KINETICS OF MOLYBDATE AND PHOSPHATE SORPTION BY SOME CHILEAN ANDISOLS

Cinética de adsorción de molibdato y fosfato en algunos Andisoles chilenos

Erika Marina Vistoso G.[1], Nanthi S. Bolan[2], Benny K. G. Theng[3], María de la Luz Mora[4]

[1]National Institute for Agricultural Research (INIA), Remehue Research Centre, P.O. Box 24-O, Osorno, Chile.
[2]Centre for Environmental Risk Assessment, University of South Australia, SA 5095, Australia
[3]Landcare Research, Private Bag 11052, Manawatu Mail Centre, Palmerston North 4442, New Zealand
[4]Departamento de Ciencias Químicas, Facultad de Ingeniería, Ciencias y Administración, Universidad de la Frontera, P.O. Box 54-D, Temuco, Chile. Corresponding author: mariluz@ufro.cl

ABSTRACT

The kinetics for the sorption of molybdate and phosphate by four Chilean Andisols have been determined. About 55% of the molybdate and 61% of the phosphate was sorbed in the first 0.5 h, after which sorption slowly increased, reaching 90% for molybdate and 97% for phosphate after 72 h. At the same time, OH^- ions were released into the external solution, raising its pH by 0.85 units for molybdate and by 0.65 units in the case of phosphate. These observations indicated that both anions were sorbed by a ligand exchange mechanims. Among the five kinetic models examined (Table, 2), the Elovich equation gave the best fit of the experimental data (R^2 = 0.93 to 0.97, standard error = 0.35 to 0.94). The sorption rate constant (α) for both anions was related to the organic matter (OM) content of the soils, especially the content of Al- and Fe-humus complexes. The α values for molybdate were 2.24×10^{15} mmol kg^{-1} h^{-1} for the Vilcún soil (15% OM), 2.49×10^{12} mmol kg^{-1} h^{-1} for the Pemehue soil (16% OM), 8.76×10^{10} mmol kg^{-1} h^{-1} for the Osorno soil (20% OM), and 3.11×10^7 mmol kg^{-1} h^{-1} for the Piedras Negras soil (24% OM). The corresponding values for phosphate were 3.89×10^7, 5.21×10^{10}, 3.11×10^{12} and 1.08×10^{16} mmol kg^{-1} h^{-1}. The desorption rate constant (β) for the four soils (in the above order) ranged from 0.47 to 0.28 for molybdate, and 0.22 to 0.39 mmol kg^{-1} h^{-1} for phosphate. The results suggest that the mineralogical composition and organic matter content of the Andisols control the kinetics for the sorption of both molybdate and phosphate. Molybdate appeared to have a high affinity for Fe- and Al-oxides, while phosphate was largely sorbed to Fe-and Al-humus complexes.

Keywords: Al- and Fe-oxide, Chilean Andisols, kinetic model, molybdate and phosphate.

RESUMEN

Se determinaron las cinéticas de adsorción de molibdato y fosfato en cuatro Andisoles Chilenos. Cerca del 55% del molibdato y 61% del fosfato fueron adsorbidos en las primeras 0,5 h; después la adsorción aumentó lentamente, donde se adsorbió aproximadamente el 90% del molibdato y el 97% del fosfato después de 72 h. Al mismo tiempo, aumentó la concentración de iones OH⁻ en la solución de suelo, aumentando el pH en 0,85 unidades para molibdato y en 0,65 unidades en el caso de fosfato. Estas observaciones indican que ambos aniones son adsorbidos por el mecanismo de intercambio de ligandos. Entre los cinco modelos cinéticos examinados (Tabla 2), la ecuación de Elovich mostró los mejores ajustes de los datos experimentales (R^2 = 0,93 a 0,97; SE = 0,35 a 0,94). La velocidad de adsorción (α), para ambos aniones, se relacionó con el contenido de materia orgánica (MO) de los suelos, especialmente con los contenidos de los complejos humus-Al y humus-Fe. Los valores de α para molibdato fueron $2,24 \times 10^{15}$ mmol kg^{-1} h^{-1} en el suelo Vilcún (15% MO); $2,49 \times 10^{12}$ mmol kg^{-1} h^{-1} en el suelo Pemehue (16% MO); $8,76 \times 10^{10}$ mmol kg^{-1} h^{-1} en el suelo Osorno (20% MO), y $3,11 \times 10^7$ mmol kg^{-1} h^{-1} en el suelo Piedras Negras (24% MO). Los valores correspondientes para fosfato fueron $3,89 \times 10^7$; $5,21 \times 10^{10}$; $3,11 \times 10^{12}$; y $1,08 \times 10^{16}$ mmol kg^{-1} h^{-1}. La velocidad de desorción (β) en los cuatro suelos (en el orden anterior) fluctuó en el rango de 0,47 a 0,28 para molibdato, y 0,22 a 0,39 mmol kg^{-1} h^{-1} para fosfato. Los resultados sugieren que la composición mineralógica y el contenido de materia orgánica de estos Andisoles controlan la cinética de adsorción de molibdato y fosfato. Molibdato parece tener mayor afinidad por los óxidos-Fe y óxidos-Al, mientras que fosfato es mayormente adsorbido por los complejos humus-Fe y humus-Al.

