



# Sulfate adsorption and its relationships with properties of representative soils of the São Paulo State, Brazil

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## Abstract

Relationships between sulfate adsorption and physical, electrochemical and mineralogical properties of representative soils of the São Paulo State, Brazil, were evaluated. Ten subsurface soil samples were characterized for particle size distribution, electrochemical and mineralogical properties and for their capacities of sulfate adsorption. The experimental results were submitted to analysis of variance and to correlation and regression analyses. The composition of the clay fraction was more important than the absolute clay content for sulfate adsorption. Although correlation analyses showed that dithionite- and ammonium-oxalate-extractable iron and aluminum were similarly related to sulfate adsorption, regression analyses indicated that the retention of sulfate was dependent mainly on  $Fe_o$  and  $Al_o$ . When the adsorption was evaluated in the clay fraction, the kaolinite content was associated with low capacities of sulfate adsorption; however, no relationship was observed between the kaolinite soil content and the sulfate adsorption by the whole soil. No significant effects on sulfate adsorption were observed for individual hematite and goethite soil contents; on the other hand, the sum of hematite and goethite contents was related to sulfate adsorption. Soil pH in 1 M NaF ( $pH_{NaF}$ ) was strongly related to sulfate adsorption and was influenced by soil properties very similarly to sulfate adsorption. Thus, it can be used as an estimator of the sulfate adsorption capacity of weathered subsoils. Finally, the current rules for gypsum amendments of agricultural soils of the São Paulo State should be revised. In this context, more research involving the use of  $pH_{NaF}$  as an ancillary criterion for defining gypsum requirement should be encouraged.

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## 1. Introduction

Sulfate is the most abundant form of sulfur found in soils under aerobic conditions and the main ionic species of this element that is absorbed by plants. The sulfate interactions with the soil solid phase influence

not only its mobility, but also its availability to plants. Barrow (1969) found for Australian soils that the adsorption by soil reduced the uptake rate of sulfate by grass species. Similarly, Ribeiro et al. (2001) have recently verified different efficiencies for chemical extractants commonly used to measure the soil content of plant available sulfur due to differences related to the sulfate adsorption capacities of some Brazilian soils.

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In the agricultural regions of the tropics, additions of sulfate to soil are made mainly through fertilization and amendment with gypsum, a byproduct of phosphoric acid plants that is composed of nearly 95%  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Many studies have shown cation leaching occurrence due to soil amendment with gypsum (Pavan et al., 1984; Alva and Gascho, 1991).

There are many factors that influence sulfate adsorption by soils, including mineralogical composition, content and nature of organic matter, pH and the presence of other ions. Soil pH is inversely correlated to sulfate adsorption (Marsh et al., 1987; Zhang and Yu, 1997). For variable charge soils, this fact would be related to the increase of positive surface charges as pH decreases. Organic matter can influence sulfate adsorption through two opposite mechanisms. There is the possibility of competition for adsorption sites between organic anions and sulfate. Most studies demonstrate that the organic ions are preferentially adsorbed over sulfate by clay minerals and oxides (Martinez et al., 1998; Liu et al., 1999). On the other hand, the formation of Al– and Fe–humus complexes (Shoji and Fujiwara, 1984) and the inhibition of the crystallization of Al and Fe oxides caused by the organic matter (Huang and Violante, 1986; Schwertmann, 1985) increase the reactive surfaces toward sulfate adsorption.

The presence of other ions also influences sulfate adsorption by soils. Bolan et al. (1993) for New Zealand soils and Marcano-Martinez and McBride (1989) for Brazilian soils verified increases in sulfate adsorption as adsorbed calcium increased, which, however, was not observed by Agbenin (1997) for soils from Nigeria. On the other hand, phosphate adsorption decreases the sulfate adsorption (Bolan et al., 1988).

In view of the above-mentioned information, it can be concluded that the surface soils present unfavorable conditions for sulfate adsorption due to additions of phosphate and lime as well as the adoption of practices that increase the soil organic matter contents. Motavalli et al. (1993) and Dynia and Camargo (1995) observed increases in sulfate leaching due to the above-mentioned practices in some Brazilian Oxisols. Therefore, it seems more useful to study the sulfate adsorption in subsurface soil samples.

Unlike phosphate, there is lack of more detailed information about the influence of soil properties

on sulfate adsorption by variable charge soils. Thus, we studied the relationships between sulfate adsorption and physical, electrochemical and mineralogical properties of subsurface soil samples collected in representative soils of the São Paulo State, Brazil.

