

Sulfate desorption from representative soils of the São Paulo State, Brazil

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Abstract. We determined the sulfate desorption in representative soils of the São Paulo State, Brazil, and related it to the soil affinity for sulfate ions as estimated by the parameters k_L and n_F of the Langmuir and Freundlich equations, respectively. Although the parameters k_L and n_F were well correlated, the nonlinear decay of the sulfate desorption with the increase in the soil affinity by sulfate was better defined when the affinity was estimated by the parameter k_L . Despite this, results of multiple regression linear analyses carried out for both k_L and n_F were quite similar and allowed us to verify that sulfate desorption tends to increase in subsurface soil layers as they become less acidic and/or have their phosphate-extractable sulfur contents increased through successive fertilisations and/or amendments with S-containing products. At the same time, sulfate desorption in these soils tends to be restrained by the advance of weathering.

Additional keywords: sulfate adsorption sites, Langmuir and Freundlich equations, tropical soils.

Introduction

Sulfate desorption by tropical soils remains a little studied theme although it plays an important role not only in sulfur availability to plants but also in environmental quality. Of the available data, some information is related to sulfate desorption by synthetic minerals of relevance to tropical soils, such as kaolinite (Aylmore *et al.* 1967) and goethite (Turner and Kramer 1992). On the other hand, studies dealing with soils have used different sulfate extractants such as water (Bornemisza and Llanos 1967), 0.05 M NH_4NO_3 (Couto *et al.* 1979), and 1 M KCl (Agbenin 1997), which makes comparison of results difficult. None of above-mentioned studies investigated a possible relationship between sulfate desorption and the affinity of the adsorption sites for the sulfate ions.

São Paulo State is covered by weathered soils whose clay mineralogies comprise mainly kaolinite, gibbsite, haematite, and goethite (Schwertmann and Herbillon 1992). Other minerals such as vermiculite, illite, maghemite, anatase, and rutile as well as amorphous phases are also found in these soils, but at minor levels. In contrast to other regions of the South America, there is no record of allophane and other similar tephra-derived materials comprising part of the soils of the São Paulo State (de Oliveira 1999). It is probable, as verified by Varajão *et al.* (2002), that the small amounts of noncrystalline aluminosilicates present in the São Paulo State

soils are derived from weathering-induced destabilisation of kaolinite and/or gibbsite. The accumulation of Fe and Al oxides in these soils caused by weathering increases their sulfate adsorption capacities, which, in turn, tend to be smaller in the less weathered kaolinitic soils (Alves and Lavorenti 2004a).

The present research aims to evaluate sulfate desorption and its relationships with properties of representative soils of the São Paulo State, Brazil.

Material and methods

Because surface soils present unfavourable characteristics for sulfate adsorption, such as higher pH values (Zhang and Yu 1997) and higher phosphate and organic matter contents (Motavalli *et al.* 1993; Dynia and Camargo 1995), and thus favourable conditions for sulfate desorption, we used in the present research samples collected in the B horizon of 8 Oxisols, 3 Ultisols, and 1 Alfisol (Soil Survey Staff 1999). These soil units comprise about 74% of the mapping units of the soil map of São Paulo State (de Oliveira 1999). General information on these samples, including classification, parent materials, localisation, and depth of sampling is presented in Table 1.

The soil samples were characterised for clay content by the pipette method (Gee and Bauder 1986), phosphate-extractable S by extraction with 0.01 M $\text{Ca}(\text{H}_2\text{PO}_4)_2$ (Fox and Olsen 1964), exchangeable Al by 1 M KCl extraction (Bertsch and Bloom 1996), and remaining phosphorus (Prem) (Alvarez *et al.* 2000) by shaking 2.5 g of soil for 1 h with 25 mL of 0.01 M CaCl_2 containing 60 $\mu\text{g}/\text{mL}$ of P and determining P in equilibrium solution by colourimetry (Murphy and Riley 1962). The

Table 1. Classification, parent materials, localisation in the São Paulo State, and sampling depth of the soils