Palabras claves: Oxido de Al y Fe, andisoles chilenos, modelo cinético, molibdato y fosfato.

INTRODUCCTION

Chilean Andisols are acidic, have variable charge characteristics and a high anion sorption capacity (Mora *et al*., 2005). Andisols also have a large propensity for retaining P, Mo, and Se (Parfitt, 1978; Mora and Canales, 1995a,b; Barrow, 1999; Barrow, 2005; Vistoso *et al*., 2005; Cartes *et al*., 2005; López *et al*., 2007). Thus, farmers need to apply high rates of P and Mo fertilizers for legume production in volcanic soils of Sourthen Chile. In practice, this is done by placing the fertilizers as bands near the seed or coat over the seeds. Sorption of molybdate and phosphate by soil constituents controls the mobility and bioavailability of Mo and P in soil-solution-plant systems (Barrow, 1999). Both molybdate and phosphate are strongly sorbed to the variable charge mineral constituents (Al-oxides, Fe-oxides, allophane, imogolite) of volcanic soils (Karimian and Cox, 1978; Goldberg and Forster, 1998; Brown and Parks, 2001). The principal sorption mechanism is ligand exchange involving the formation of inner-sphere surface complexes (Zhang and Sparks, 1989; Goldberg *et al*., 2002; Goldberg *et al*., 2008). Thus, P and Mo deficiencies often occur in highly weathered acid soils.

Chemical reactions in soil, including anion sorption from aqueous solutions, occur on a millisecond time scale (Sparks, 1999). Since sorption kinetics have a controlling influence on anion mobility, transport, and bioavailability, their assessment is a prerequisite for the efficient application of Mo and P fertilizers. Various models have been used to describe the kinetics for the sorption of phosphate by soils and soil constituents (Chien and Clayton, 1980;

Aharoni *et al*., 1991; Freese *et al*., 1995). Little information, however, is available of the kinetics of molybdate sorption by soils, let alone by volcanic soils.

The aim of this research was to compare the effect of reaction time and the effect of soil properties on molybdate and phosphate adsorption in a range of Andisols from southern Chile.

Theoretical background

Many models such as the homogeneous and heterogeneous surface site models have been used to describe the sorption of Mo and P by soils (Zhang and Sparks, 1989; Sparks, 1999; McGechan and Lewis, 2002). Because of the mathematical complexity involved, sorption rates have commonly been described in terms of zero-order kinetic (1), first-order kinetic (2), and second-order kinetic (3) kinetics all of which assume that the rate of change in solute concentration is proportional to the concentration in solution and the number of empty sites on the sorbent:

$$q_t = q_o - K_o\, t \qquad (1)$$
$$ln\ q_t = ln\ q_o - K_1 t \qquad (2)$$
$$1/q_t = 1/q_o + K_2\, t \qquad (3)$$

Here q_t, and q_o denote the quantity at time (*t*) and time zero, respectively; K_o, K_1, and K_2 are the corresponding rate constants. Another kinetic model is the parabolic diffusion equation (4) which assumes that the rate-limiting step is the diffusion of anions either from the solution into the surface, or from the surface into intraparticle pores:

$$q_t = \alpha + K_d^{1/2} \qquad (4)$$

where, q_t is the sorbed amount at time *t*; and K_d are constants.
A widely used model is the Elovich equation:

