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Available phosphorus in the central area of the Argentinean Pampas. 2: Kinetics of adsorption and desorption of phosphorus under different soil and management environments

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Disponibilidad de fósforo en el área central de la Región Pampeana Argentina. 2: Cinéticas de adsorción y desorción de fósforo en distintos ambientes de suelo y manejo
Fósforo disponível na área central das Pampas Argentinas. 2: Cinética de adsorção e desorção do fósforo em diferentes solos e ambientes pedológicos

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ABSTRACT

The concentration of phosphate ions in solution is critical in defining the ability of a soil to adequately meet crop demand. That concentration is regulated by adsorption/desorption and precipitation/dissolution processes, particularly its kinetics of reaction. This work was developed in order to find the kinetic model describing the sorption/desorption of phosphate in soils of the Argentinean Pampas region, to describe the processes associated with these reactions and to define the effect of temperature on them. A bi-linear model that adequately describes the data obtained in the adsorption and desorption experiments is proposed. Thus, it was possible to clearly differentiate two different kinetic mechanisms, each characterized by different reaction rates. Two very labile pools of phosphorus were determined in these soils. The rate at which these processes occur indicates the occurrence of chemical reactions of precipitation in highly soluble compounds and surface adsorption reactions with very low binding energy, as P is quickly released into the soil solution in the desorption process. However, since the amounts of P released in the desorption process are very much less than the adsorbed, is possible to infer that both processes occur at non-equilibrium conditions and there is a lack of reversibility of the reaction P-Soil – P-Solution in the soils studied. The intensity of these processes is differentially affected by temperature and, in general, there is a positive effect of phosphorus fertilization history, although the effect of this is not clearly seen in the amounts of extractable phosphorus with the classic Bray & Kurtz N°1 method.

RESUMEN

La concentración del ion fosfato en solución es decisiva para definir la habilidad de un suelo para abastecer adecuadamente la demanda de los cultivos. Dicha concentración en solución está regulada por procesos de adsorción/desorción y precipitación/disolución, particularmente por su cinética de reacción. Este trabajo se desarrolló con el fin de hallar el modelo cinético que describa la sorción/desorción de fosfato en suelos de la región pampeana argentina, describir los procesos asociados a dichas reacciones y definir el efecto de la temperatura sobre ellas. Se propone un modelo bi-lineal que describe adecuadamente los datos obtenidos en los experimentos de adsorción y desorción. Así, se pudo diferenciar claramente dos mecanismos cinéticos distintos, cada uno caracterizado por diferente velocidad de reacción. Se determinaron dos pools muy lábiles de fósforo en estos suelos. La velocidad con la cual se producen estos

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procesos indica la ocurrencia de reacciones químicas de precipitación en compuestos altamente solubles y reacciones de adsorción superficial con muy baja energía de unión, ya que se liberan rápidamente a la solución del suelo en los procesos de desorción. Sin embargo, dado que las cantidades de fósforo liberados en el proceso de desorción son bastante menores que las absorbidas, es posible inferir que ambos procesos se producen en condiciones de no equilibrio y hay una falta de reversibilidad de la reacción P-Suelo – P-Solución en los suelos estudiados. La intensidad de estos procesos se encuentra afectada en forma diferencial por la temperatura y, en general, hay un efecto positivo de la historia de fertilización fosfatada, aunque el efecto de ésta no se observa claramente en las cantidades de fósforo extraíble con el clásico método Bray & Kurtz N°1.

RESUMO

A concentração de ião fosfato na solução do solo é decisiva para definir a capacidade deste para satisfazer adequadamente as exigências das culturas. A referida concentração na solução do solo é regulada por fenómenos de adsorção/dessorção e precipitação/dissolução, e em particular pela sua cinética de reacção. Este trabalho foi desenvolvido com o objetivo de encontrar um modelo cinético que descreva a sorção/dessorção de fosfato em solos da região das Pampas Argentinas, os processos associados com estas reacções e para definir o efeito da temperatura sobre estes processos. É proposto um modelo bi-linear que descreve adequadamente os dados obtidos nos ensaios de adsorção e de dessorção. Assim, foi possível diferenciar claramente dois mecanismos cinéticos distintos, cada um deles caracterizado por uma velocidade de reacção diferente. Foram determinadas duas "pools" muito lábeis de fósforo nesses solos. A velocidade a que estes processos se desenvolvem indicam a ocorrência de reacções químicas de precipitação de compostos altamente solúveis e reacções de adsorção de superfície com muito baixa energia de ligação já que se libertam muito rapidamente para a solução do solo nos processos de dessorção. No entanto, uma vez que as quantidades de P libertadas no processo de dessorção são significativamente mais baixas que a absorção, é possível inferir que ambos os processos ocorrem em condições de não equilíbrio e que existe uma falta de reversibilidade da reacção de P-Solo–P-Solução nos solos estudados. A intensidade destes processos é diferencialmente afetada pela temperatura e, em geral, ocorre um efeito positivo do historial da adubaçãofosfatada efetuada embora este efeito não seja claramente observado nas quantidades de fósforo extraível obtidas pelo método clássico de Bray & Kurtz No. 1.

