# EFFECT OF pH, PHOSPHATE AND/OR MALATE ON SULFATE SORPTION ON ANDISOLS

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**Efecto del pH, fosfato y/o malato sobre la adsorción de sulfato en Andisoles**

## ABSTRACT

The sulfate sorption was studied on Andisols with variable mineralogical composition and low organic matter content in presence and absence of phosphate or malate ligands at different pH. Crystalline clay mineralogy was similar for all the studied samples, except for the 2C horizon of the pedon 2, which did not show crystalline minerals. The soil samples showed content of allophane ranging from 16% to 42%. The sulfate adsorption decreased when descending the first 3 horizons (A1, 2A2 and 3Bw1) of the pedon 1. This behavior was attributed to the decreasing organic carbon content. At different pH sulfate sorption was drastically decreased by increasing the pH from 4.0 to 7.0, precisely by 80% for sample 5 to 100% for sample 1. Experiments on the competitive sorption of phosphate and sulfate on volcanic soils were carried out. Sulfate sorption was reduced even in the presence of low concentrations of phosphate ions (phosphate/sulfate molar ratio $<< 1$). Sulfate sorption was influenced by many factors as the organic carbon content, pH, the mineralogical composition of soil samples and the order of sulfate and phosphate addition into the soils. Sulfate competes with phosphate particularly when added before phosphate and at low pH values (pH $< 4.5$). Phosphate more than malate affected the kinetics of sulfate sorption onto a volcanic soil containing a large amount of allophanic materials.

## RESUMEN

La adsorción de sulfato fue estudiada en Andisoles con una composición mineralógica variable y bajo contenido de materia orgánica en presencia y ausencia de fosfato o malato a diferentes pH. La mineralogía de las arcillas cristalinas fue similar para todos las muestras estudiadas, excepto para el horizonte 2C del pedon 2, la cual no mostró minerales cristalinos. Las muestras de suelo presentaron contenidos de alofán en el rango de 16 a 42 %. La adsorción de sulfato incrementó al descender los primeros 3 horizontes (A1, 2A2 and 3Bw1) del pedon 1. Este comportamiento fue atribuído a la disminución del contenido de carbono orgánico. A diferentes pH la adsorción de sulfato fue drásticamente disminuída el aumento del pH desde 4,0 a 7,0, desde un 80 % para la muestra 5 a 100 % para la muestra 1. La adsorción de sulfato fue reducida incluso en presencia de bajas concentraciones de iones fosfato (razón molar fosfato/sulfato 1). Experimentos de adsorción competitiva de fosfato y sulfatos fueron realizado en suelos volcánicos. La adsorción de sulfato fue influenciada por muchos factores, como el contenido de materia orgánica, pH, composición mineralógica de los suelos y el orden de adición de sulfato y fosfato en los suelos. Sulfato compite con fosfato particularmente cuando es adicionado antes que fosfato y a bajos valores de pH (pH 4,4). Fosfato más que malato afectó la cinética de la adsorción de sulfato en un suelo volcánico conteniendo una gran cantidad de materiales alofánicos.

## INTRODUCTION

Volcanic ash soils (Andisols) may adsorb high amounts of phosphate and sulfate for the presence of short-range ordered variable charge minerals (allophane, imogolite, Al and Fe oxides) characterized by high surface area and reactivity (Parfitt, 1990; Huang and Violante, 1986; Mora and Canales, 1995; Vacca *et al*., 2003). Gunjigake and Wada (1980) indicated that the more reactive forms of aluminium in fixing phosphate anions in Andisols are the following: i) allophane and imogolite; ii) allophane-like components; iii) aluminium associated with humic substances and iv) aluminium present in the interlayers of expandable phyllosilicates.