$$dq/dt = \alpha\ exp\ (\beta\text{-}q) \qquad (5)$$

where, *q* is the sorbed amount at time (*t*); α and β are constants. Equation (5), originally developed to describe the kinetics for the chemisorption of gases to solid surfaces, was modified by Chien and Clayton (1980) who assumed that the activation energy of sorption increases linearly with surface coverage. The α parameter can be considered as the initial rate constant since $dq/dt \rightarrow \alpha$ when $q \rightarrow 0$. This means that the rapid initial sorption is not governed by the exponential law. Assuming that $q = 0$ at $t = 0$, and integrating equation (5) yields:

$$q = (1/\beta)\ ln\ (1 + \alpha\beta t) \qquad (6)$$

By assuming that $\alpha\beta t \gg 1$, equation (6) may be further simplified to:

$$q t = (1/\beta)\ ln\ (\alpha\beta) + (1/\beta)\ ln\ t \quad (7)$$

where, *q* is the amount of anion sorbed at time (*t*), α and β are parameters and K_{eq} is the equilibrium constant (calculated by α/β). Chien and Clayton (1980) determined α and β (7), and used these parameters to compare the kinetics of phosphate release and sorption in soils.

Materials and methods

Soils
Four Andisols (Vilcún, Pemehue, Osorno and Piedras Negras) with contrasting chemical properties were sampled from locations in Southern Chile (37° 35'–44° 04' LS and 70° 50'–71° 35' LW). The samples were taken from 0–20 cm, air-dried and sieved 2 mm . The chemical characteristics of the soils were determined according to the methods described by Sadzawka *et al*. (2006). Soil pH (water) was measured potentiometrically using a soil:solution ratio of 1:2.5. Organic matter was estimated by a modified Walkley-Black wet digestion method adapted for Chilean soils by Sadzawka *et al*. (2006). The different forms of Al and Fe oxides in the soils were determined by selective extraction (dissolution) with acid ammonium oxalate

Table 1. Chemical characteristics, concentrations of different forms of Al, Si and Fe, and contents of allophane and ferrihydrite of the four studied Andisols.

Tabla 1. Características químicas, concentraciones de las diferentes formas de Al, Si, Fe y, contenidos de alofán y ferrihidrita de los cuatro Andisoles estudiados.

Soil	Vilcún	Pemehue	Osorno	P. Negras
pH (water)	5.47 ± 0.01	5.41 ± 0.06	4.81 ± 0.02	5.40 ± 0.02
Organic matter (g kg^{-1})	140 ± 1.26	150 ± 0.58	210 ± 1.16	240 ± 1.41
Al$_o$ (g kg^{-1})	14.10 ± 0.01	29.80 ± 0.04	30.70 ± 0.06	32.50 ± 0.13
Fe$_o$ (g kg^{-1})	8.90 ± 0.05	10.30 ± 0.05	11.50 ± 0.01	11.90 ± 0.04
Si$_o$ (g kg^{-1})	5.70 ± 0.06	9.103 ± 0.07	17.10 ± 0.10	19.30 ± 0.05
Al$_d$ (g kg^{-1})	23.00 ± 0.07	21.90 ± 0.05	18.50 ± 0.03	16.30 ± 0.04
Fe$_d$ (g kg^{-1})	56.30 ± 0.10	51.31 ± 0.08	37.60 ± 0.07	37.10 ± 0.02
Al$_p$ (g kg^{-1})	6.60 ± 0.02	10.10 ± 0.03	14.30 ± 0.01	14.60 ± 0.03
Fe$_p$ (g kg^{-1})	7.10 ± 0.01	6.80 ± 0.02	8.70 ± 0.04	10.40 ± 0.05
Allophane (g kg^{-1}) [1]	28.50 ± 0.38	54.60 ± 0.44	85.50 ± 0.52	96.50 ± 0.45
Ferrihydrite (g kg^{-1}) [2]	15.10 ± 0.90	17.50 ± 0.70	19.60 ± 0.30	20.20 ± 0.60

[1] Calculated by a factor depending on the Al/Si molar ratio (Parfitt and Wilson, 1985).
[2] Calculated by multiplying Fe$_o$ by 1.7 (Parfitt and Childs, 1988).

(Al$_o$, Fe$_o$), dithionite-citrate-bicarbonate (Al$_d$, Fe$_d$), and Na-pyrophosphate (Al$_p$, Fe$_p$) as described by Blakemore *et al.* (1987). The concentrations of Al and Fe in the various extracts were determined by atomic absorption spectrophotometry (AAS). Allophane and ferrihydrite contents were calculated using the methods proposed by Parfitt and Wilson (1985) and Parfitt and Childs (1988). The chemical characteristics of the soils together with the concentrations of different forms of Al, Fe, and Si, and the contents of allophane and ferrihydrite, are listed in Table 1.

