

Factors affecting phosphorus-sorption in loess soils of the semi-arid Argentina

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INTRODUCTION. — Deficiencies of phosphorus to plants in non fertilized- and long- term cultivated soils of the Semiarid Pampa of Argentina (SAP) increased dramatically in the last years (MONTROYA *et al.*, 1999). Future behavior of phosphates in soils of this region will depend on the effect of cultivation upon some soil properties which determine P-sorption, like organic matter-, lime-, and both amorphous and crystalline Al oxides contents (BUSCHIAZZO *et al.*, 1990).

Agriculture decreases significantly OM contents in soils of this region (BUSCHIAZZO *et al.*, 1991, HEPPER *et al.*, 1996), though it is still not known how OM decreases affect P- sorption. This fate is important because sorbed P is mostly exchangeable, and therefore available to plants in these soils (PRÜEB *et al.*, 1992).

Higher P-sorption rates after OM losses were shown by some authors (GÜLÜT and SAYIN, 1986; Gessa *et al.*, 1978). This occurs when organic matter blocks soil active anion sorption sites of the soil. P-sorption decreases after OM losses were also find in other soils when the formation of organomineral complexes increases the amount of anion sorption sites (SAMPLE *et al.*, 1986) or when organic acids inhibited the crystallization of Fe- and Al oxides (SCHWERTMANN *et al.*, 1968), compounds with high phosphate sorption capacity (BORGGAARD *et al.*, 1990).

The loessial parent materials of the soils of the semiarid Pampas contain variable amounts of volcanic ashes. Their weathering produced large amounts of amorphous aluminium oxides and high phosphate sorption (BUSCHIAZZO *et al.*, 1997). These oxides can form complexes with OM (TOKASHIKI and WADA, 1975; FREESE *et al.*, 1991). Therefore we hypothesized that P-sorption will be highly affected by organic matter and contents of Al- and Fe oxides in soils of the semi-arid Pampas. As OM is highly dependent on soil texture (BUSCHIAZZO *et al.*, 1991) we expected a different effect of OM losses on P-sorption in different textured soils.

The objective of this study was to evaluate how OM and amor-

phous and crystalline oxides affect P-sorption in soils of the semiarid Pampa of Argentina.

MATERIALS AND METHODS. — A-horizons of five Entic Haplustolls of the SAP, selected on the basis of their texture, were studied. Main characteristics of the soils are shown in Table 1. One mixed sample composed by three subsamples from each A-horizon was used for this study. Soil samples were air dried, sieved through a 2 mm sieve, and analyzed for clay contents (pipette method); carbonate (calcimetry); pH (1:2.5 soil-water extract, potentiometric); organic matter (OM) (WALKLEY and BLACK, 1934); acid oxalate soluble iron (Fe_o) and aluminium (Al_o) (SCHLICHTING *et al.*, 1995), boiling acid oxalate soluble iron (Fe_{os}) and aluminium (Al_{os}) (FISCHER and FECHTER, 1982). Each Fe and Al fraction was determined by atomic absorption spectrometry.

All soil samples were treated separately for removal of organic matter, active and crystalline oxides. For OM-removal (H₂O₂) a soil sample was treated with 30% H₂O₂ in a 1:1 soil: solution during 24 h at 60-70°C. Samples were then centrifuged, filtered, washed with 1 mol dm⁻³ NaCl solution, and dried at 50°C (KUNZE and DIXON, 1986).

For removal of active oxides (AcOx) 2g of air dried soil were dark shaken for 1 h with 100 ml of a 0,15 mol dm⁻³ oxalic acid and 0,2 mol dm⁻³ ammonium oxalate solution, centrifuged and filtered. Residues were washed three times with 1 mol dm⁻³ NaCl solution, and dried at 50°C (SCHLICHTING *et al.*, 1995).