Phosphate ions should be able to form very strong inner-sphere complexes, whereas sulfate may form only outer-sphere complexes on variable charge minerals (Parfitt, 1990; Zhang and Sparks, 1990). However, there is some evidence by X-ray absorption fine-structure (XAFS) that sulfate can also be adsorbed as an inner-sphere complex. Turner and Kramer (1991) and Sparks (1999) demonstrated that sulfate may be adsorbed on variable charge minerals forming at all, pH values, both inner-sphere and outer-sphere $SO_4$ sorption complexes with the former becoming more dominant with decreasing pH and increasing sulfate concentrations. Peak *et al*. (2001) demonstrated that sulfate forms inner-sphere monodentate surface complexes on hematite, but on goethite it forms only outer-sphere surface complexes at pH 6.0 and a mixture of outer-sphere and inner-sphere surface complexes below pH 6.0. According to these authors sulfate forms outer-sphere surface complexes on ferrihydrite.

Violante *et al*. (1996) and Liu *et al*. (1999) demonstrated that sulfate adsorbed on the external surfaces of variable charge minerals may be easily replaced by phosphate, whereas sulfate present in the network of metal oxides (e.g. Al-hydroxy sulfate precipitates) cannot be completely removed. Organic substances play a very important role on phosphate and sulfate sorption on soil components (Violante *et al.*, 1996; Jara *at al.*, 2006), but studies on the competitive sorption of these anions on soil samples characterized by differences in chemical and mineralogical properties have received scant attention. Recently, Mora *et al*. (2005) studied the effect of organic matter content

and soil chemical properties on sulfate sorption in Chilean Andisols. The increasing of organic matter decreased the sulfate adsorption.

The aim of the present work was to study the factors that influence the sulfate sorption, as pH, mineralogical properties, organic carbon content and presence of phosphate or malate on Italian Andisols.

**MATERIALS AND METHODS**

Five soils (Andisols) derived from volcanic materials present in the caldera of Roccamonfina volcano (Central-Southern Italy) were selected. The samples 1-4 were collected from the horizons A1, 2A2, 3Bw1

and 4Bw2 of an Eutric Fulvudand (Pedon 1), sample 5 was collected from a 2C horizon of an Eutric Pachic Fulvudand (Pedon 2) (Vacca et al., 2003). Bulk samples were air-dried and crushed to pass a 2-mm sieve. All analyses were performed on air-dried <2-mm soil according to the procedures published by Ministry for Agricoltural and Forestry Policy (2000). Soil pH was measured by potentiometry in soil: solution suspensions of 1:2.5 $H_2O$, and 1:50 1 M NaF. Organic C was estimated by wet digestion with a Walkley-Black procedure. The allophane content was estimated from selective dissolution extracts (Parfitt, 1990) (Table 1). The chemical and mineralogical properties were described in a previous work (Vacca et al., 2003).

**Table 1:** Chemical and mineralogical properties of soil samples.
**Cuadro 1:** Propiedades químicas y mineralógicas de las muestras de suelo.

| Samples Horizons | pH $H_2O$ | pH NaF | Organic Carbon (g kg$^{-1}$) | Allophane (%) | Mineralogy (c) (< 0.002 mm) |
|---|---|---|---|---|---|
| 1) A1 (a) | 6,7 | 10,9 | 184 | 17 | P1, M, Ht, Ch, or Vt, HIV |
| 2) 2A2 (a) | 6,7 | 11,3 | 74 | 16 | P1, M, Ht, Ch, or Vt, HIV |
| 3) 3Bw1 (a) | 6,4 | 11,3 | 37 | 27 | P1, M, Ht, Ch, or Vt, HIV |
| 4) 4Bw 2 (a) | 6,1 | 11,2 | 12 | 23 | P1, M, Ht, HHt, Ch, or Vt, HIV |
| 5) 2C (b) | 5,5 | 11,0 | 2 | 42 | ———— |

(a) Horizons of Pedon 1 (Vacca et al., 2003)
(b) Horizon of Pedon 2 (Vacca et al., 2003)
(c) Abbreviations: Ch = chlorite; HHt = hydrated halloysite; HIV = hydroxy interlayered vermiculite, Ht, = halloysite; M = mica; Pl = plagioclase; Vt = vermiculite.