KEY WORDS
Phosphorus fertilization, phosphorus sorption, kinetic models, Argentinean Mollisols

PALABRAS CLAVE
Fertilización fosfatada, sorción de fósforo, modelos cinéticos, Mollisoles de Argentina

PALAVRAS-CHAVE
Adubação fosfatada, sorção de fósforo, modelos cinéticos, Molissolos da Argentina

1. Introduction

From the point of view of plant nutrition, the concentration of phosphate ions in solution is critical in defining the ability of a soil to adequately supply crop demand. This concentration in solution is regulated by adsorption/desorption and precipitation/dissolution reactions (Horta and Torrent 2007; Limousin et al. 2007; Abolfazli et al. 2012; Pinto et al. 2013). Adsorption experiments with different reaction times provide plenty of information about the speed of these processes. Usually it is assumed that the phosphorus missing from the solution in the first 24 hours is due to rapid adsorption processes, which are reversible and occur on the solids surfaces (Taddesse et al. 2008). The disappearance at subsequent times takes place because of slower, generally irreversible, chemical processes (McGechan and Lewis 2002). The adsorption on the surface of solids occurs so quickly it can be considered instantaneous, resulting in an equilibrium condition (Atkins and de Paula 2006). However, in fast processes a slower change in the solid/liquid interface delays the equilibrium. This is a consequence of the time required for phosphorus to dissolve and come into contact with adsorption sites within, which depends on diffusive flux of phosphate ions in the soil solution (Limousin et al. 2007). Adsorption processes could be fast (when adsorption occurs on the surface of the particles) or slow (when adsorption occurs inside the particles). These processes are often difficult to differentiate and can be considered as a continuous one (Addiscott and Thomas 2000; Antelo et al. 2007; Limousin et al. 2007). This variation in adsorption rate is attributed to the existence of at least two pools of phosphorus with different degrees of availability, from each of which the fast and slow desorption will be produced, respectively (Silva Rossi et al. 2013).

Koopmans et al. (2004) studied the kinetics of desorption in short periods of time (reversible process of rapid adsorption) as a way to assess a dynamic bioavailability index to determine whether kinetics of phosphorus desorption limits plant uptake.

Temperature variation is the factor that has the most contradictory results in kinetic processes. Jiang et al. (2008), Mezenner and Bensmaili (2009), Ciopec et al. (2011) and Shen et al. (2011) reported increases in phosphorus adsorption with increases in temperature but other authors have found contrasting results (Jin et al. 2005; Huang et al. 2011).

The availability of different phosphate compounds in soil depends on the phosphorus fertilization history and the time since the fertilizer application (Bermúdez and Mallarino 2007; Vázquez et al. 2011; Pinto et al. 2013) and therefore it can be assumed that both (phosphorus fertilization history and the time since the fertilizer application) will also affect the kinetics of these processes.

In the central area of the Pampas region of Argentina, there is a lack of information about the kinetics and thermodynamics of adsorption and desorption processes of phosphorus, and how they are affected by different management history. In soils of the Argentinean Pampas region Mendoza (1986) studied models for the P adsorption. Then, Hevia et al. (2000) performed studies on the kinetics of adsorption of phosphorus with minimal soil: solution contact times (12 h) and at ambient temperature, evaluating only the linear relationship between adsorption and contact time. There is an evident lack of information about P adsorption/desorption kinetics in the literature regarding the soils of Argentina.

It was hypothesized that in the same type of soil, phosphorus adsorption kinetics decrease with prior history of fertilization and increase with temperature. An opposing relationship occurs with the processes of nutrient release in soil. Thus, this work was carried out in order to find the kinetic model that describes the sorption/desorption of phosphate in soils of the Argentina Pampas region, describe the processes associated with these reactions and define the effect of temperature on them.

2. Materials and Methods

The work was carried out in three soils, classified as Typic Argiudoll (La Chispa, Santa Fe, Argentina, 33°32'28" S, 61°59'45" O), Typic Hapludoll (Teodelina, Santa Fe, Argentina, 34°14'13" S, 61°29'58" O) and Entic Haplustoll (Canals, Córdoba, Argentina, 33°31'18" S, 62°33'3" O) according to Soil Taxonomy (Soil Survey Staff 2014). They belong to long term trials from AACREA South of Santa Fe and IPNI Southern Cone, under zero tillage and crop rotation systems (wheat, soybean and corn). The experimental design was in blocks with completely randomized plots, with three replications for treatments in each location. We studied plots that were annually fertilized during seven agricultural seasons (38 kg P/ha/year, added as monoammonium phosphate $NH_4H_2PO_4$, which exceeds the crop requirements by 10%). We also used control plots in each location that 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 a wheat crop (December 2008). The following composite samples were obtained: ((3 crops + 1 control plot) x 3 replicates) x 3 sites (soils). In each of these samples, the following analysis were performed: particle size analysis through the pipette method (Day 1986), soil pH with glass electrode in a 1:2.5 (w/w) soil-water suspension, soil organic matter (SOM) through the Walkley and Black procedure (Nelson and Sommers 1996). To determine the effect of agricultural management on the SOM, labile fraction and stable fraction of the organic matter contents were determined by physical fractionation (Irizar et al. 2010). 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), exchangeable cations: calcium and magnesium were determined by EDTA titration, and potassium (K^+) and sodium (Na^+) by flame photometry. Exchangeable acidity was analyzed by H^+ displacement with KCl 1 M followed by acid/base titration (Thomas 1996) and extractable phosphorus with the Bray & Kurtz N° 1 (P-Bray 1) method (Kuo 1996).