Soil	Classification	Parent material	Localisation	Depth (m)
1	Rhodic Acrudox	Basalt	Ribeirão Preto	1.00–1.40
2	Rhodic Eutrudox	Basalt	Iracemápolis	1.00–1.10
3	Rhodic Hapludox	Basalt	Luís Antonio	0.80–1.00
4	Rhodic Acrudox	Basalt	Luís Antonio	1.50–1.70
5	Xanthic Acrustox	Basalt	Guaira	1.00–1.30
6	Typic Hapludox	Schist	Piracicaba	1.00–1.10
7	Typic Hapludox	Sandstone	Piracicaba	1.00–1.10
8	Typic Hapludox	Sandstone	São Carlos	0.80–1.00
9	Typic Hapludalf	Diabase	Piracicaba	0.30–0.40
10	Typic Hapludult	Sandstone	Pindorama	1.00–1.20
11	Typic Hapludult	Sandstone	Vera Cruz	1.00–1.20
12	Typic Hapludult	Schist	Rio Claro	0.70–0.80

soil pH was measured in water ($\text{pH}_{\text{H}_2\text{O}}$), in 0.01 M CaCl_2 ($\text{pH}_{\text{CaCl}_2}$), and in 1 M KCl (pH_{KCl}) at 1:2.5 soil(g)/solution (mL) ratio. Soil pH was also determined after shaking 0.5 g of soil for 1 h with 20 mL of 1 M NaF (pH_{NaF}) (Bolland *et al.* 1996). The ΔpH index was calculated from the difference between pH_{KCl} and $\text{pH}_{\text{H}_2\text{O}}$ and the point of zero salt effect (PZSE) was determined using the modified potentiometric titration method as detailed by Alves and Lavorenti (2005).

The Si, Fe, and Al contents associated with secondary minerals were determined in extracts obtained after boiling both 1 g of soil for 30 min in 20 mL of 9 M H_2SO_4 (Fe and Al) and the remaining solid for 1 min in 150 mL of 0.2 M NaOH (Si). The acid extracts were analysed for Fe and Al by atomic absorption spectroscopy, whereas Si was quantified in the alkaline extracts by colourimetry (EMBRAPA 1997). With these data, the weathering indices Ki ($\text{SiO}_2/\text{Al}_2\text{O}_3$, mol/mol) and Kr [$\text{SiO}_2/(\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3)$, mol/mol] were calculated (EMBRAPA 1999). The clay contents of kaolinite, gibbsite, haematite, goethite, and ammonium-oxalate-extractable Al (Al_o) were determined as detailed by Alves and Lavorenti (2004b).

Sulfate adsorption isotherms were obtained by shaking 2.5 g of soil for 24 h with 25 mL of eleven 0.01 M CaCl_2 solutions containing SO_4^{2-} added as K_2SO_4 . The initial SO_4^{2-} concentrations were defined considering the potential adsorption of the soils as estimated by the remaining phosphorus (Prem) (Alvarez *et al.* 2000). The following ranges were used: 0–156 $\mu\text{g}/\text{mL}$ for soils 1, 2, 3, 5, 6, and 12 (Prem 0.1–3.8 $\mu\text{g}/\text{mL}$); 0–120 $\mu\text{g}/\text{mL}$ for soils 3, 8, and 9 (Prem 4.1–7.7 $\mu\text{g}/\text{mL}$); 0–66 $\mu\text{g}/\text{mL}$ for soil 10 (Prem 21.8 $\mu\text{g}/\text{mL}$); and 0–48 $\mu\text{g}/\text{mL}$ for soils 7 and 11 (Prem 36.1 $\mu\text{g}/\text{mL}$). After shaking, the suspensions were filtered through a Whatman 42 filter, and the solutions were analysed for sulfate by BaSO_4 turbidimetry (Chesnin and Yien 1950). The amount of sulfate adsorbed was calculated from the difference between the initial and final sulfate concentrations. The results were fitted to the Langmuir and Freundlich equations, given, respectively, by:

$$q = \frac{k_L cb}{1 + k_L c} \quad (1)$$

where q is adsorbed sulfate ($\mu\text{g}/\text{g}$), k_L is a parameter related to affinity of the soil by sulfate ($\text{mL}/\mu\text{g}$), c is equilibrium concentration of sulfate ($\mu\text{g}/\text{mL}$), and b is maximum capacity of sulfate adsorption ($\mu\text{g}/\text{g}$); and:

$$q = k_F c^{1/n_F} \quad (2)$$

where q is adsorbed sulfate ($\mu\text{g}/\text{g}$), k_F is a constant [$(\mu\text{g}^{(1-1/n)} \text{mL}^{1/n})/\text{g}$], c is equilibrium concentration of sulfate ($\mu\text{g}/\text{mL}$), and n_F is a constant (dimensionless).