## 2. Material and methods

The studied soils are Oxisols, Ultisols and Entisols (Soil Survey Staff, 1998), which comprise 82% of the mapping units of the soil map of the São Paulo State (de Oliveira, 1999). Detailed information on the soils including classification, localization, depth of sampling and parent materials are presented in Table 1. Soil samples were air-dried and crushed to pass through a 2-mm sieve prior to analyses.

The texture was determined by the pipette method (Gee and Bauder, 1986), organic carbon by the Walkley and Black method (Nelson and Sommers, 1982), available P, K, Ca and Mg by extraction with ion-exchange resin (van Raij et al., 1986), phosphate-extractable S by extraction with 0.01 M  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  (Fox et al., 1964), exchangeable Al by 1 M KCl extraction (Bertsch and Bloom, 1996) and equilibrium phosphorus (Prem) by shaking 2.5 g of soil for 1 h with 25 ml of 0.01 M  $\text{CaCl}_2$  containing  $60 \mu\text{g P ml}^{-1}$  and determining P in equilibrium solution (Alvarez V. et al., 2000).

The Si, Fe and Al contents associated to secondary minerals were determined after boiling in 1:1  $\text{H}_2\text{SO}_4$  at a 1:20 soil/solution ratio (EMPRAPA, CNPS, 1997)

Table 1

Classification, parent materials, localization in the São Paulo State and sampling depth of the studied soils

Soil	Classification	Parent material	Localization	Depth (cm)
1	Rhodic Acrudox	Basalt	Ribeirão Preto	100–140
2	Rhodic Hapludox	Basalt	Luis Antonio	80–100
3	Rhodic Acrudox	Basalt	Luis Antonio	150–170
4	Xanthic Acrustox	Basalt	Guaira	100–130
5	Typic Hapludox	Sandstone	Piracicaba	100–110
6	Typic Hapludult	Sandstone	Pindorama	100–120
7	Typic Hapludult	Sandstone	Vera Cruz	100–120
8	Typic Hapludult	Schist	Rio Claro	70–80
9	Typic Hapludult	Basalt	Piracicaba	100–110
10	Typic Quartzipsamment	Sandstone	São Pedro	80–100

and the weathering indices  $K_i$  ( $\text{SiO}_2/\text{Al}_2\text{O}_3$ ,  $\text{mol mol}^{-1}$ ) and  $K_r$  ( $\text{SiO}_2/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ ,  $\text{mol mol}^{-1}$ ) were calculated. Dithionite- and oxalate-extractable Fe and Al were determined in the clay fraction ( $< 2 \mu\text{m}$ ) separated by gravity settling (Jackson, 1969) according to Buurman et al. (1996) ( $\text{Fe}_d$  and  $\text{Al}_d$ ) and McKeague and Day (1966) ( $\text{Fe}_o$  and  $\text{Al}_o$ ). The soil pH was measured in 0.01 M  $\text{CaCl}_2$  (pH  $\text{CaCl}_2$ ), water (pH  $\text{H}_2\text{O}$ ) and 1 M  $\text{KCl}$  (pH  $\text{KCl}$ ) at 1:2.5 soil/solution ratios (EMPRAPA, CNPS, 1997). Additionally, soil pH was also determined after shaking 0.5 g soil for 1 h with 20 ml of 1 M  $\text{NaF}$  (Bolland et al., 1996). Values of the  $\Delta\text{pH}$  index were calculated from the difference between pH  $\text{KCl}$  and pH  $\text{H}_2\text{O}$  according to Mekaru and Uehara (1972). The anion exchange capacity (AEC) was determined following the method outlined by Gillman (1979), which briefly consist of equilibrating the soil at its natural pH with 0.002 M  $\text{BaCl}_2$ , extracting the  $\text{Cl}^-$  ions with 0.005 M  $\text{MgSO}_4$  and determining the amount of desorbed  $\text{Cl}^-$ , which corresponds to AEC.

Kaolinite and gibbsite contents were determined in the deferrified clay fraction by differential thermal analysis (Tan et al., 1986) and corrected to the total clay fraction considering the weight difference of the clay fraction before and after iron oxides removal. Clay contents of hematite (Hm) and goethite (Gt) were estimated from the ratio  $\text{Hm}/\text{Hm} + \text{Gt}$  and the difference  $\text{Fe}_d - \text{Fe}_o$ . The ratio  $\text{Hm}/\text{Hm} + \text{Gt}$  was calculated using the following equation:

$$R = \frac{0.708A_{\text{Hm}104}}{A_{\text{Gt}110} + 0.708A_{\text{Hm}104}} \quad (1)$$

where  $R = \text{Hm}/\text{Hm} + \text{Gt}$ ;  $A_{\text{Hm}104}$  and  $A_{\text{Gt}110}$  = respective areas under hematite (104) and goethite (110) X-ray diffraction (XRD) peaks. The factor 0.708 corresponds to the ratio  $A_{\text{Gt}110}/A_{\text{Hm}104}$  found by Jones (1981) in a 1:1 mixture of hematite and goethite.