2.1. Kinetics of phosphorus adsorption

To evaluate P adsorption kinetics, we used batch methods (Sparks 1985), in which the P present in a solution of a given concentration is exchanged with the adsorbent (soil). The experiment was carried out using stirred polypropylene centrifuge tubes. In short, 2.5 g of air dried soil sieved through a 2 mm sieve was treated with 25 ml of 2 μmol L^{-1} KCl solution with concentrations of 30, 32 and 16 mg P/L for the Argiudoll, Hapludoll and Haplustoll respectively. These are the concentrations at which 50% of the Langmuir Qmax for each soil is reached (Silva Rossi et al. 2013). Each of the soil samples, with indicated P rates, was incubated at temperatures of 10, 25 and 40 °C. This temperature range was used in order to simulate environmental effects in winter, summer and even more extreme conditions. The soil samples were stirred with the solutions of different phosphorus concentration at different time intervals between 30 seconds and 96 hours: 0.008, 0.08, 0.166, 0.25, 0.5, 1, 2, 3, 4, 6, 20, 48, 72 and 96 h, at the three temperatures. After each of these periods the samples were centrifuged at 3000 rpm for 5 minutes, an aliquot of the suspension was taken, transferred to a 15 ml centrifuge tube and re-centrifuged for 5 minutes at 3700 rpm to remove traces of particles in suspension; from that solution an aliquot for determining the concentration of P was taken and the remainder on the soil was calculated in each period. The analysis of P in solution was performed by the ascorbic acid method (Kuo 1996).

From the samples exposed to different soil:solution contact intervals for P adsorption, as described above, the supernatant solution was entirely removed. The tubes were then kept in incubation until the end of the test, to perform desorption experiments. This was done to avoid differences in contact time among tubes between the soil and the P solution remaining in soil pores.

2.2. Kinetics of desorption of phosphorus

To determine the kinetics of desorption, upon completion of the maximum adsorption period, all the tubes from the adsorption experiment were centrifuged, the supernatant was removed and the soil was dried at 40 °C in order to facilitate a homogeneous drying in all of the samples. After that, the soil of each tube was dispersed using a glass rod. Then each sample was subjected to phosphorus desorption processes with a solution of KCl 2 μmol L^{-1}, in a soil:solution ratio of 1:10. These desorption processes were conducted at different soil:solution contact intervals: 0.5, 1, 2, 4, 7, 24, 32, 48, 72 and 96 hours, at 10, 25 and 40 °C. After each of these periods the P concentration in solution was measured as in the adsorption experiments.

2.3. Analysis of results

It was previously demonstrated that in the studied soils the experimental results were not adjusted to classical kinetic Elovich or Freundlich models, because the parameters presented high correlation coefficients between them (Silva Rossi 2011). Therefore, the kinetics of adsorption and desorption of P were modeled using SigmaPlot (SPSS Science 2000) adjusting a bi-linear model regression. A model that adjusted the data to two linear sections of different slopes was developed. In a first section:

$$P_{ad/des} = a + (b \cdot time) \qquad [1]$$

For time < *ti*.

In the second section:

$$P_{ad/des} = a + b\,ti + d \cdot (t - ti) \qquad [2]$$

In these expressions $P_{ad/des}$ is the concentration of phosphorus adsorbed or desorbed, "*a*" and "*b*" are the interception and slope, respectively, of the linear regression from the first section, the constant "*ti*" is the time at which ends the first reaction stage, and "*d*" is the slope of the second stage of the linear regression.

The concentration of $P_{ad/des}$ in "*ti*" is: $P_{ad/des} ti = (a + b \cdot ti)$. So, *ti* is obtained from:

$$ti = (P_{ad/des} - a)/b$$

The kinetic parameters were analyzed by multivariate analysis of principal components to describe the relationship among kinetic parameters, soils and temperature treatments, and with analysis of variance (Fisher LSD) to determine differences between means. The statistical analysis was performed using InfoStat (Di Rienzo et al. 2013).

3. Results and Discussion

3.1. Soil properties

Table 1 shows the values of pH, extractable phosphorus with Bray & Kurtz N° 1 method (P-Bray 1), total SOM, stable SOM (S-SOM) and labile SOM (L-SOM), cation exchange capacity (CEC), exchangeable cations and exchangeable acidity for each treatment. Also, percentages of sand, silt and clay are listed for each soil, P fertilization treatment and climatic conditions.

The presence of iron and aluminum oxides and hydroxides is one of the main causes of P adsorption in acid soils of the orders Alfisol, Oxisol and Ultisol (Horta and Torrent 2007; Vázquez et al. 2011; Pinto et al. 2013). On the other hand, in the Mollisol soils order of the central area of Argentina Gorgas and Tassile (2006) and Hang et al. (2015) showed that the Fe/Al oxide contents are not significant.

Abolfazli et al. (2012) studied the effects of phosphorous fertilizer in alkaline (pH = 7.33) and acidic (pH = 3.34) soils; they showed that Ca-P was the predominant form of P in calcareous soil, while Fe-P and Al-P were only dominant in acidic soils. Millán et al. (2010) indicated that below pH 5 the dominant metal in solution is Al^{3+} whereas at higher pH values (5.5-5.8 up to 7.5), this element (Al^{3+}) is drastically reduced. The pH values of the soils under study, between 6.0 and 6.6 (Table 1), were above the range designated by Millán et al. (2010) for P-Al and below the conditions of alkalinity reported by Abolfazli et al. (2012) that facilitate P-Ca linkage.