Sorption kinetics
The kinetics of molybdate and phosphate sorption by the four Andisols were determined at 298 K using the batch method. A background electrolyte solution (0.1 M KCl) containing 5.0 mmol L^{-1} of molybdate (as Na$_2$MoO$_4$x2H$_2$O) or phosphate (as

K$_2$HPO$_4$) was added in duplicate to polypropylene centrifuge tubes at soil:solution ratio of 1:20. The pH was adjusted to 5.0 by addition of dilute HCl or KOH solution in a N$_2$ atmosphere so as to eliminate CO$_2$. The tubes were shaken for 72 h and the end of the reaction time, the suspensions were centrifuged at 10,000 g for 10 minutes and aliquots of the supernatants were analyzed. The concentration of Mo in the equilibrium solution was determined by AAS and that of P by colorimetry (Murphy and Riley, 1962).

Kinetic modelling
The following models were used to describe the sorption of Mo and P: zero-order kinetic (1), first-order kinetic (2), second-order kinetic (3), parabolic diffusion (4), and Elovich equation (7).

Statistical analysis

The experimental data were statistically analyzed using SPSS version 13. The fit of each kinetic model was evaluated by the determination coefficient (R^2) and standard error (SE) of Chien and Clayton (1980). The values of R^2 and SE were used to compare the applicability of the different models at a confidence level of 95%. Furthermore, the parameters of the Elovich equation model were correlated with the chemical properties of the Andisols.

RESULTS AND DISCUSSION

Sorption kinetics

The initial step of molybdate sorption by the Vilcún and Pemehue soils was faster than that by the Osorno and Piedras Negras soils samples (Figure 1). In accord with Barrow´s (1999) studies with the same anions but with other soils, the sorption of phosphate by the Andisols was twice as rapid as that of molybdate, except for the Vilcún soil. Sorption increased with time, reaching an apparent equilibrium after 72 h. The sorption of both molybdate and phosphate showed two clearly defined steps: A fast initial reaction (up to 30 minutes), followed by a slow adsorption (up to 72 h). About 55.4% of the total amount of molybdate and 61.7% of the total amount of phosphate, were sorbed after 30 minutes. At 72 h, 89.7% of molybdate and 96.8% of phosphate were sorbed. Similar results were obtained by Zeng *et al*. (2003) for the sorption of phosphate by two Andisols. The same pattern was observed for the sorption of molybdate and phosphate by Al- and Fe-hydroxides, goethite, and acid soils (Bolan *et al*., 1985; Zhang and Sparks, 1989; Freese *et al*., 1995; Barrow, 1999; Brinton and O'Connor, 2003; do Carmo Horta and Torrent, 2007). Barrow (1999) has suggested that the "slow" reaction is due to diffusion of sorbed anions from surface sites into micropores within the structure of the soil constituents.

There was a steady increase in the pH of the supernatant solution as sorption progressed. After 72 h the pH of the equilibrium solution increased by 0.85 units for molybdate and 0.65 units for phosphate (Figure 2). These observations is supported by the literature because sorption occurs by ligand exchange mechanism; that is, the replacement of hydroxyl groups, exposed on surface sites, by either molybdate or phosphate in solution (Zhang and Sparks, 1989; Barrow, 1999; Goldberg *et al*., 2008).

We tested five different kinetics models using the least square regression analysis to describe the sorption of molybdate and phosphate in the Andisols (Table 2). The fitting by the linear models (equations 1, 2, 3 and 4) were unsuccessful in that the R^2 were low (0.32–0.68) with, high SE (1.12–2.67). Similarly, Bolan *et al*. (1985) and Zeng *et al*. (2003) found that the sorption of phosphate could not be adequately described by a zero-, first-, or second- order kinetic; nor by the parabolic diffusion model. No information, however, is available on modelling the kinetics for the sorption of molybdate by Andisols.

We have fitted the sorption data to the Elovich equation (Figure 3) where the R^2 values were highest (0.92) and SE lowest (0.94) (Table 2). Other have obtained similar results (Freese *et al*. (1995), Zeng *et al*. (2003) and Li *et al*. (2005) obtained similar results for different types of soils.