For removal of active and crystalline oxides (BAcOx) the method given by FISCHER and FECHTER (1982) was used: 2g of air-dried soil stood in contact for 6 minutes with 100 ml of a solution composed by 0,15 mol dm⁻³ oxalic acid, and 0,2 mol dm⁻³, and 6 minutes with the same solution under boiling conditions. Samples were then centrifuged, filtered and residues were washed three times with 1 mol dm⁻³ NaCl solution, and dried at 50°C.

P-sorption isotherms were carried out at 20°C on both untreated and treated soils. Maximum P concentration in the equilibrium solution was 22 µg ml⁻¹. More details of the method used for P-sorption isotherms were given in BUSCHIAZZO *et al.* (1990).

Table — Main characteristics of the studied soils.

Soil	clay	CaCO ₃	pH	OM	Fe _o	Al _o	Fe _{os}	Al _{os}
		%						
	5.4	0.06	8.1	1.24	325	1100	13075	2900
2	6.5	nd	6.3	1.22	915	700	14575	3050
3	7.8	0.65	8.3	1.82	425	1850	12625	5000
4	16.9	0.01	6.3	3.53	1500	1550	19470	4200
5	20.8	0.01	6.8	2.70	1165	1450	12500	5000

nd: no detect

Fitting of P-sorption data to the linear transformation of Freundlich equation ($\ln x = \ln a + b \ln c$, BARROW, 1978) were analyzed by linear regression analysis. From Freundlich equation the values of constants a and b , and the slope of the curve at a P concentration of 0.3 g P ml^{-1} (BC 0.3) in the equilibrium solution, were calculated. Treatment effects on a , $1/b$, and BC 0.3 were analyzed with one way ANOVA, taking the soils as replicates. When ANOVA was significant at a 0.05 level, the Dunnett mean-comparison test was carried out to compare the constants in treated and untreated samples.

Relationships between a , b , and BC 0.3 with soil properties were analyzed by simple regression analysis.

RESULTS AND DISCUSSION. — Fitting of sorption isotherms to Freundlich equation were significant in most treated and untreated soils (Table 2). This allowed to use the constants a , $1/b$ and BC 0.3 derived from this equation to study the influence of selected soil properties on P-behavior.

Values of a , $1/b$ and BC0.3 are presented in Fig. 1. In no treated samples the constant BC0.3 increased (between 3 and 3.4) and $1/b$ decreased (between 3.4 and 1.2) from coarse to fine textured soils, while a values did not show any agreement with soil textural changes. Constant a is directly related to the capacity of the soil to

Table 2. — Correlation coefficients (r) and standard deviations (SD) of P-sorption isotherms adjusted to the Freundlich equation carried out on untreated soil samples and on boiling acid oxalate- (BAcOx), acid oxalate- (AcOx) and water peroxide (H_2O_2) treated soil samples.

Soil		Treatment			
		Untreated	BAcOx	AcOx	H_2O_2
	r	0.978**	0.915*	0.987**	0.976**
	SD	0.1208	0.1520	0.0514	0.1163
2	r	0.989**	0.925*	0.972**	0.883
	SD	0.0612	0.2690	0.1388	0.2577
3	r	0.994***	0.920*	0.997***	0.965**
	SD	0.0599	0.1301	0.0306	0.1803
4	r	0.986**	0.976**	0.943*	0.987**
	SD	0.0980	0.1513	0.2377	0.1065
5	r	0.995***	0.995***	0.963**	0.991***
	SD	0.0585	0.890	0.1664	0.0923