Table 1. Characteristics of the soils used in this study: pH, P by Bray & Kurtz N° 1 (P-Bray 1), total SOM, stable SOM (S-SOM) and labile SOM (L-SOM), cation exchange capacity (CEC), exchangeable cations, sand, silt and clay values in each of the soils and treatments. Data are presented as means with its standard deviation (in parentheses). N = 3. Different letters indicate the minimum significant difference in P-Bray 1, 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 (1:2.5)	6.6 (0.12)	6.5(0.10)	6.4(0.12)	6.3(0.09)	6.1(0.10)	6.0(0.11)
P-Bray 1 (mg kg^{-1})	8.1*b*	14.5*b*	10.7*b*	25.9*a*	12.2*b*	28.3^{a}
SOM (g kg^{-1})	29.9(5.5)	25.6(4.7)	20.6(6.2)	26.1(7.1)	29.6(5.5)	27.2(5.8)
S-SOM (g kg^{-1})	26.3(4.8)	24.1(5.7)	19.9(3.6)	23.7(4.4)	25.3(5.2)	26.4(4.1)
L-SOM (g kg^{-1})	3.6(0.3)	1.5(0.2)	0.7(0.1)	2.4(0.2)	4.3(0.3)	0.8(0.3)
Ca^{2+} (cmol kg^{-1})	9.4(0.3)	9.2(0.5)	8.4(0.5)	8.5(0.4)	11.2(0.5)	10.9(0.5)
Mg^{2+} (cmol kg^{-1})	2.1(0.2)	2.2(0.2)	2.0(0.1)	2.1(0.1)	2.6(0.3)	2.6(0.3)
K^{+} (cmol kg^{-1})	1.5(0.1)	1.5(0.1)	1.4(0.1)	1.4(0.1)	1.5(0.1)	1.5(0.1)
Na^{+} (cmol kg^{-1})	0.1(0.02)	0.1(0.01)	0.1(0.02)	0.1(0.02)	0.1(0.01)	0.1(0.01)
H^{+} (cmol kg^{-1})	1.0(0.2)	1.0(0.2)	1.3(0.4)	1.4(0.4)	1.8(0.5)	1.7(0.4)
CEC ($cmol_c$ kg^{-1})	14.1(1.5)	14.0(1.2)	13.2(1.2)	13.5(1.0)	17.2(1.7)	16.8(1.6)
Sand (g kg^{-1})	502.0(7.1)	648.0(9.3)	318.0(5.2)			
Silt (g kg^{-1})	326.0(5.1)	224.0(4.5)	454.0(5.5)			
Clay (g kg^{-1})	172.0(8.3)	128.0(5.0)	228.0(6.4)			

The short-term availability of P for crops is strongly influenced by biochemical processes that affect soil organic matter (Von Wandruszka 2006). The SOM consists of different chemical compounds and states of decomposition. It can be fractionated into labile and stable (recalcitrant) SOM (Martínez et al. 2008; Galantini and Suner 2008; Irizar et al. 2010). In our study the SOM contents ranged from 20.6 to 29.9 g kg^{-1}. These values correspond to a medium to low range according to Conti (2000). Also, there were no statistically significant differences in the content of S-SOM or L-SOM, respectively, between fertilized and unfertilized treatments in the three soils.

3.2. Adsorption and desorption kinetics

Results of the kinetics of adsorption and desorption of phosphorus, for different soils, treatments and temperatures, are showed in **Figures 1, 2 and 3**, adjusted to the bi-linear models as described. There are two different process speeds that were also observed by Horta and Torrent (2007). Both speeds are correlated with the slopes estimated through the bi-linear model fitted to the experimental data.

For the same soil treatment and temperature, important changes in the kinetics were

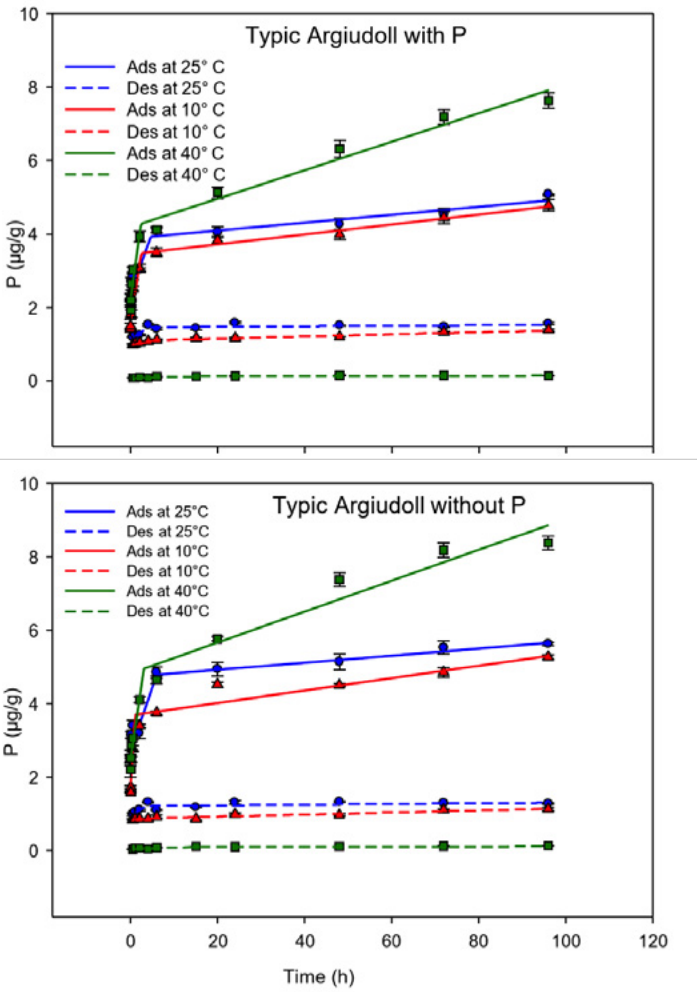

Figure 1. Kinetics of adsorption (Ads) and desorption (Des) of phosphorus in a Typic Argiudoll with and without P treatment, at temperatures of 10, 25 and 40 °C. Error bars represent the standard deviation of the experimental data.

adequately described by the bi-linear model. Previous studies in the soils of this study demonstrated that experimental results were not adjusted to classical kinetic Elovich or Freundlich models, because its parameters presented high correlation coefficients between them (Silva Rossi 2011). On the other hand, the bi-linear model shows higher R^2 values, p values below 0.001 and a random distribution of errors of predicted vs. observed data. Besides its robustness, the bi-linear model brings a description of important kinetic parameters: rates of adsorption/desorption processes for the fast and slow reactions involved, parameters *b* and *d*, respectively. These are the slopes of two lines which indicates the rates at which each adsorption and desorption processes occurred. Also, it estimates the time at which the rate of the processes changes from fast to slow, *ti*. It also allowed the estimation of concentrations at the start of reactions or during changes in reaction rates. Time intervals at which these changes occurred were also identified.