For soils that had goethite and hematite, the following equations were used:

$$\text{Gt} = \frac{\text{Fe}_d - \text{Fe}_o}{\frac{160(1-x)}{160 - 58x} \frac{R}{(1-R)} + \frac{80(1-y)}{89 - 29y}} \quad (2)$$

where Gt = goethite clay content (%);  $\text{Fe}_d$  = clay content of dithionite-extractable iron (%  $\text{Fe}_2\text{O}_3$ );  $\text{Fe}_o$  = clay content of ammonium-oxalate-extractable iron

(%  $\text{Fe}_2\text{O}_3$ );  $x$  and  $y$  = respective aluminum substitution in hematite and in goethite ( $\text{mol mol}^{-1}$ ).

$$\text{Hm} = \frac{R}{1-R} \text{Gt} \quad (3)$$

where Hm = hematite clay content (%).

For soils that did not have hematite, the goethite clay content was determined with the following equation:

$$\text{Gt} = (\text{Fe}_d - \text{Fe}_o) \frac{(89 - 29y)}{80(1-y)} \quad (4)$$

Eqs. (2), (3) and (4) were derived considering that the respective unit cells of Al-substituted hematite and goethite are given by  $\text{Fe}_{(2-2x)}\text{Al}_{2x}\text{O}_3$  and  $\text{Fe}_{(1-y)}\text{Al}_y\text{OOH}$  and that the iron content associated to hematite plus goethite corresponds to  $\text{Fe}_d - \text{Fe}_o$ .

The aluminum substitutions were determined from XRD data for hematite according to Schwertmann et al. (1979) and for goethite according to Schulze (1984). The XRD analyses were performed on random powder samples of the clay fraction after boiling in 5 M  $\text{NaOH}$  for concentration of iron oxides (Kämpf and Schwertmann, 1982). The patterns were recorded with a Siemens D5000<sup>®</sup> computer-oriented diffractometer using monochromated  $\text{CoK}\alpha$  radiation at 25 mA and 35 kV. The scans were obtained from  $20^\circ$  to  $45^\circ 2\theta$  at a speed of  $0.6^\circ 2\theta/\text{min}$ , and both peak positions and raw areas were determined using the EVA 3.09<sup>®</sup> software.

Sulfate adsorption isotherms were determined by shaking 2.5 g of soil for 24 h with 25 ml of eleven 0.01-M  $\text{CaCl}_2$  solutions containing  $\text{SO}_4^{2-}$  added as  $\text{K}_2\text{SO}_4$ . The initial  $\text{SO}_4^{2-}$  concentrations were defined considering the potential adsorption of the soils as estimated by equilibrium phosphorus (Prem) (Alvarez V. et al., 2000). The following ranges were used: 0–156  $\mu\text{g ml}^{-1}$  for soils 1, 3, 4, 8 and 9 (Prem 0.1–2.1  $\mu\text{g ml}^{-1}$ ); 0–120  $\mu\text{g ml}^{-1}$  for soil 2 (Prem 4.1  $\mu\text{g ml}^{-1}$ ); 0–66  $\mu\text{g ml}^{-1}$  for soil 6 (Prem 21.8  $\mu\text{g ml}^{-1}$ ); and 0–48  $\mu\text{g ml}^{-1}$  for soils 5, 7 and 10 (Prem 36.1–43  $\mu\text{g ml}^{-1}$ ). After shaking, the suspensions were filtered through a Whatman 42<sup>®</sup> filter, and the solutions were analyzed for sulfate by  $\text{BaSO}_4$  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 through nonlinear regression analysis (SAS, 1994).

The Langmuir equation is given by:

$$q = \frac{kcb}{1 + kc} \quad (5)$$

where  $q$  = adsorbed sulfate,  $\mu\text{g g}^{-1}$ ;  $k$  = parameter related to affinity of the soil by sulfate,  $\text{ml } \mu\text{g}^{-1}$ ;  $c$  = equilibrium concentration of sulfate,  $\mu\text{g ml}^{-1}$ ; and  $b$  = maximum capacity of sulfate adsorption,  $\mu\text{g g}^{-1}$ .