## Phosphate and sulfate sorption isotherms

Three hundred mg of soil samples were equilibrated with KCl 0.02 M at pH 4.5. Suitable amounts of 0.1 mol $L^{-1}$ solutions containing sulfate or phosphate were then added in order to have an initial sulfate or phosphate concentration in the range 5 x $10^{-4}$ to $10^{-2}$ mol $L^{-1}$. The pH of each suspension was kept at the initial value by adding 0.1 or 0.01 mol $L^{-1}$ HCl or NaOH. The suspensions were shaken for 24 h. The final suspensions (20 mL) were centrifuged at 10,000 *g* for 20 min. and filtered through a 0.22-$\mu$m membrane filter.

## Sorption of sulfate as a function of pH

Suitable amounts of sulfate 0.1 mol $L^{-1}$ were added to 300 mg of each soil sample in reaction flasks at three different pH values (3.5, 4.5, 5.5). The pH of each suspensions was kept at the initial value by adding 0.1 or 0.01 mol $L^{-1}$ KCl or NaOH. The suspensions were shaken for 24 h. The final suspensions (20 mL) were centrifuged at 10,000 *g* for 20 min. and filtered through a 0.22-$\mu$m membrane filter.

## Competitive sorption of phosphate and sulphate

Competitive sorption of phosphate and sulfate, added as a mixture, was carried out by adding suitable amounts of sulfate in the presence of increasing quantities of phosphate to achieve initial phosphate/sulfate molar ratios ranging from 0 to 1.0. The pH of each suspension was kept constant at pH 4.5 for 24 h by adding 0.1 or 0.01 mol $L^{-1}$ HCl or NaOH. The final suspensions (20 mL) were centrifuged at 10,000 *g* for 20 min, and filtered through a 0.22-$\mu$m filter. Some experiments, (Andisol 5) were carried out by adding suitable amounts of sulfate in the presence of increasing quantities of phosphate to achieve initial phosphate/sulfate molar ratios ranging from 0 to 2.0. at different pH values (2.5, 3.5, 4.5). Further experiments (Andisol 5) were carried out at pH 4.5 by adding sulfate 24 h before phosphate at initial phosphate/sulfate molar ratio ranging from 0 to 2. Phosphate and sulfate were determined in the supernatant as described below.

## Kinetics of sorption of sulfate in the presence of phosphate and malate

We also studied the kinetics of sorption of sulfate at pH 4.5 alone and in the presence of phosphate or malate on Andisol 5. At 300 mg of soil samples suitable amounts of $SO_4$ (150 mmol $kg^{-1}$) were added in reaction flasks at initial $SO_4/PO_4$ or Mal (malato) molar ratio of 2 . The suspensions were shaken from 0.08 to 168 h. The final suspensions (20 mL) were centrifuged at 10.000 g for 20 min, and filtered through a 0.22-$\mu$m filter.

## Phosphate and sulfate determination

Phosphate and sulfate were determined by ion chromatography, using a Dionex DX-300 Ion Chromatograph (Dionex Co, Sunnyvale, CA), an IonPac AS4A column (4.0 mm), an eluent of $Na_2CO_3$ and $HNaCO_3$ at a flow rate of 2 mL $min^{-1}$, and a CD20 Conductivity Detector combined with autosuppression.
The standard concentrations were 0.2 to 2 mmol $L^{-1}$ for phosphate and sulfate. The amount of ligands adsorbed was determined by the difference between the initial and final concentrations. The data are the mean of two or three determinations. Coefficients of variation ranged from 1.5 to 5%.