In both adsorption and desorption processes for the three soils, temperatures and fertilization treatments, the largest proportion of P adsorbed and/or released came in a very short period of time (less than 6 hours), described by the first part of the model. The high reaction rate was

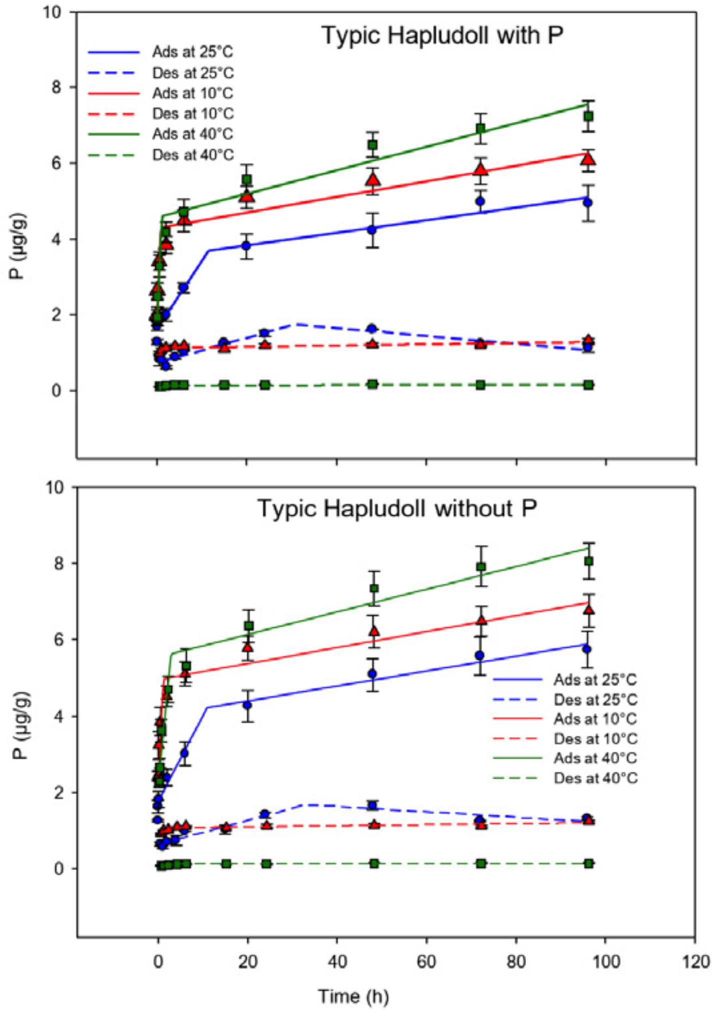

Figure 2. Kinetics of adsorption (Ads) and desorption (Des) of phosphorus in a Typic Hapludoll with and without P treatment, at temperatures of 10, 25 and 40 °C. Error bars represent the standard deviation of the experimental data.

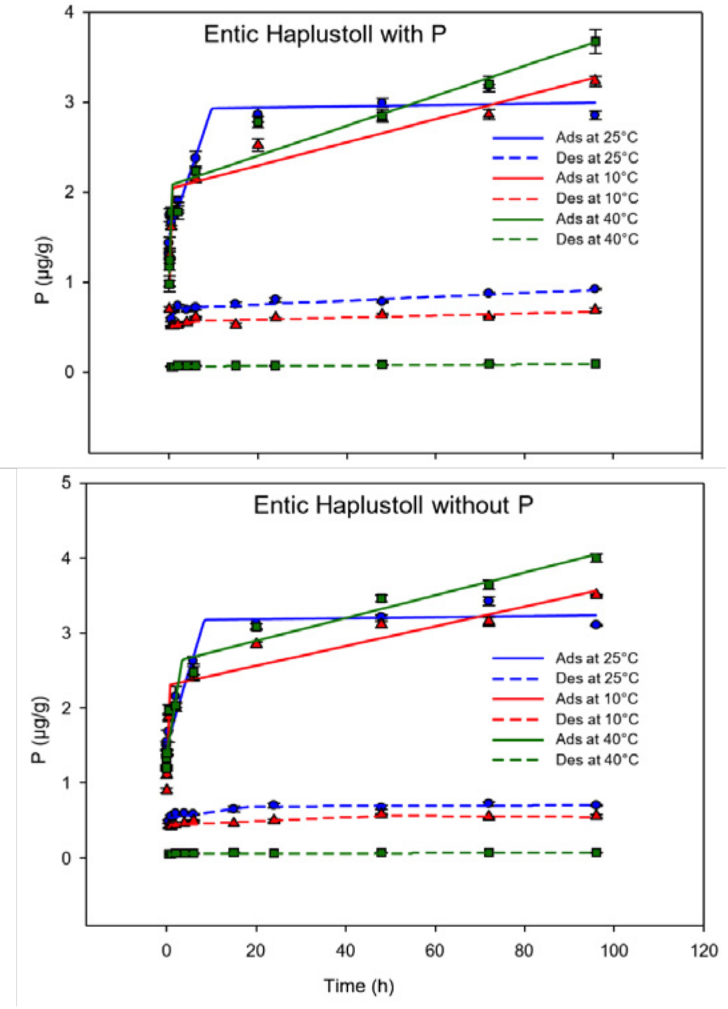

Figure 3. Kinetics of adsorption (Ads) and desorption (Des) of phosphorus in an Entic Haplustoll with and without P treatment, at temperatures of 10, 25 and 40 °C. Error bars represent the standard deviation of the experimental data.