The Freundlich equation is expressed by:

$$q = kc^{1/n} \quad (6)$$

where  $q$  = adsorbed sulfate,  $\mu\text{g g}^{-1}$ ;  $k$  = constant,  $\mu\text{g}^{(1-1/n)} \text{g}^{-1} \text{ml}^{1/n}$ ;  $c$  = equilibrium concentration of sulfate,  $\mu\text{g ml}^{-1}$  and  $n$  = constant, dimensionless.

The goodness of fit of the Langmuir and Freundlich equations was verified using the approaches adopted by Mead (1981) and Raven and Hossner (1994) for comparisons of nonlinear fittings. The standard error of the estimate (S.E.) was also determined using the following equation:

$$\text{S.E.} = \left[ \sum (q - q^*)^2 / (n - 2) \right]^{1/2} \quad (7)$$

where  $q$  = measured sulfate adsorption;  $q^*$  = predicted sulfate adsorption; and  $n$  = number of isotherm points.

The sulfate adsorption was also determined by shaking 0.5 g of clay for 1 h with 25 ml of 0.01 M  $\text{CaCl}_2$  containing  $30 \mu\text{g SO}_4^{2-} \text{ml}^{-1}$ . The suspensions were filtered and analyzed for sulfate as outlined above. The amounts of sulfate adsorbed were calculated from the difference between the initial and final sulfate concentrations.

All determinations were performed with three replications. The experimental data were submitted to analysis of variance and to correlation and regression analyses using the Statistical Analysis System—SAS® software, version 6.11.

### 3. Results and discussion

#### 3.1. Soil properties

Texture and some chemical and electrochemical properties of the soils are summarized in Table 2. In general, most of the soils are acid, of low fertility and

Table 2  
Electrochemical, chemical and physical properties of the soils

Soil	pH	$\Delta\text{pH}^a$	AEC <sup>b</sup> ( $\text{cmol}_c \text{kg}^{-1}$ )	OC ( $\text{g kg}^{-1}$ )	P ( $\text{mg dm}^{-3}$ )	S- $\text{SO}_4^{2-}$ ( $\text{mg dm}^{-3}$ )	K ( $\text{cmol}_c \text{dm}^{-3}$ )	Ca ( $\text{cmol}_c \text{dm}^{-3}$ )	Mg ( $\text{cmol}_c \text{dm}^{-3}$ )	Al ( $\text{cmol}_c \text{dm}^{-3}$ )	Texture ( $\text{g kg}^{-1}$ )		
											CaCl <sub>2</sub>	NaF	Sand
1	5.0	10.4	0.1	0.57	6.0	5	0.05	0.4	0.1	0	133	338	529
2	4.3	10.3	-0.1	0.43	4.5	2	0.03	0.3	0.1	0.07	292	165	543
3	5.4	10.7	0.4	0.79	4.9	3	0.11	0.4	0.1	0	44	309	647
4	5.6	10.4	0.9	0.81	2.0	3	0.21	0.4	0.1	0	519	157	324
5	4.8	9.3	-1.0	0.12	2.1	2	0.15	0.8	0.2	0	667	89	244
6	4.0	9.5	-1.2	0.09	1.5	2	0.12	1.0	1.3	0.82	574	79	347
7	3.7	8.8	-0.7	0.04	2.1	2	0.09	0.4	0.2	0.66	747	48	205
8	5.2	9.7	-0.8	0.36	3.0	3	0.05	6.3	1.7	0	217	308	475
9	3.8	10.0	-1.1	0.60	2.4	2	0.09	0.7	0.4	2.54	210	158	632
10	4.0	9.0	-0.5	0.02	0.6	4	0.03	0.6	0.1	0.09	914	75	11

<sup>a</sup>  $\Delta\text{pH}$  = pH KCl – pH H<sub>2</sub>O (Mekaru and Uehara, 1972).

<sup>b</sup> AEC = anion exchange capacity.