## RESULTS AND DISCUSSIONS

Crystalline clay mineralogy was similar for all the studied samples, except for the 2C horizon of the pedon 2 (sample 5), which did not show crystalline minerals (Table 1).The soil samples showed content of allophane ranging from 16% (sample 2) to 42% (sample 5).
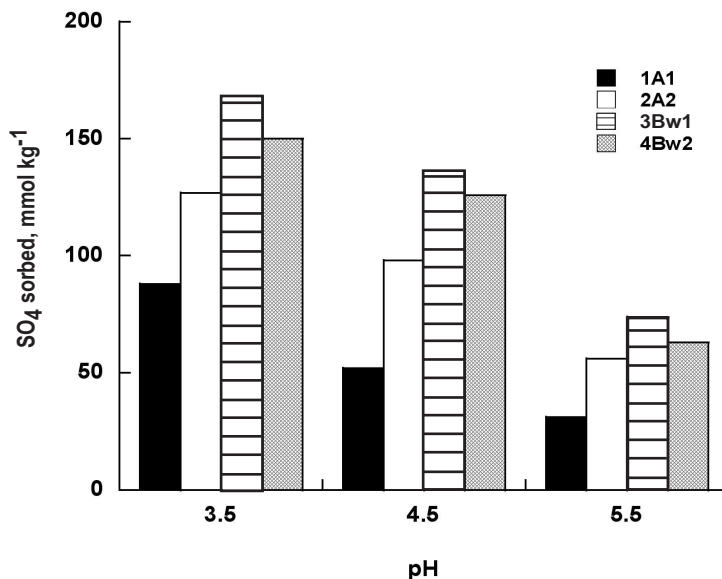
**Figure 1**: Sulfate ($SO_4$) sorption (mmol kg$^{-1}$) at pH 3.5, 4.5 and 5.5, on selected soil samples of the horizons A1, 2A2, 3Bw1 and 4Bw2 (samples 1-4) of an Eutric Fulvudand (Pedon 1). Sulfate added was 466 mmol kg$^{-1}$.
**Figura 1:** Adsorción de sulfato (mmol kg$^{-1}$) a pH 3.5, 4.5 y 5.5 en muestras de suelo seleccionadas de los horizontes A1, 2A2, 3Bw1 y 4Bw2 (muestras 1-4) de un Eutric Fulvudand (Pedon 1). La cantidad de sulfato adicionado fue 466 mmol kg$^{-1}$.

## Sorption of sulfate on Andisols

Figure 1 shows the sorption of sulfate onto soil samples of Pedon 1 (samples 1-4) at three different pH values (3.5, 4.5, and 5.5).

If we consider the first 3 horizons (A1, 2A2 and 3Bw1) of the pedon 1, the increase in sorption of sulfate appears evident along the profile (Figure 1). This behaviour was attributable to a decrease in C content (184, 74, and 37 g kg-1, respectively in horizons A1, 2A2 and 3Bw1; Table 1). It is well know that organic samples (humic and fulvic acids as well as low molecular mass organic ligands), sorbed on variable charge minerals or present in organo-mineral complexes prevent sulfate sorption competing for

sorption sites (Violante *et al*., 2002). The increase of sulfate sorption in the 3Bw1 sample must be also attributed to a greater percentage of allophanic materials (27% vs 16-17% in the first two horizons).