The evaluation of the sulfate desorption had 3 steps. First, the release of the 0.01 M CaCl_2 extractable SO_4^{2-} , which includes both soluble and labile sulfate fractions (Tabatabai 1982), was determined. For this, 2.5-g soil samples and 25 mL of 0.01 M CaCl_2 were added to 50-mL centrifuge tubes, which were shaken for 24 h and centrifuged. The supernatants were filtered and analysed for SO_4^{2-} by BaSO_4 turbidimetry (SO_4^{2-} soluble). Second, 2.5-g soil samples and 25 mL of 0.01 M CaCl_2 containing 60 $\mu\text{g}/\text{mL}$ of SO_4^{2-} were added to pre-weighed 50-mL centrifuge tubes, which were shaken for 24 h and centrifuged. The supernatants were filtered for SO_4^{2-} determination and the tubes containing the soil plus entrapped solution were weighed. The adsorbed sulfate was calculated as the difference between the added and final sulfate concentrations (SO_4^{2-} adsorbed). In the final step, volumes of 0.01 M CaCl_2 were added to the tubes containing the soil plus entrapped solution so that the final volume (added + entrapped) was 25 mL. The tubes were shaken for 24 h and centrifuged, and the supernatants were filtered and analysed for SO_4^{2-} . Values were corrected considering the sulfate amounts of the entrapped solutions (SO_4^{2-} recovered). The desorbed sulfate was calculated as follows:

$$\text{SO}_4^{2-} \text{ desorbed } (\mu\text{g}/\text{g}) = \text{SO}_4^{2-} \text{ recovered } (\mu\text{g}/\text{g}) - \text{SO}_4^{2-} \text{ soluble } (\mu\text{g}/\text{g}) \quad (3)$$

Taking into consideration the direct relationship verified between the amounts of adsorbed and desorbed sulfate, we calculated a relative desorption index given by:

$$\text{SO}_4^{2-} \text{ desorption } (\%) = \frac{[\text{SO}_4^{2-} \text{ desorbed } (\mu\text{g}/\text{g}) / \text{SO}_4^{2-} \text{ adsorbed } (\mu\text{g}/\text{g})] \times 100}{1} \quad (4)$$

All determinations were performed in triplicate and the experimental data were submitted to both correlation and regression analyses using SAS Version 6.11.

Results and discussion

Soil and clay properties

Soil and clay properties are summarised in Table 2, where it can be seen that most soils were acidic ($\text{pH}_{\text{CaCl}_2} \leq 5$), clayey (clay > 350 g/kg) (EMBRAPA 1999), poor in organic carbon (1.5–7.8 g/kg), and had no exchangeable Al. In contrast to soils 1, 3, 4, and 12, the others presented high contents of phosphate-extractable S ($\text{S} > 10 \text{ mg}/\text{dm}^3$) (Van Raij *et al.* 1996). Among these soils, 3 Oxisols (soils 2, 6, and 8) and 1 Alfisol (soil 9), the only ones sampled in cultivated areas, showed higher values of S, which may be due to the sulfate leaching from the plowed layer after applications of S-containing fertilisers.

The ΔpH values indicate the presence of negative surface charge in all samples (Mekaru and Uehara 1972), except for the soils 1, 4, and 5, whose PZSE values were higher than $\text{pH}_{\text{H}_2\text{O}}$, indicating positive balance of charges (Van Raij and Peech 1972). The pH_{NaF} values ranged from 8.8 in soil 11 to 10.7 in soil 4, in agreement with the respective highest clay contents of kaolinite and gibbsite shown by these soils (Alves and Lavorenti 2004b). Although pH_{NaF} is a suitable indicator of both phosphate (Singh and Gilkes 1991) and sulfate (Alves and Lavorenti 2004a) adsorption capacities

Table 2. Selected soil and clay properties

Al³⁺, exchangeable Al (cmol_c/dm³); S, phosphate-extractable S (mg/dm³); pH, pH measured in 0.01 M CaCl₂; ΔpH, difference between pH_{KCl} and pH_{H₂O}; PZSE, point of zero salt effect; Prem (μg/mL), remaining phosphorus given by the P in the equilibrium solution after shaking soil for 1 h with a 0.01 M CaCl₂ solution containing 60 μg P/mL at 1 : 10 soil (g)/solution (mL) ratio; Ki, weathering index given by 1.7 SiO₂/Al₂O₃; Kr, weathering index given by 1.7 SiO₂/(Al₂O₃ + 0.64 Fe₂O₃) where SiO₂, Al₂O₃, and Fe₂O₃ are the respective soil contents of Si, Al, and Fe associated with secondary minerals; Ka, kaolinite clay content; Gb, gibbsite clay content; Hm, haematite clay content; Gt, goethite clay content; Al_o, ammonium-oxalate-extractable Al clay content (g/kg)