* $p < 0.10$; ** $p < 0.05$; *** $p < 0.01$; $n = 4$

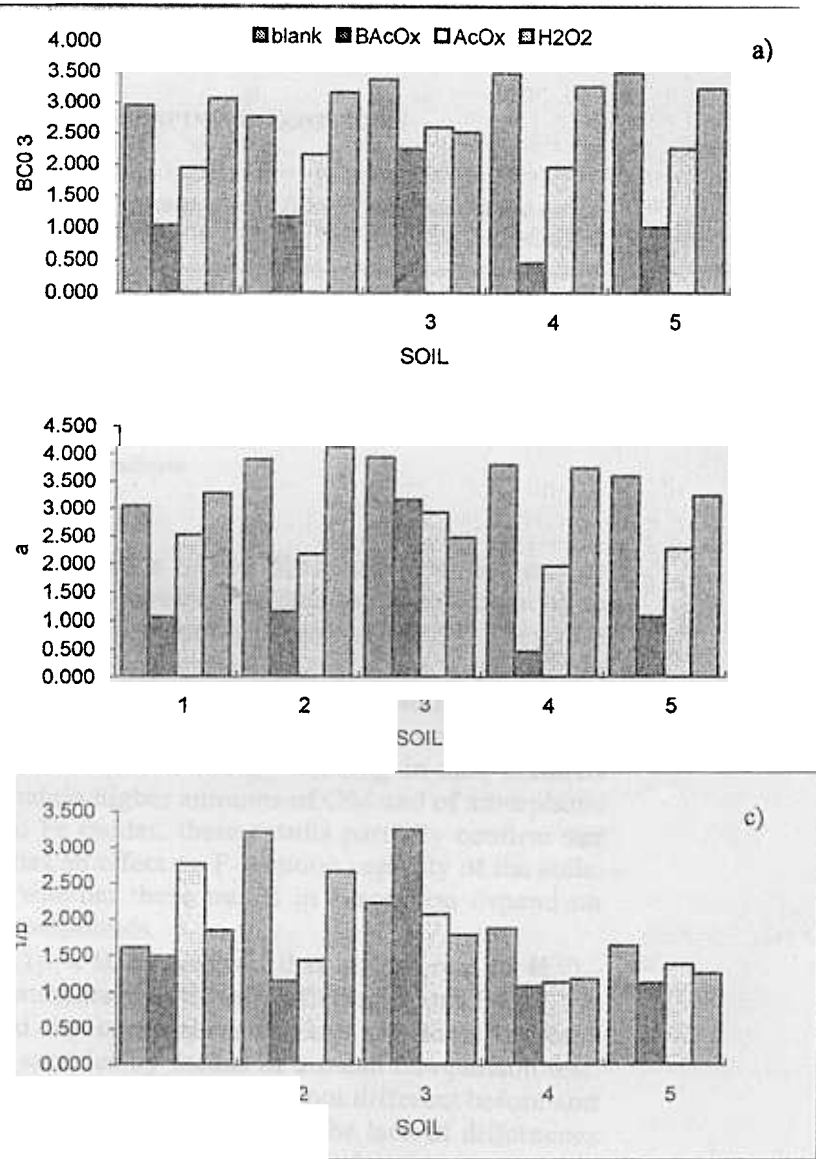


Figure Values of constants a) BC0.3, b) a and c) 1/b deduced from Freundlich equation

Table 3. — Mean comparison tests (Dunnett) of a , $BC0.3$ and $1/b$ of treated and untreated soil samples.

Treatment		$BC0.3$
BAcOx	**	
AcOx	**	
H ₂ O ₂	ns	

significant at $p < 0.01$; ns: not significant

sorb phosphates, $1/b$ is an index of soil phosphate-retention energy (MEAD, 1981), and $BC0.3$ is inversely related to the soil capacity to liberate phosphate to the soil solution (HOLFORD, 1979). Therefore former results indicate that P-retention capacity of the soils will not be related to soil texture, but the ability of the soil to liberate phosphate to the soil solution will be lower in fine than in coarse textured soils because of higher retention energy existing in fine textured soils. As finer soils contain higher amounts of OM and of amorphous and crystalline Al and Fe oxides, these results partially confirm our assumption that OM has an effect on P-sorption capacity of the soils. It remains uncertain whether these trends in P-sorption depend on OM or on other soil compounds.

ANOVA analysis ($p < 0.05$) showed that at less one of H₂O₂-AcOx- or BAcOx treatments significantly affected a and $BC0.3$ but not $1/b$. This allowed the comparison of both constants between untreated and treated samples by means of a mean comparison test. This analysis showed that a and $BC0.3$ were not different before and after H₂O₂-treatment in most soils (Table 3). The lack of differences among treated and untreated soil samples were related to the variable behavior of both constants after the H₂O₂-treatment, because they increased in some soils and decreased in others, without any relationship with soil texture. Our hypothesis that OM variations should affect P behavior in the studied soils according to their texture cannot be confirmed with present results. The source of variations of phosphorus behavior in these soils associated to OM losses must be therefore further studied.