Sorption experiments were also carried out at different pH values (pH ranging from 4.0 to 8.0) on the samples 1 and 5 characterized by different chemical, physico-chemical and mineralogical properties (Tables 1-2) (Figure 2). On these soil samples sulfate sorption drastically decreased by increasing the pH from 4.0 to 7.0, precisely by 80% for sample 5 to 100% for sample 1. Hingston *et al*. (1972) also showed that sulfate sorption on goethite decreased with an increase in pH up to 8.0, beyond which no sorption occurred. The
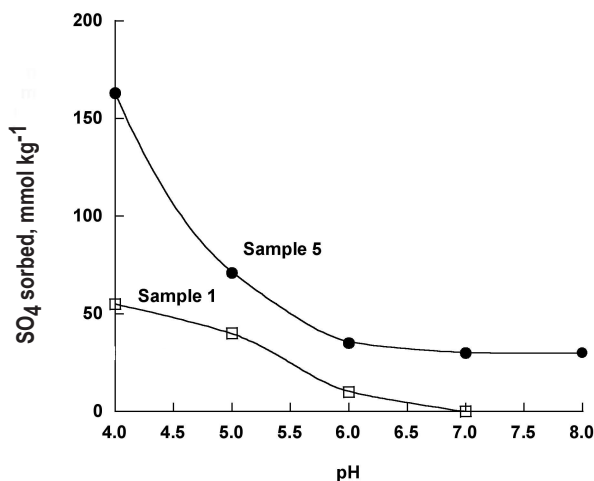
**Figure 2:** Influence of pH on the sulfate (SO4) sorption on andisols 1 and 5. Sulfate added was 466 mmol $kg^{-1}$.
**Figura 2:** Influencia del pH sobre la adsorción de sulfato (SO4) sobre los Andisoles 1 y 5. La cantidad de sulfato adicionado fue 466 mmol $kg^{-1}$.

negligible sorption of sulfate on variable charge minerals and soils at pH > 7.0 has been widely documented (Couto *et al.*, 1979; Pasricha and Fox, 1993; Violante *et al.*, 1996; Liu *et al.*, 1999).

**Sorption of sulfate in the presence of phosphate**

Experiments were carried out on the sorption of sulfate in the presence of phosphate at pH 4.5 on selected soil samples (samples 1-4). The anions were added as a mixture at initial phosphate/sulfate molar ratios (R) ranging from 0 to 1 and sulfate was added at its maximum surface coverage on each sample (Figure 3). Sulfate sorption was strongly inhibited by the presence of phosphate even at R << 1. In fact, at R = 0.2 we observed a decrease of sulfate sorption of about 10% for sample 1 and about 40-45% for samples 2-4 (Figure 3).
The decrease of sulfate sorption on soil samples cannot be attributed only to competition in sorption between phosphate and sulfate, because the sulfate sorption decrease was much greater than the amounts of phosphate added and sorbed (data not shown). A possible explanation of these findings is that phosphate sorption on soil samples decreased their surface charge and point of zero charge (PZC), preventing the fixation of sulfate ions on more negative surfaces (Parfitt, 1990; Violante and Pigna, 2002). According to Barrow (1992) the competition of anions for sorption sites of variable charge minerals was largely through changes in the electric potential of the surface. Recently, Violante and Pigna (2002) demonstrated that competition for sorption sites is a very important mechanisms, but certainly reduction in the surface charge of the sorbents is also very significant, particularly when a ligand (phosphate in our study) is sorbed more strongly than the other anion (sulfate in our study).
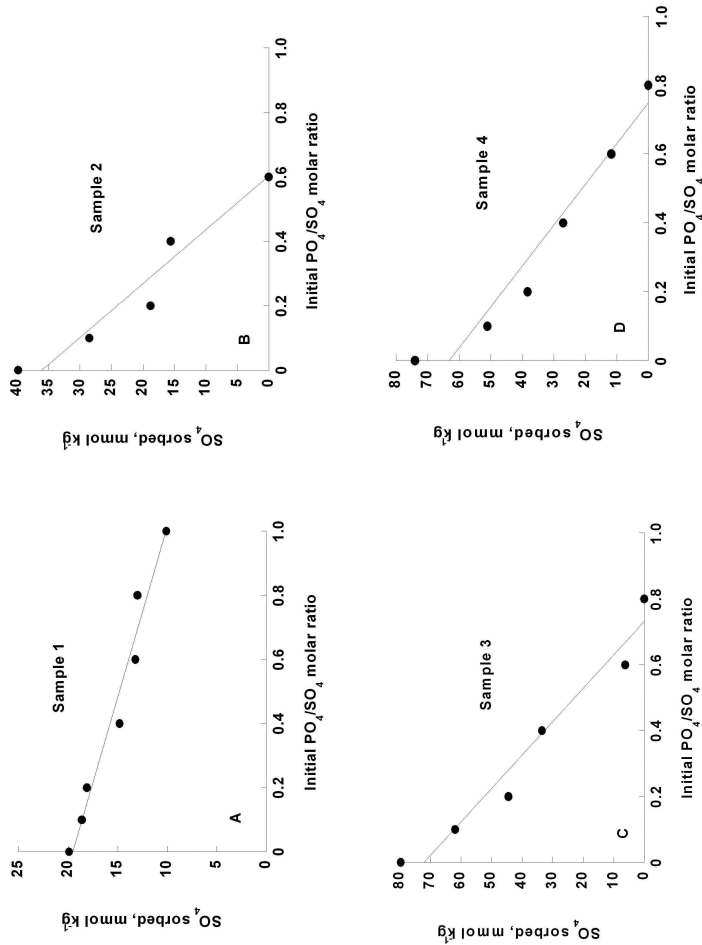
**Figure 3**: Sulfate ($SO_4$) sorption (mmol kg$^{-1}$) onto samples 1-4 at pH 4.5 in the presence of increasing concentration of phosphate ($PO_4$). $PO_4/SO_4$ molar ratio ranging from 0 to 1. Sulfate added was 200 mmol kg$^{-1}$.
**Figura 3:** Adsorción de sulfato ($SO_4$) en las muestras 1-4 a pH 4.5 en presencia de concentraciones crecientes de fosfato ($PO_4$). La razon molar $PO_4/SO_4$ fue entre 0 y 1. La cantidad de sulfato adicionado fue 200 mmol kg$^{-1}$.