Kinetic constants from the Elovich equation

The Elovich parameters for the sorption of molybdate and phosphate are listed in Table 3. Except for the Vilcún and Pemehue soils, the values of sorption rate constant (α) for phosphate were much higher than those for molybdate. This agrees with Barrow (1999) who indicates that the reactivity of phosphate in soil is much higher than that of molybdate. Piedras Negras soil gave a higher α value for phosphate than the other soils. According to the parameters estimated
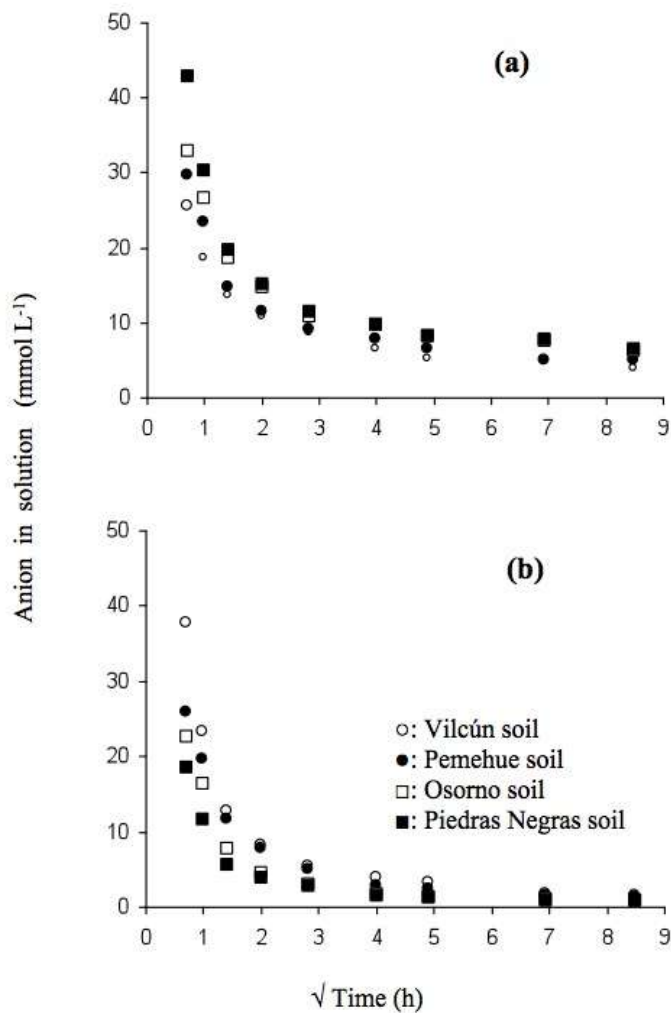
Figure 1: Effect of time on sorption of molybdate (a) and phosphate (b) by Vilcún, Pemehue, Osorno and Piedras Negras soils at 298 K in the presence of 0.1 M KCl as background electrolyte.