Soil	Al ³⁺	S	Clay (g/kg)	pH	ΔpH	PZSE	pH _{NaF}	Prem	Ki	Kr	Ka	Gb (%)	Hm	Gt	Al _o
1	0	5	529	5.0	0.1	5.6	10.4	1.0	0.72	0.42	23.4	45.9	22.4	3.3	13
2	0	37	481	5.5	-0.8	5.8	10.3	3.1	1.14	0.71	40.5	24.5	20.5	3.7	11
3	0.07	2	543	4.3	-0.1	4.5	10.3	4.1	0.97	0.61	40.8	33.7	21.1	0.9	10
4	0	1	647	5.4	0.4	6.1	10.7	0.3	0.49	0.30	15.0	54.3	22.4	4.0	16
5	0	17	324	5.6	0.9	7.0	10.4	0.1	0.85	0.60	29.7	35.7	0	20.7	12
6	0.01	109	774	4.9	-0.8	4.1	10.3	3.8	1.44	1.18	52.2	11.9	2.3	11.0	08
7	0	35	244	4.8	-0.9	3.5	9.3	36.1	1.65	1.29	63.2	1.0	2.1	8.5	06
8	0	78	421	4.8	-0.4	4.5	10.3	7.7	0.69	0.56	25.6	55.3	0.2	16.0	11
9	0	102	597	5.0	-0.6	4.8	9.8	5.3	1.56	1.00	53.4	2.3	12.8	8.4	07
10	0.80	15	347	4.0	-1.1	2.9	9.5	21.8	1.75	1.48	60.1	0.2	0.3	8.5	07
11	0.70	22	205	3.7	-0.8	3.5	8.8	36.1	1.81	1.56	77.3	0	1.4	5.6	06
12	0	7	475	5.2	-0.8	4.0	9.7	2.1	1.63	1.12	53.0	0	2.3	12.5	09

of non-allophanic tropical soils and has good correlation to the remaining phosphorus (Prem) ($r = -0.88$, $P < 0.01$), its low coefficient of variation (CV) of 6% within the soil set evaluated reveals that its capacity to separate soils into classes of anion adsorption is much lower than that of Prem, with CV 133%.

The Ki and Kr indexes are used in the Brazilian System of Soil Classification to characterise the soil weathering status. As weathering increases, there is a progressive silica loss from clay minerals and a concomitant accumulation of iron and aluminum oxides. Therefore, the lower the Ki and Kr values, the more weathered is the soil. The Ki range (0.49–1.81) shows the wide variation in weathering status of the studied soils, whereas Kr values separate them into oxidic (Kr < 0.75) and kaolinitic (Kr > 0.75), which agrees the clay mineralogy data (Table 2). The correlations between Ki index and both kaolinite ($r = 0.97$, $P < 0.01$) and gibbsite clay contents ($r = -0.99$, $P < 0.01$) are in line with the above-mentioned weathering trends.

Adsorption isotherms and sulfate desorption

The absence of zero within the confidence intervals associated with both parameters k_L and b of the Langmuir equation and parameters k_F and n_F of the Freundlich model (Table 3) reveals that their estimates were statistically adequate. The affinity of the soil for sulfate ranged from 0.0163 mL/μg (soil 2) to 0.1493 mL/μg (soil 3) when estimated by the Langmuir parameter k_L and from 1.7247 (soil 2) to 3.1859 (soil 4) when estimated by the parameter n_F of the Freundlich equation.

As verified in other studies (Marcano-Martinez and McBride 1989; Bolan *et al.* 1993), the lower mean square error values associated with the Freundlich model indicate

that it fitted better the experimental data for all samples, excepted for soils 2, 5, 8, and 9 (Table 3). Despite this, parameters k_L and n_F were well correlated ($r = 0.88$, $P < 0.01$), in agreement with Holford (1982) regarding the usefulness of the empirical Freundlich n_F parameter as an affinity index. The maximum capacity of sulfate adsorption, given by the parameter b , ranged from 179 μg/g (soil 7) to 965 μg/g (soil 12) and was better correlated to Prem ($r = -0.86$, $P < 0.01$) than to pH_{NaF} ($r = 0.62$, $P < 0.05$), probably due to the greater sensitivity of the former to the soil contents of ammonium oxalate extractable Al (Al_o) (Alves and Lavorenti 2004c), which, in turn, exerted greater effect on sulfate adsorption by most of the soils studied (Alves and Lavorenti 2004a).