**Effect of pH on the competitive sorption of sulfate and phosphate**

Experiments on sorption of sulfate in the presence of increasing amounts of phosphate (R ranging from 0 to 2) were carried out at different acid pH values (pH 2.5, 3.5 and 4.5) on Andisol 5  (Figure 4). It has been found that the lower the pH the greater the capacity of sulfate to compete with phosphate. For example, at R = 1, phosphate inhibited sulfate sorption of 30 % at pH 2.5 versus 40 and 94 % at pH 3.5 and 4.5, respectively. A possible explanation of these findings is that sulfate forms inner-sphere complexes particularly at low pH values (Turner and Kramer, 1991; Sparks, 1999). Peak *et al.* (2001) found that sulfate formed

a second bidentate binuclear surface complex on goethite at pH 3.5. Evidently, particularly at low pH values sulfate ions form strong complexes on some surface sites from which they cannot be easily desorbed in spite that phosphate and some organic ligands are more able to remove sulfate at acidic than neutral or alkaline environment (Jara *et al.*, 2006).

Liu *et al.* (1999) found that at pH 4.5 oxalate up to oxalate/sulfate molar ratio of 2 (r) strongly inhibited the sorption of sulfate, but at r>2 the sorption of sulfate remained practically constant. These authors concluded that 25-30% of sulfate was sorbed so strongly onto goethite that even large amounts of oxalate (r = 3.33) were not able to replace it.
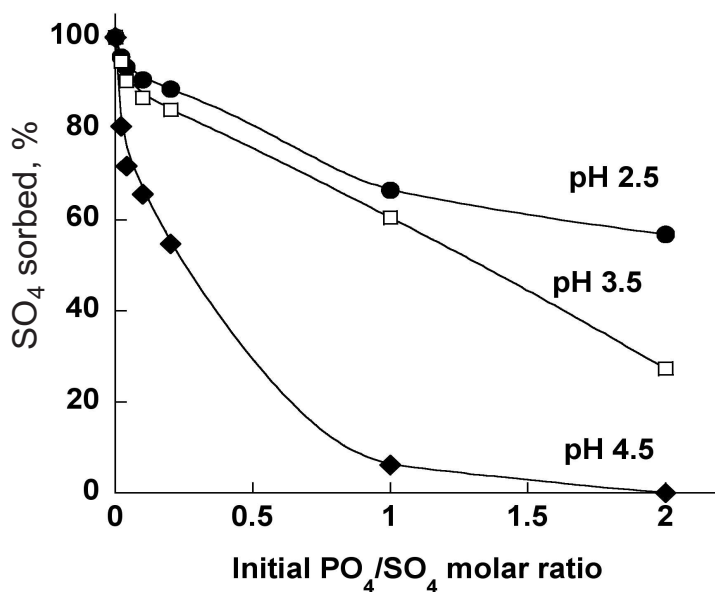