AcOx and BAcOx treatments, which removed amorphous and crystalline Al and Fe oxides, respectively, lowered significantly a and $BC0.3$ in relation to untreated samples in all studied soils. Values of

a decreased 20 to 88% after BAcOx treatment, and 17 to 48% after AcOx treatment. BC0.3 decreased 33 to 87% after BAcOx treatment, and 21 to 44% after AcOx treatment. The largest a and BC0.3 variations occurred in soils 4 and 5. These soils had the finest textures, and presented the higher amounts of amorphous and crystalline Fe and Al oxides. Such results indicate that P-sorption, as well as the ability of the soil to liberate P to the soil solution, were highly influenced by the amount of amorphous and crystalline Al and Fe oxides. On the other hand the retention energy of P by soils remained unchanged.

Correlation analysis showed that no significant relationships exists between a, BC0.3 or 1/b and any of the studied soil properties. This was surprising, as we expected high correlations with for amorphous Al and Fe contents. Probably the reduced number of soils studied did not allow us to built a significantly relationship among these variables. Studied soils content higher Al₀ than Fe₀ contents (Table 1), indicating that amorphous Al-oxides predominate over amorphous Fe-oxides. It is known that amorphous Al or Fe oxides show higher P-retention capacity than crystalline oxides because of their higher specific surface (BORGGAARD *et al.*, 1990). Therefore it can be inferred that BAcOx- and AcOx treatments reduced P-sorption in the studied soils because of they solubilized the amorphous Al-oxides rather than amorphous Fe-oxides.

CONCLUSIONS. — From present results it can be concluded that organic matter does not affect none of the studied P-behavior parameters (P-sorption, P buffer capacity and P- sorption energy) in the same way in different textured soils. It was not possible to deduce the origin of these variations from present results. The effect of OM on P-sorption parameters must be further studied.

Amorphous and crystalline Al- and Fe oxides are the soil compounds which mostly affect P-behavior parameters, as they increase the P-sorption and decrease the P-buffer capacity. P-sorption energy was the same with different contents of such oxides.

ACKNOWLEDGMENTS. — This study was financed by Facultad de Agronomia, Universidad Nacional de La Pampa, Project N° 2/96, and SECYT, Argentina, Project PICT97 N° 461.

Ing. Agr. Francisco Babinec carried out the statistical analysis of results.

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ABSTRACT.— Previous results showed that phosphorus-sorption strongly correlated with contents of active Al-, and Fe-oxides, and organic matter (OM) in soils of the Semiarid Argentinian Pampas. Objective of this study was to determine the relative influence of these soil compounds on P-sorption. It was hypothesized that contents of OM and Al- and Fe oxides should decrease P-sorption in the studied soils. With this purpose sorption isotherms were carried out on non treated soils and on soil samples pretreated with H₂O₂ (OM destruction), acid oxalate (AcOx, destruction of amorphous oxides), and boiled acid oxalate (BAcOx, destruction of crystalline oxides). Results showed that OM destruction did not affect none of the constants deduced from Freundlich isotherm (a, 1/b and BC0.3). This was probably due to the variable effect of OM on these constants in each soil. On the other hand constant a decreased 20 to 88% after elimination of crystalline oxides, and 17 to 48% after elimination of amorphous oxides, BCO.3 decreased 33 to 87% after elimina-

tion of crystalline oxides, and 21 to 44% after elimination of amorphous oxides, and 1/b remained unchanged. Such results indicate that P-sorption (a), as well as the ability of the soil to liberate P to the soil solution (BCO.3) were highly influenced by the amount of amorphous and crystalline Al and Fe oxides, and that the retention energy of P (1/b) remained unchanged.