Sulfate desorption ranged from 4.8% (soil 5) to 28.4% (soil 9) (Table 3). The highest goethite clay content of soil 5 may explain the low reversibility of sulfate adsorption verified in this soil, in agreement with the high irreversibility of sulfate adsorption for a synthetic goethite verified by Turner and Kramer (1992). The highest desorption verified in soil 9 may be attributed in part to the abundance in its clay fraction of kaolinite, a mineral that has a low capacity for sulfate adsorption and whose sulfate adsorption–desorption curves do not show hysteresis (Aylmore *et al.* 1967). Another factor that probably contributed to the high sulfate desorption shown by this soil is its higher phosphate-extractable S content.

The sulfate desorption is a relative index and is thus dependent on the surface properties related to the sulfate adsorption sites. The sulfate desorption decay with the increase in the soil affinity by sulfate was better defined by the relationship between k_L and sulfate desorption than that observed between n_F and sulfate desorption (Fig. 1).

Table 3. Parameters of the Langmuir (k_L and b) and Freundlich (k_F and n_F) equations and sulfate desorption (%)
 MSE_L and MSE_F, mean square errors calculated in the analysis of variance of the nonlinear regression analyses of the Langmuir and Freundlich models, respectively. Values in parentheses are the lower and upper limits of 95% confidence intervals

Soil	k_L (mL/ μ g)	b (μ g/g)	MSE _L	k_F [μ g ^(1-1/n) mL ^{1/n} /g]	n_F	MSE _F	Sulfate desorption
1	0.1052 (0.0884–0.1220)	577 (554–600)	720	132 (118–145)	3.1076 (2.8583–3.3568)	677	6.4
2	0.0163 (0.0102–0.0224)	678 (552–803)	377	30 (19–41)	1.7247 (1.4684–1.9810)	441	20.4
3	0.1493 (0.1093–0.1893)	720 (676–767)	3039	174 (164–185)	3.0199 (2.8744–3.1654)	433	6.5
4	0.1384 (0.1172–0.1596)	628 (605–651)	853	156 (144–168)	3.1859 (2.9805–3.3912)	568	5.0
5	0.1245 (0.1123–0.1367)	618 (603–633)	346	150 (134–166)	3.1837 (2.8969–3.4705)	1040	4.8
6	0.0340 (0.0235–0.0446)	693 (610–774)	557	64 (52–76)	2.0960 (1.8948–2.2971)	283	20.5
7	0.0564 (0.0270–0.0858)	179 (136–222)	114	17 (13–22)	1.7962 (1.5225–2.0701)	72	7.8
8	0.0405 (0.0139–0.0671)	456 (347–565)	862	41 (14–68)	1.9853 (1.3280–2.6425)	1197	16.4
9	0.0270 (0.0105–0.0436)	544 (397–691)	653	40 (16–62)	1.9174 (1.3703–2.4645)	919	28.4
10	0.0999 (0.0805–0.1193)	255 (239–272)	109	22 (17–28)	2.2563 (2.0929–2.4196)	85	9.6
11	0.0800 (0.0461–0.1139)	180 (149–211)	178	97 (87–107)	1.9181 (1.6352–2.2010)	135	5.9
12	0.0438 (0.0375–0.0501)	965 (912–1018)	807	81 (69–92)	2.0634 (1.9491–2.1778)	684	8.7