**Figure 4:** Sulfate (SO4) sorption (%) on sample 5 at pH 2.5, 3.5 and 4.5, in the presence of increasing concentration of phosphate (PO4). The % SO4 sorbed as referred to sulfate sorbed in the absence of phosphate. Sulfate added was 466 mmol kg^{-1}.
**Figura 4:** Adsorción de sulfato (SO4) sobre la muestra 5 a pH 2.5, 3.5 y 4.5, en presencia de concentraciones crecientes de fosfato (PO4). El % SO4 es referido al sulfato adsorbido en ausencia de fosfato. La cantidad de sulfato adicionado fue 466 mmol kg^{-1}.

**Effect of sequence addition**

When sulfate was added 24 h before phosphate (SO4 before PO4 system) (Figure 5) greater quantities of sulfate were sorbed on Andisol 5 with respect to the quantities fixed when phosphate and sulfate were added as a mixture (SO4 + PO4 systems). At R = 0.1, 0.2, and 1 the sulfate sorption decreased, respectively, of 10, 22, and 70% in SO4 before PO4 system versus 34, 45, and 94% in the PO4 + SO4 systems.

Similar results were found studying the competitive sorption of sulfate and phosphate on to a Al-Si and Fe-Al-Si allophane (Pigna *et al*, 2003). Different processes may concur in the sorption reactions of different ligands on soil components, as i) the kind of surface complexes formed by the anions when added as a mixture in different amounts, ii) the change in the surface charge after anions adsorption and iii) the effect of time on competition (Violante and Pigna, 2002).
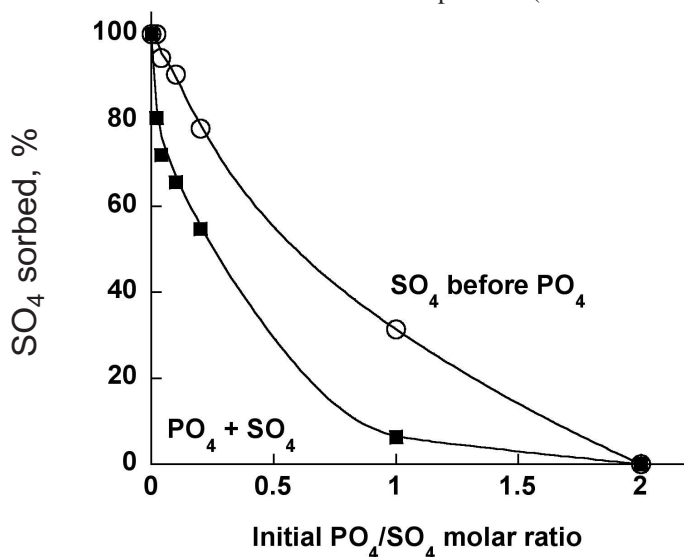


**Figure 5:** Sulfate (SO4) sorption on sample 5, at pH 4.5, in the presence of increasing concentration of phosphate (PO4). The anions were added together (PO4 + SO4 system) or by adding sulfate 24 hours before phosphate (SO4 before PO4 system). Sulfate added was 466 mmol kg$^{-1}$.
**Figura 5:** Adsorción de sulfato sobre la muestra 5 a pH 4.5 en presencia de concentraciones crecientes de fosfato (PO4). Los aniones fueron adicionados juntos (sistema SO4 + PO4) o por adición de sulfato 24 horas antes que fosfato (sistema SO4 antes que PO4). La cantidad de sulfato adicionado fue 466 mmol kg$^{-1}$.