evident by the fact that in the first minute of contact 30 to 50% of P adsorbed in 96 hours of the test disappeared from the soil solution. In desorption, during the first 30 minutes 70% of total P desorbed was released to the soil solution. This high reaction rate indicates the occurrence of different processes: in the first step, precipitation reactions between phosphate ions and desorbed exchangeable calcium ions form very labile compounds (i.e. di-hydrated calcium phosphate), which occurs within the first minute of soil-solution contact (Álvarez et al. 2004). This is a mechanism facilitated by the high degree of calcium saturation (> 70%) of the exchange complex (**Table 1**) that provides a soil solution with a high concentration of calcium ions. The second step would be based on surface physical adsorption reactions. In turn, this behaves as a substrate from which a rapid release of phosphate is produced by means of dissolution and desorption mechanisms. This stage is followed by a relatively slower one, in which the solubility of the resulting phosphate compounds is less in comparison (Guppy et al. 2005; Horta and Torrent 2007).

Table 2 shows the parameters of the phosphorus adsorption kinetics for different soils, treatments and temperatures.

Table 2. Parameters of the phosphorus adsorption kinetics for the different soils; *a*: intercept, P initially adsorbed at $t = 0$, *b*: slope of the first stage, t_i: time at which the first reaction stage ends, *d*: slope of the second stage, Pad(t_i): concentration of phosphorus adsorbed at t_i estimates for each soil, treatment and temperature (T). N = 3 replicates for each estimation. Different letters indicate minimum significant differences, LSD Fisher Test ($p < 0.05$)

Soil(1)	Treatment	T (°C)	*a*	*b*	t_i (h)	*d*	Pad(t_i) (µg/g)
TA	With P	10 °C	1.66e	0.77d	2.37e	0.014e	3.48d
TA	Without P	10 °C	1.84e	2.01b	0.93f	0.017d	3.71d
TH	With P	10 °C	2.08d	2.77a	0.81f	0.021c	4.31c
TH	Without P	10 °C	2.58b	2.66a	0.90f	0.021c	4.97b
EH	With P	10 °C	0.93g	1.44c	0.78f	0.013e	2.05f
EH	Without P	10 °C	1.06g	1.69b	0.74f	0.013e	2.31f
TA	With P	25 °C	2.42b	0.33e	4.58d	0.011e	3.93d
TA	Without P	25 °C	2.78a	0.33e	6.00c	0.010e	4.77b
TH	With P	25 °C	1.65e	0.18e	11.42a	0.017d	3.70d
TH	Without P	25 °C	1.76e	0.22e	10.91a	0.020c	4.22c
EH	With P	25 °C	1.52f	0.15e	9.59b	0.001f	2.93e
EH	Without P	25 °C	1.52f	0.20e	8.41b	0.001f	3.18e
TA	With P	40 °C	2.30c	0.86d	2.32e	0.039a	4.29c
TA	Without P	40 °C	2.54b	0.80d	3.01e	0.042a	4.97b
TH	With P	40 °C	1.99d	2.68a	0.98f	0.031b	4.62b
TH	Without P	40 °C	2.49b	1.17c	2.68e	0.030b	5.64a
EH	With P	40 °C	1.07g	1.42c	0.71f	0.017d	2.08f
EH	Without P	40 °C	1.40f	0.36e	3.44e	0.015e	2.65e

(1) TH: Typic Hapludoll, EH: Entic Haplustoll, TA: Typic Argiudoll.

The ANOVA performed on the parameters of adsorption kinetics showed significant differences by soil effect ($p < 0.001$), treatment ($p < 0.01$) and the soil-temperature interaction ($p < 0.001$). The amount of phosphorus initially adsorbed (a) in the Typic Argiudoll increased with temperature in the treatments without phosphorus application. In the Entic Haplustoll most adsorption occurred at 25 °C without differences due to fertilization history. The greatest effect of the soil × temperature interaction was observed in the Typic Argiudoll at 25º and 40 ºC.

The initial rate of phosphorus release (b) in the Typic Argiudoll and Entic Haplustoll increased between 10 and 25 °C and with the fertilization history. Due to the interaction soil × temperature, higher rates of adsorption in the first stage were observed in the Typic Hapludol at 10 °C and the lowest in the Typic Argiudoll and Entic Haplustoll. The speed of the second adsorption stage (d) only increased by the effect of lower fertilization history in the Typic Argiudoll at 10 ºC.

These analyzes show the complex relationships between soil type, history of phosphate fertilization, temperature and the kinetics of phosphorus adsorption. Therefore, in these soils we could not clearly elucidate the effect of temperature on phosphorus adsorption kinetics due to the high variability of the results. The same contrasting effect of temperature on P adsorption was observed by Mezenner and Bensmaili (2009), Shen et al. (2011) and Huang et al. (2011).

The parameters of the phosphorus desorption kinetics for different soils, treatments and temperatures are detailed in **Table 3**.

The ANOVA performed on the parameters of desorption kinetics showed significant statistical differences by soil effect ($p < 0.001$), treatment

($p < 0.01$) and the soil × temperature interaction ($p < 0.001$), which is similar to what was found for adsorption kinetics parameters. The effect of temperature variation shows a rather variable influence, as was the case in the adsorption process. That was not the case reported by Pignatello (2000) for organic compounds, where desorption consistently increased when temperature rose.