Figura 1: Efecto del tiempo sobre la adsorción de molibdato (a) y fosfato (b) en los suelos Vilcún, Pemehue, Osorno y Piedras Negras, a 25 ± 0,1°C en presencia de 0,1 M KCl como electrolito de soporte.
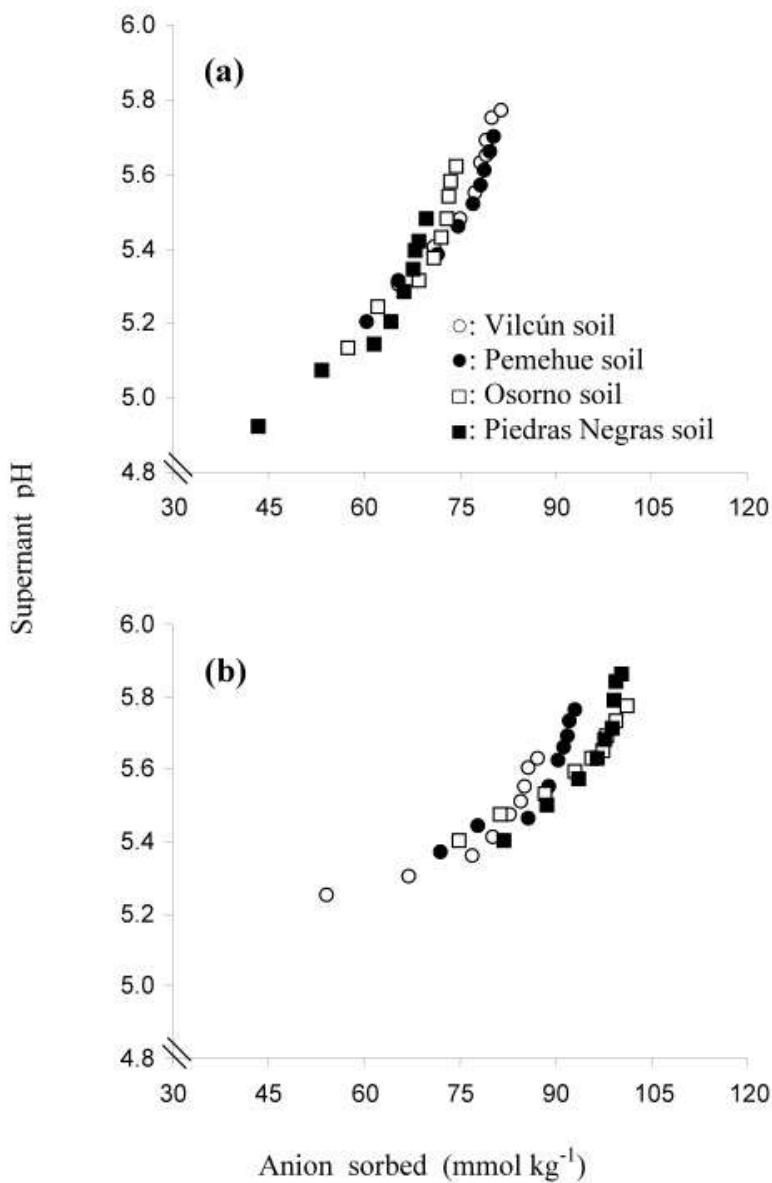
Figure 2: Relationship between supernatant pH and amount of molybdate (a) and phosphate (b) sorbed by Vilcún, Pemehue, Osorno and Piedras Negras soils at 298 K in the presence of 0.1 M KCl as background electrolyte.

Figura 2: Relación entre el pH del sobrenadante y la cantidad adsorbida de molibdato (a) y fosfato (b) en los suelos Vilcún, Pemehue, Osorno and Piedras Negras, a 25 ± 0,1°C en presencia de 0,1 M KCl como electrolito de soporte.
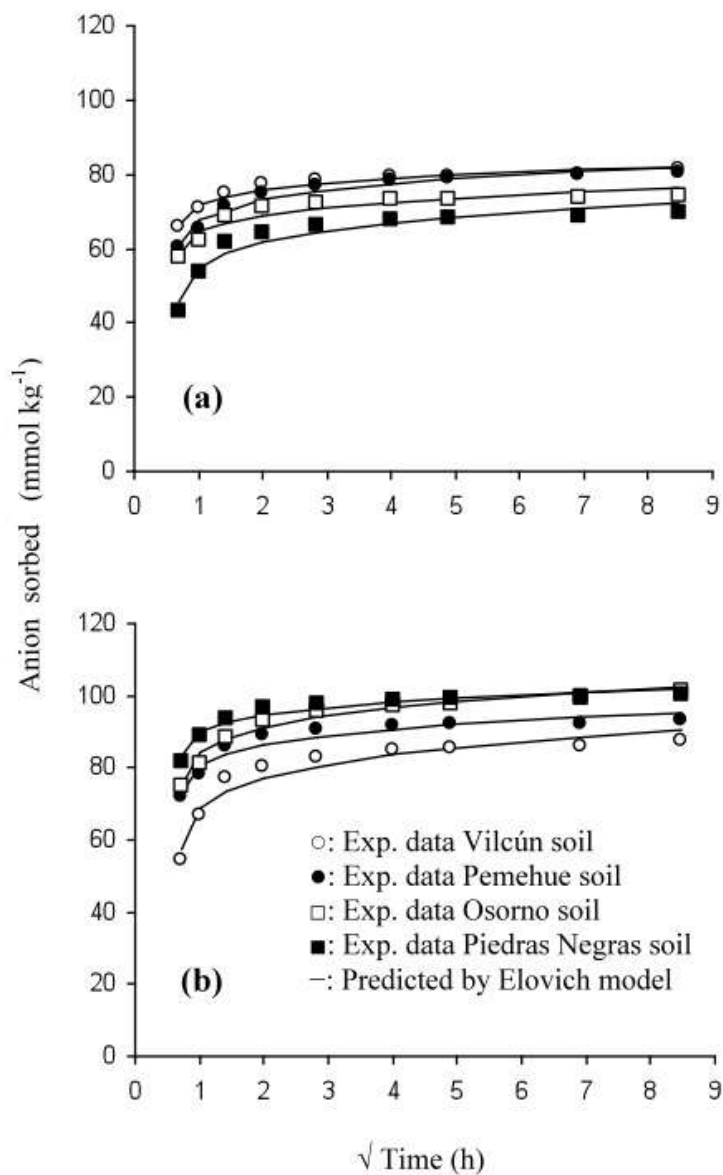
Figure 3: Kinetic data for the sorption of molybdate (a) and phosphate (b) by Vilcún, Pemehue, Osorno and Piedras Negras soils at 298 K in the presence of 0.1 M KCl, showing the closeness of fit to the Elovich equation (solid lines).

