46

Most studies have shown that clay content is one of the most influential soil properties in regards to P sorption (Cox, 1994; Maguire et al., 2001; see also Penn et al., 2005). However, several studies indicated no direct effects of clay on P sorption and that this relationship was highly influenced by the indirect effects of Al_{ox} and Fe_{ox} (Zhang et al., 2005; Ige et al., 2007). The current study is in line with these findings, particularly when the short-term indices are considered (Table 2). Wang et al. (2000) observed that the inclusion of clay physical properties improved the prediction of the P buffer capacity. In our models, although the specific surface area showed significant correlation with most P sorption indices (Table 2), neither this parameter nor the clay pore area improved the predictions obtained from the variable clay content by itself (Table 2).

The P availability indices Bray-P and Mehlich-3 P did not exhibit a significant association with any of the indices when considered as single variables in the linear correlation analyses. However, Bray-P did enter as predictive variable in the stepwise equations for b_{45}, with a positive sign. This may be due to the degree of saturation of the P retention sites at high soil P levels, reducing the probability that the new added P was retained by the soil matrix.

Comparison Northern vs. Southern Pampean Soils

In previous work we found that soils located in the southern part of the Pampean Region had a higher P sorption capacity than those located north (Rubio et al., 2008a). In line with these results, here we found that southern soils exhibited higher S_{max} than the northern ones. Almost all evaluated soil properties contributed to explain the higher soil P sorption capacity of the southern soils. The largest difference between zones was observed by S_{max} (57%), followed by b_{45} (41%). Those properties that represent the physical capacity to retain more P, such as clay content, C content, specific clay surface area and clay pore area, showed higher values in the southern soils. Similarly, those properties related to the presence of trivalent or divalent cations also indicated a higher affinity for P in the southern soils. All these soil properties are related to the parental material rather to agricultural management or other anthropogenic effects. Therefore, the differences in P sorption observed between zones would have been determined by the particular loess material deposited in each one. In line with this hypothesis, Zarate (2003) observed that the parental loess of southern Pampa soils has a predominance of volcaniclastic materials derived from the Patagonian Andean Mountains. In contrast, the northern Pampa soils are characterized not only by this material but also by two other sources (Sierras Pampeanas and the Parana Basin) containing metamorphic and igneous rocks with lower capacity to bind P (Zarate, 2003).

In a previous work, we proposed several equations for predicting b_{45} (the index more useful to optimize the plant requirements of P) in Pampean Mollisols that included the variables Bray-P, clay, and a dummy variable (zone) representing the geographical location of the soil (north or south; Rubio et al., 2008a). Here, we improved this prediction models by identifying which variables are responsible for the observed differences between zones. Additionally, specific equations for each zone are provided for estimating b_{45} and the other P sorption indices (Table 3). Applying the equation for b_{45}, the southern Pampa soils need on average 5.4 kg fertilizer P per hectare to raise soil Bray-P by 1 mg kg^{-1}, whereas the northern Pampa soils need less: 4.2 kg (assuming a bulk density of 1.2 Mg m^{-3} in the top 20 cm; see Rubio et al., 2008b).

Our results could be extrapolated to other Mollisols, but should be used with caution in other soil types, especially given the significant differences in P fractions and P sorption characteristics across different soils. While it may be more reliable to determine P sorption directly by the individual evaluation of P sorption indices for each soil, the estimation of P sorption capacity from soil properties may be a good alternative for agronomic purposes. The information obtained from this research can strengthen P fertilization programs by providing a methodology to estimate fertilizer P requirements to attain optimum crop yields while reducing environmental risks.

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