While studies of P adsorption isotherms are recorded in Argentine soils since the 80s (Mendoza 1986) there are no articles about the kinetics of the P desorption process in these soils. With regard to the data obtained in this work, Lookman et al. (1995) observed similar desorption kinetics in 36 soils from Belgium and 8 from Germany. These authors attributed the differences in rates of desorption to the type of pool to which the P added in the pre-incubation was adsorbed, distinguishing between a very labile pool with a very high rate, and one of lower solubility. The release rate slowly increased to 1600 hours of experiment.

Table 3. Parameters of the phosphorus desorption kinetics for the different soils; *a*: intercept, P initially desorbed at $t = 0$, *b*: slope of the first stage, t_i: time at which ends the first reaction stage, *d*: slope of the second stage, Pad(t_i): concentration of phosphorus desorbed at ti estimates for each soil, treatment and temperature (T). N = 3 replicates for each estimation. Different letters indicate minimum significant differences, LSD Fisher Test ($p < 0.05$)

Soil$^{(1)}$	Treatment	T (°C)	*a*	*b*	t_i (h)	*d*	Pad(t_i) (μg/g)
TA	With P	10 °C	1.66e	0.77d	2.37e	0.014e	3.48d
TA	Without P	10 °C	1.84e	2.01b	0.93f	0.017d	3.71d
TH	With P	10 °C	2.08d	2.77a	0.81f	0.021c	4.31c
TH	Without P	10 °C	2.58b	2.66a	0.90f	0.021c	4.97b
EH	With P	10 °C	0.93g	1.44c	0.78f	0.013e	2.05f
EH	Without P	10 °C	1.06g	1.69b	0.74f	0.013e	2.31f
TA	With P	25 °C	2.42b	0.33e	4.58d	0.011e	3.93d
TA	Without P	25 °C	2.78a	0.33e	6.00c	0.010e	4.77b
TH	With P	25°C	1.65e	0.18e	11.42a	0.017d	3.70d
TH	Without P	25°C	1.76e	0.22e	10.91a	0.020c	4.22c
EH	With P	25°C	1.52f	0.15e	9.59b	0.001f	2.93e
EH	Without P	25°C	1.52f	0.20e	8.41b	0.001f	3.18e
TA	With P	40°C	2.30c	0.86d	2.32e	0.039a	4.29c
TA	Without P	40°C	2.54b	0.80d	3.01e	0.042a	4.97b
TH	With P	40°C	1.99d	2.68a	0.98f	0.031b	4.62b
TH	Without P	40°C	2.49b	1.17c	2.68e	0.030b	5.64a
EH	With P	40°C	1.07g	1.42c	0.71f	0.017d	2.08f
EH	Without P	40°C	1.40f	0.36e	3.44e	0.015e	2.65e

$^{(1)}$ TH: Typic Hapludoll, EH: Entic Haplustoll, TA: Typic Argiudoll.

The complex relationships between the parameters of the kinetics of adsorption and desorption of phosphorus, different soil types, fertilization treatments and temperature, can be described more clearly with a multivariate principal component analysis. In the biplot in **Figure 4**, a clear association between the amounts of phosphorous adsorbed at the beginning of the process (*a*) and that adsorbed when the rate of adsorption (*Pti*) changes is observed. However, there is no association between the adsorbed amounts and rates at which these processes occur, which is evident in the right angle between the vectors.

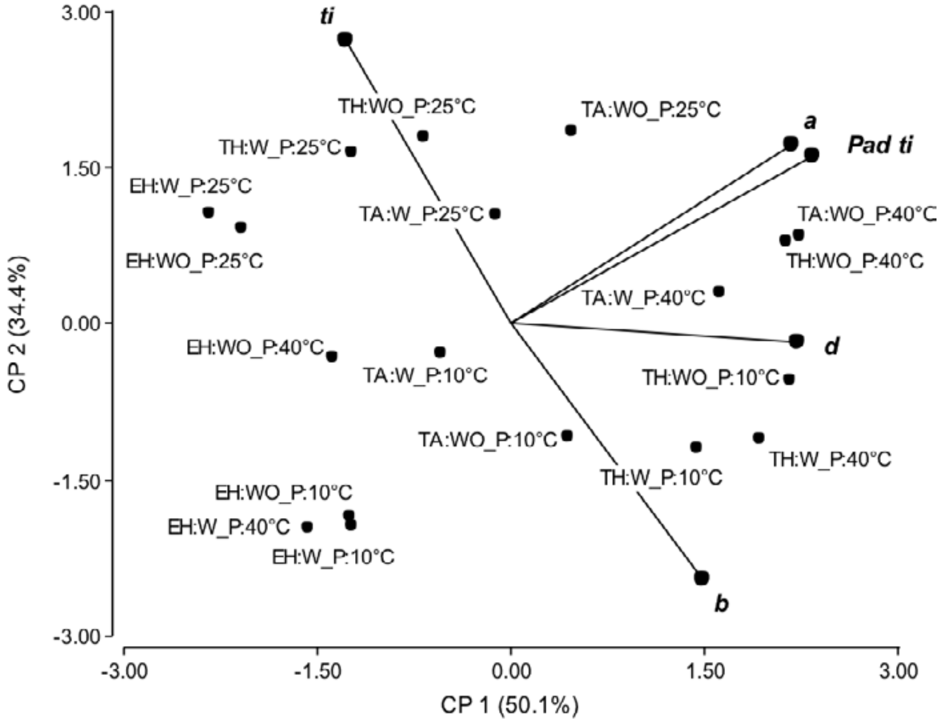

Figure 4. Biplot for the relationship between soils (TH: Typic Hapludoll, EH: Entic Haplustoll, TA: Typic Argiudoll), treatments (W_P: with P; WO_P: without P) and temperature and the adsorption kinetics parameters (*a*: intercept, P initially adsorbed at *t* = 0, *b*: slope of the first stage, t_i: time at which ends the first reaction stage, *d*: slope of the second stage, Pad(t_i): concentration of phosphorus adsorbed at t_i).