Figura 3: Datos cinéticos de la adsorción de molibdato (a) y fosfato (b) en los suelos Vilcún, Pemehue, Osorno and Piedras Negras, a 25 ± 0,1°C en presencia de 0,1 M KCl como electrolito de soporte, mostrando los datos modelados con la ecuación de Elovich (líneas sólidas).

Table 2. Values of determination coefficient (R^2) and standard error (SE) obtained from the model kinetic fitting to the experimental data for the sorption of molybdate and phosphate by four Andisols.

Tabla 2. Valores de coeficientes de determinación (R^2) y error estándar (ES) de diferentes modelos cinéticos obtenidos de los datos experimentales en la adsorción de molibdato y fosfato en cuatro Andisoles.

Soil	Sorption kinetics for molybdate		Sorption kinetics for phosphate	
	SE	R^2	SE	R^2
Zero-order				
Vilcún	1.116	0.430	2.161	0.349
Pemehue	1.530	0.432	1.474	0.360
Osorno	1.176	0.361	2.054	0.479
Piedras Negras	1.729	0.350	1.257	0.371
First-order				
Vilcún	1.094	0.421	2.069	0.334
Pemehue	1.483	0.419	1.430	0.356
Osorno	1.144	0.351	1.992	0.464
Piedras Negras	1.655	0.335	1.231	0.364
Second-order				
Vilcún	1.073	0.413	1.988	0.321
Pemehue	1.438	0.406	1.393	0.341
Osorno	1.115	0.342	1.934	0.450
Piedras Negras	1.590	0.322	1.207	0.356
Parabolic diffusion				
Vilcún	1.331	0.611	2.667	0.533
Pemehue	1.862	0.633	1.815	0.549
Osorno	1.452	0.550	2.439	0.675
Piedras Negras	2.134	0.533	1.542	0.558
Elovich equation				
Vilcún	0.670	0.962	0.529	0.933
Pemehue	0.885	0.926	0.924	0.970
Osorno	0.352	0.960	0.935	0.928
Piedras Negras	0.824	0.934	0.570	0.949

Tabe 3. Values of the parameters (α, β, K$_{eq}$) derived from fitting the experimental data for the sorption of molybdate and phosphate by four Andisols to the Elovich kinetic model.

Tabla 3. Valores de los parámetros (α, β, K$_{eq}$) derivados de los datos experimentales de la adsorción de molibdato y fosfato en cuatro Andisoles a partir del modelo cinético de Elovich.

Soil	Parameters (mmol kg^{-1} h^{-1})		Keq
	α	β	
Sorption kinetics for molybdate			
Vilcún	2.24×10^{15}	0.473	4.73×10^{15}
Pemehue	2.49×10^{12}	0.419	5.94×10^{12}
Osorno	8.76×10^{10}	0.347	2.52×10^{11}
Piedras Negras	3.11×10^{7}	0.280	1.11×10^{8}
Sorption kinetics for phosphate			
Vilcún	3.89×10^{7}	0.224	1.73×10^{8}
Pemehue	5.21×10^{10}	0.270	1.93×10^{11}
Osorno	3.11×10^{12}	0.336	9.25×10^{12}
Piedras Negras	1.08×10^{16}	0.394	2.74×10^{16}

by the Elovich equation (Table 3) it can be inferred that the α values for phosphate and molybdate depend on the soil type. The β values did not vary much between the four soils, while the sorption rate constants (α) were higher than the desorption constants (β). Since β values for molybdate were higher than those for phosphate, the availability of molybdate in these Andisols would be higher than that of phosphate.