**Kinetics of sorption of sulfate in the presence of phosphate and malate**

We also studied the kinetics sorption of sulfate on Andisol 5 at pH 4.5, when added alone (150 mmol kg$^{-1}$) or in the presence of phosphate or malate (SO4/PO4 or Mal molar ratio of 2). The kinetics was evaluated using first order, Parabolic diffusion, and Elovich kinetics models (data not shown).

The kinetics of sulfate sorption alone or in the presence of foreign ligands (PO4, Mal) could be explained best by Elovich kinetic model. The sorption of sulfate on the sample increased with time, reaching maximum 88 mmol kg$^{-1}$ after 168 h (Figure 5). The

presence of low amounts of PO4 or Mal strongly prevented SO4 sorption even though many sites were still available for SO4 sorption. In the presence of PO4 or Mal the maximum amount of SO4 sorbed was reached after 24-48 h, no further increase was observed even after 48 h (Figure 6).

Compared to the SO4-alone, about 70% of SO4 was sorbed in the presence of PO4, and 86% in the presence of Mal after 168 h. However, after 360 h of reaction the amounts of SO4 sorbed in the presence of PO4 or Mal did not increase further (data not shown).
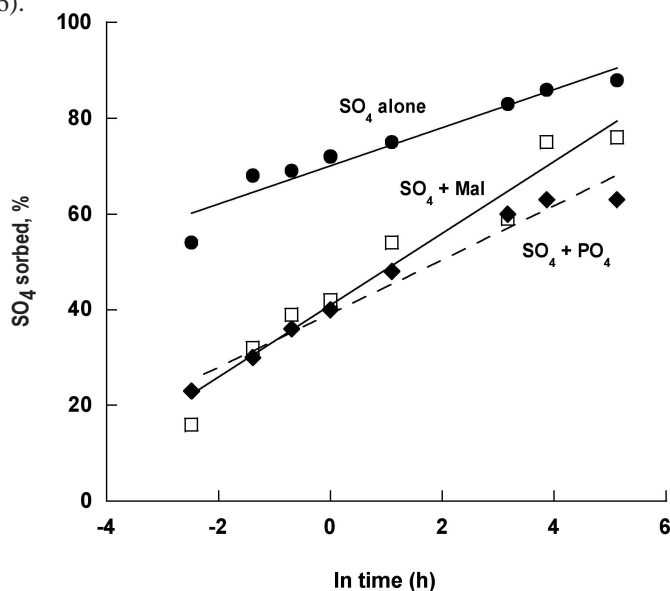


**Figure 6:** Effect of time on the kinetic sorption of sulfate (SO4) on andisol 5 at pH 4.0 when added alone (150 mmol kg$^{-1}$) and in the presence of phosphate (PO4) or malate (Mal). Initial SO4/PO4 or Mal molar ratio of 2. The kinetics were fitted using Elovich model.

**Figura 6:** Efecto de tiempo sobre la cinética de adsorción de sulfato (SO4) sobre Andisol 5 a pH 4.0 cuando fue adicionado solo (150 mmol kg$^{-1}$) y en presencia de fosfato (PO4) o malato (Mal). Razon molar inicial SO4/PO4 o Mal de 2. Las cinéticas fueron ajustadas usando el modelo de Elovich.

## CONCLUSIONS

In this study on the sorption of sulfate on Andisols we have found that: i) sulfate sorption was strongly prevented by phosphate even at phosphate/sulfate molar ratios << 1; ii) pH strongly influenced the competition in sorption between phosphate and sulfate; at very low pH values (< 4.5) sulfate anions competed with phosphate probably forming inner-sphere complexes; iii) when sulfate was added before phosphate (SO4 before PO4 system) more sulfate was sorbed than when sulfate was added with phosphate or after phosphate; iv) in the presence of phosphate or malate the kinetics of sulfate sorption on Andisol was retarded (phosphate > malate).

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