A negative association exists between the more rapid absorption rate and the time at which the speed change occurs (*b* and *ti*), this means that when one increases the other decreases, which is observed by the plane angle between the vectors; this was not observed for the Typic Argiudoll at 10 °C, where the Without-P treatment is located at relatively higher values of the adsorption rate (*b* and *d*), indicating an effect of temperature on the adsorption kinetics in interaction with the soil fertilization history. Relationships between the parameters describing the kinetics and soils vary widely in the Typic Hapludoll due to differences in fertilization history and/or management at the three temperatures. On this type of soil, the effect of temperature is greater for 25 °C than for 10 and 40 °C. The multivariate analysis of principal components (with two components) used in this work explained 83.8% of the total variability observed. This analysis reveals a complex relationship between soil fertilization history, temperature and the parameters that describe the kinetic processes.

Analysis of the parameters that explain the kinetics of desorption depending on the fertilization history and the temperature (with two components) explained 81.7% of the total variability. **Figure 5** shows a poor association between the amounts of phosphorus initially released (*a*) into the soil solution (at t = 0) and when the speed changes (at t = *ti*), in comparison with the observed in adsorption. It was observed a positive association between the fastest release rate (*b*) and the initial amount desorbed (a) (see the acute angle between the vectors). On the other hand, there was a lack of association between the amounts released at t = *ti* (*Pdes ti*) and the rate of the second step of desorption (*d*). For all soils and treatments together, there was no clear relationship between the soil and the parameters for the effect of temperature, because the scores of soils and treatments were not placed as a function of temperature, as it was observed in adsorption.

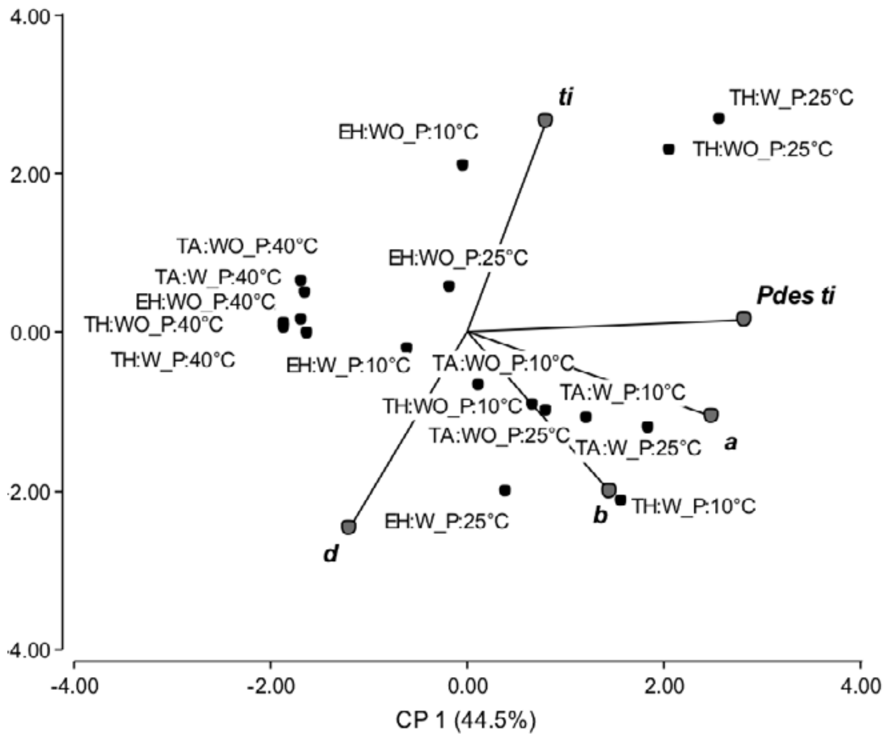

Figure 5. Biplot for the relationship between soils (TH: Typic Hapludoll, EH: Entic Haplustoll, TA: Typic Argiudoll), treatments (W_P: with P; WO_P: without P) and temperature and the desorption kinetics parameters (*a*: intercept, P initially desorbed at $t = 0$, *b*: slope of the first stage, t_i: time at which ends the first reaction stage, *d*: slope of the second stage, Pad(t_i): concentration of phosphorus desorbed at t_i).

The fertilization history was more important than the type of soil in determining the kinetic processes for both adsorption and desorption. For this reason, each soil with its history and/or fertility treatment should be considered here as a soil environment. Thus, six different soil environments, instead of three soils that received different treatments. Kinetic processes in turn have been differentiated according the temperature and processes considered (adsorption or desorption). These occurred according to the kinetic parameters considered, in conjunction with the environment, indicating the existence of multiple and complex interactions.

4. Conclusions

The proposed bi-linear kinetic model adequately described the data obtained in the experiments of adsorption and desorption. It allowed the distinction of two different kinetic mechanisms or processes, each characterized by different reaction rates (speeds). The different rates of the kinetic processes allowed the identification of at least two very labile phosphorus pools in these soils.

The rate at which the processes of adsorption and desorption occurred indicate precipitation in highly soluble compounds, and surface adsorption reactions with very low binding energy, quickly released into the soil solution in the desorption process.

Since the amounts of P released in the desorption process were much less than the adsorbed, it was possible to infer that both processes occurred at non-equilibrium conditions and that there was a lack of reversibility of the reaction P-Soil – P-Solution in the soils studied.

The intensity of these processes changed as a function of temperature and, in general, there was a positive effect of P fertilization history, although this effect was not clearly seen in the amount of extractable phosphorus detected by the Bray & Kurtz Nº 1 method.

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