The equilibrium constants (K_{eq}) for molybdate increased as the organic matter content of the soils decreased, while the K_{eq} values for phosphate showed the opposite tendency (Table 3). The K_{eq} values indicate that the molybdate sorption capacity of these Andisols is related to the content of free Al- and Fe-oxides (Al$_d$, Fe$_d$). In contrast, the K_{eq} values for phosphate are related to the content of Al- and Fe-humus complexes (Al$_p$, Fe$_p$). These results suggest that Al- and Fe-humus complexes control the kinetic behaviour of these anions.

Many workers (Barrow, 1970; Karimian and Cox, 1978; García-Rodeja and Gil-Sotres, 1997; Goldberg and Forster, 1998; Brown and Parks, 2001; Hirade and Uchida, 2004; Goldberg *et al.*, 2008) have shown that molybdate and phosphate in soil are strongly sorbed to, and associated with, Al- and Fe-oxides. Being rich in free Al- and Fe-oxides (and allophane), volcanic soils generally have a high capacity for sorbing molybdate and phosphate. For this reason,

Table 4. Values of correlation coefficient (r) relating some soil properties to the Elovich (α, β) parameters.

Tabla 4. Valores de coeficientes de correlación (r) entre algunas propiedades del suelo y los parámetros de Elovich (α, β).

Sorption kinetic of molybdate									
Parameter	OM[1]	Al$_o$ [2]	Fe$_o$ [2]	Al$_d$ [3]	Fe$_d$ [3]	Al$_p$ [4]	Fe$_p$ [4]	Allophane [5]	Ferrihydrite [6]
α	ns	-0.991*	ns	0.666*	0.737*	ns	ns	ns	-0.866*
β	-0.980*	ns	-0.966*	0.992**	0.950*	-0.951*	ns	-0.980*	-0.963*
Sorption kinetic of phosphate									
Parameter	OM[1]	Al$_o$[2]	Fe$_o$[2]	Al$_d$[3]	Fe$_d$[3]	Al$_p$[4]	Fe$_p$[4]	Allophane[5]	Ferrihydrite[6]
α	ns	0.765*	ns	ns	ns	0.561*	0.864*	0.654*	ns
β	0.983*	ns	0.966*	-0.994**	-0.953*	0.952*	ns	0.981*	0.963*

(**), significant at < 0.01; (*), significant at < 0.05; ns = not significant.

the phytoavailability of Mo and P in Chilean Andisols would be low. The present results are consistent with this expectation.

Relationship between kinetic constants and various soil properties

As already mentioned, Al- and Fe-oxides in soils are very reactive toward molybdate and phosphate. Table 4 gives the coefficients for the correlations between soil properties and the Elovich parameters for the sorption of molybdate and phosphate. The results lend further support to the hypothesis that the rate of molybdate sorption (α) is positively correlated with free Al- and Fe-oxides (Al$_d$, Fe$_d$) and negatively correlated with Al$_o$ and ferrihydrite contents (p<0.05). In contrast, the α values for phosphate were positively correlated with the content of poorly crystalline Al-oxides (Al$_o$), allophane, and Al- and Fe-humus complexes (Al$_p$, Fe$_p$). On the other hand, the rate of desorption (β) for molybdate was positively correlated with Al$_d$ and Fe$_d$ and negatively correlated with organic matter, Fe$_o$, Al$_p$, allophane and ferrihydrite contents. The correlation coefficients relating phosphate β values to

soil properties were similar in magnitude to those of molybdate, but with an opposite sign. The results for phosphate are in line with previous measurements of the kinetics of phosphate sorption and release (García-Rodeja and Gil-Sotres, 1997; Zeng *et al.*, 2003; do Carmo Horta and Torrent, 2007).

CONCLUSIONS

The content of free Fe and Al oxides appears to be the principal factor affecting the rate and capacity of molybdate sorption by Chilean Andisols. In the case of phosphate, on the other hand, it is the content of allophane, Al-humus and Fe-humus complexes that has a controlling influence on sorption and release. From the correlation between the Elovich parameters and soil properties we infer that availability of Mo in Andisols is higher than that of P. Nevertheless, Mo availability in volcanic soils may be inadequate for crop production. The high, negative correlation between the desorption constant for molybdate and the content of allophane or ferrihydrite further

suggests that plant roots are not very efficient in taking up Mo. Thus, volcanic soils may not be able to supply sufficient Mo to meet the requirement of legumes for nitrogen fixation.

ACKNOWLEDGEMENTS

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