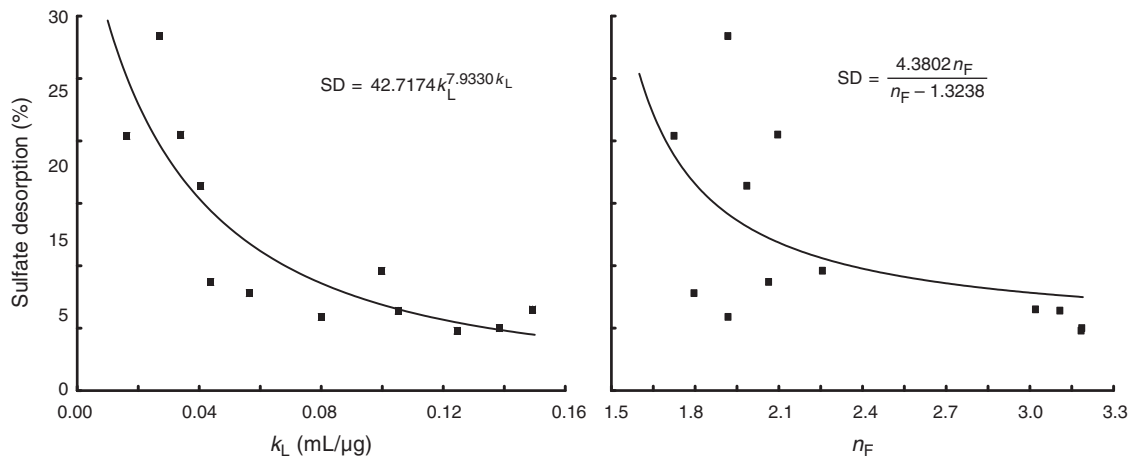


Fig. 1. Relationships between the soil–sulfate affinity parameters k_L and n_F and the sulfate desorption.

Considering the magnitudes of the affinity indices k_L and n_F are defined not only by the adsorbate type but also by the surface properties of the adsorbent, multiple regression analyses were carried out to assess the influence of the phosphate-extractable S soil contents, pH_{H2O}, and PZSE on both k_L and n_F . The choice of these soil properties was based on the premise that they would be related to the behaviour of the anionic adsorption sites towards sulfate retention, as

will be detailed later in this discussion. In fact, the predictor variables ln S, pH_{H2O}, and PZSE were able to explain, on average, 86% of the variation of both k_L and n_F (Table 4).

According to Neter *et al.* (1990), when the predictor variables of a multiple regression model are correlated among themselves, multi-collinearity among them is said to exist. In this case, the following problems can occur in the multiple regression analysis: (i) parameter estimates may not be

Table 4. Results of the multiple regression analyses relating the parameters k_L and n_F to the phosphate-extractable S soil content (S), soil pH measured in water (pH_{H₂O}), and point of zero salt effect (PZSE) values

$k_L = a_0 + a_1 \ln S + a_2 \text{pH}_{\text{H}_2\text{O}} + a_3 \text{PZSE}$ and $n_F = b_0 + b_1 \ln S + b_2 \text{pH}_{\text{H}_2\text{O}} + b_3 \text{PZSE}$. VIF, variance inflation factor; SC, standardised coefficient. k_L model: F -value = 25.8, $P > F = 0.0002$, $R^2 = 0.87$, $n = 12$. n_F model: F -value = 21.6, $P > F = 0.0003$, $R^2 = 0.85$, $n = 12$

Coefficient	Value	Std error	<i>t</i>	<i>P</i> > <i>t</i>	VIF	SC
a_0	0.3342	0.0504	6.624	0.0002	0.0000	0.0000
a_1	-0.0145	0.0041	-3.572	0.0073	1.5025	-0.4738
a_2	-0.0542	0.0119	-4.556	0.0019	1.7538	-0.6529
a_3	0.0167	0.0053	3.318	0.0139	1.6610	0.4376
b_0	4.1592	0.6930	6.002	0.0003	0.0000	0.0000
b_1	-0.1435	0.0557	-2.575	0.0329	1.5025	-0.3699
b_2	-0.5633	0.1634	-3.447	0.0087	1.7538	-0.5350
b_3	0.3567	0.0731	4.880	0.0012	1.6610	0.7369

significant, even though a definite statistical relationship exists, and (ii) a parameter estimate may have a sign that is different from expected. One way of detecting multi-collinearity consists of calculating the variance inflation factors (VIF), which measure the inflation of the variances for the regression coefficients above that expected if there were no correlation among the predictor variables; a VIF value > 10 indicates the presence of strong multi-collinearity. For both k_L and n_F , the VIF values were < 10 for all model parameters, revealing the absence of multi-collinearity among them. Therefore, the signs of the coefficients in both k_L and n_F models have reliable physical meanings. The analysis of the standardised coefficients, estimates whose magnitudes are not affected by the scales of measurements of the various model variables (SAS 1991), indicates that pH_{H₂O} had a greater negative impact on both k_L and n_F than did the logarithm of phosphate-extractable S (Table 4).

Multiple regression results showed that the affinity of the soil to sulfate increases with the lowering of both phosphate-extractable S and pH_{H₂O} values and with an increase in PZSE values. Therefore, sulfate desorption tends to be lower in acidic soils presenting low levels of adsorbed sulfate and high PZSE values. Despite the lack of experimental evidence, some assumptions can be made in order to explain this desorptive behaviour.

The negative effect of the logarithm of the native phosphate-extractable S content on the soil affinity of sulfate, favouring its desorption, agrees in part with the presupposition of the Freundlich equation related to the logarithmic fall in the enthalpy of adsorption with surface coverage (Bohn *et al.* 1979). The non significance found for phosphate-extractable S when its logarithm form was not considered in the multiple regression of n_F against S, pH_{H₂O}, and PZSE seems to reinforce its assumption. Thus, this could explain the lower values shown by both k_L and n_F parameters for the soils 2, 6, 8, and 9, which presented higher contents of phosphate-extractable S.

Based on experimental data which showed that sulfate adsorption by variable charge soils results both in small surface hydroxyl release (OH⁻/SO₄²⁻ equivalent ratio ≪ 1) and in surface charge change much larger than that expected if the ligand exchange with surface OH groups was the main mechanism of sulfate adsorption, Zhang and Yu (1997) considered that sulfate adsorption by such soils takes place mainly through the substitution of OH₂⁺ surface groups by the sulfate ions. Thus, considering the preference for sulfate ions by the surface water molecules, it can be hypothesised that the OH₂⁺ → SO₄²⁻ exchange results in more stable bindings than those formed from OH⁻ → SO₄²⁻ exchange. In this context, and as at low pH values the number of OH₂⁺ surface groups tends to be higher than that of OH groups, the surface affinity by sulfate would be greater in acidic than in alkaline soils. This could explain the negative impact of pH_{H₂O} on the surface affinity by sulfate shown by the multiple regression models and, by consequence, the smaller tendency for sulfate desorption in acidic soils.

The positive impact of PZSE on both k_L and n_F and, by consequence, its restrictive role on sulfate desorption can be explained by the fact that the more weathered the soil, the greater its number of easily ionisable OH surface groups. As verified by Alves and Lavorenti (2005) for some soils of the São Paulo State, Brazil, most of them evaluated in the present study, low PZSE values are essentially due to higher soil contents of kaolinite, a mineral whose edge single OH groups coordinated with Si⁴⁺, the silanol groups (SiOH), protonate only at low pH values (Sparks 1995). On the other hand, OH groups coordinated with both Al³⁺ (AlOH) and Fe³⁺ (FeOH) can be protonated at higher pH values, conferring to the soils not only higher PZSE values but also a greater number of OH₂⁺ surface groups capable of being exchanged by sulfate ions, even at higher soil pH values. Therefore, in soils presenting higher PZSE values, the greater availability of OH₂⁺ groups may favour the establishment of more stable binding between sulfate ions and adsorption

sites, limiting sulfate desorption. The correlations of PZSE with both Ki ($r = -0.77$, $P < 0.01$) and Kr ($r = -0.82$, $P < 0.01$) indices show that kaolinite destabilisation and the concomitant accumulation of Fe and Al oxides contribute to the increase in the soil affinity by sulfate ions and so to lowering SO_4^{2-} desorption.

Finally, taking into consideration the high positive correlation between the differences (PZSE – $\text{pH}_{\text{H}_2\text{O}}$) and ($\text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$) (ΔpH) ($r = 0.97$, $P < 0.01$), it can be hypothesised that both phosphate-extractable S and the pH values measured in both water and in 1 M KCl, all of them routinely determined in the laboratory for soil fertility evaluation, could be used as predictor variables of the tendency of sulfate desorption by non-allophanic tropical soils. In fact, the multiple regression of n_{F} against $\ln S$ and ΔpH ($n_{\text{F}} = 3.0766 - 0.1621 \ln S + 0.6383 \Delta\text{pH}$) was able to explain 86% of the n_{F} variation; however, the possible usefulness of S and ΔpH as easily determinable sulfate desorption estimators should be better evaluated.

Conclusions

The sulfate desorption in subsurface layers of non-allophanic tropical soils tends to increase as these soils become alkaline and their phosphate-extractable S contents are increased by successive fertilisations and/or amendments with S-containing products. At same time, the advance of weathering tends to restrict sulfate desorption by these soils.

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