Table 3

Total contents of Fe, Al and Si from sulfuric acid digestion, weathering indices Ki and Kr, dithionite- and oxalate-extractable Fe and Al, kaolinite (Ka), gibbsite (Gib), hematite (Hm) and goethite (Gt) clay contents

Soil	Whole soil					Clay fraction								
	H <sub>2</sub> SO <sub>4</sub> digestion (g kg <sup>-1</sup> )			Ki <sup>a</sup>	Kr <sup>b</sup>	Fe <sub>d</sub> (g kg <sup>-1</sup> )	Fe <sub>o</sub> (g kg <sup>-1</sup> )	Fe <sub>o</sub> /Fe <sub>d</sub>	Al <sub>d</sub> (g kg <sup>-1</sup> )	Al <sub>o</sub> (g kg <sup>-1</sup> )	Ka (%)	Gib (%)	Hm (%)	Gt (%)
	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>											
1	310	284	120	0.72	0.42	246	15	0.06	19	13	23.40	45.88	22.61	3.34
2	209	223	127	0.97	0.61	214	11	0.05	14	10	40.75	33.70	21.27	0.89
3	324	314	91	0.49	0.30	254	14	0.06	23	16	14.99	54.30	22.55	4.04
4	122	182	91	0.85	0.60	151	4	0.03	43	12	29.69	35.67	0	20.77
5	39	87	85	1.65	1.29	92	6	0.06	19	6	63.15	1.03	2.03	8.33
6	33	117	120	1.75	1.48	69	5	0.07	19	7	60.05	0.24	0.26	8.34
7	18	75	79	1.81	1.56	58	5	0.08	17	6	77.31	0	1.40	5.56
8	162	229	220	1.63	1.12	128	14	0.11	24	9	53.02	0	2.34	12.43
9	86	234	228	1.66	1.34	101	9	0.09	28	9	51.32	0.86	2.59	8.97
10	8	25	24	1.66	1.39	75	14	0.19	25	8	68.26	1.59	0.57	6.66

<sup>a</sup> Ki = 1.7(SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) (EMPRAPA, CNPS, 1997).

<sup>b</sup> Kr = 1.7(SiO<sub>2</sub>)/(Al<sub>2</sub>O<sub>3</sub> + 0.64Fe<sub>2</sub>O<sub>3</sub>) (EMPRAPA, CNPS, 1997).

poor in organic carbon (van Raij et al., 1996). The ΔpH values indicate the presence of negative net surface charge in all samples (Mekaru and Uehara, 1972), except for samples 1, 3 and 4 that have acric characteristics (FAO, 1989). The pH<sub>NaF</sub> values ranged from 8.8 to 10.7, suggesting that the F<sup>-</sup> replaces the OH<sup>-</sup> from soil minerals (Perrott et al., 1976). Samples 1, 2 and 8 are classified as clayey, whereas samples 3 and 9 as very clayey. The others have medium texture, except for the very sandy Typic Quartzipsamment (EMPRAPA, CNPS, 1999).

The Ki range (0.49–1.81) (Table 3) shows the wide variation of the weathering status of the studied soils,

whereas the Kr values separate them into oxidic (soils 1–4; Kr < 0.75) and kaolinitic (soils 5–10; Kr > 0.75) (EMPRAPA, CNPS, 1999), which agrees with the clay mineralogy as presented in Table 3, where the low Fe<sub>o</sub>/Fe<sub>d</sub> ratios also indicate predominance of hematite and goethite over poorly ordered iron phases.

### 3.2. Sulfate adsorption

The fit of the experimental data to the Freundlich equation was better for all soils, except for soils 4 and 9 for which the Langmuir equation fitted better (Table 4). Most of the data of sulfate adsorption by soils

Table 4

Results of experimental data fitting to the Langmuir and Freundlich equations

Soil	Langmuir					Freundlich				
	MSE <sup>a</sup>	S.E. <sup>b</sup>	a <sup>c</sup>	b <sup>c</sup>	R <sup>2c</sup>	MSE	S.E.	a	b	R <sup>2</sup>
1	720.1	26.8	20.9	0.95	0.9703	677.2	26.0	-9.2	1.00	0.9697
2	3038.9	55.1	47.4	0.91	0.9387	433.1	20.8	-2.2	1.00	0.9898
3	853.3	29.2	18.6	0.96	0.9720	567.7	23.8	-9.0	1.02	0.9805
4	346.1	18.6	6.6	0.99	0.9872	1039.6	32.2	-13.1	1.03	0.9617
5	114.3	10.7	4.5	0.95	0.9383	71.9	08.5	-0.7	0.99	0.9570
6	108.9	10.4	5.6	0.97	0.9823	85.4	09.2	-2.3	1.01	0.9850
7	178.0	13.3	3.2	0.97	0.9201	134.9	11.6	-0.1	1.00	0.9384
8	807.0	28.4	23.2	0.96	0.9865	684.0	26.1	-7.9	1.01	0.9869
9	499.7	22.4	0.5	1.00	0.9897	1167.9	34.2	-13.6	1.03	0.9766
10	182.0	13.5	4.3	0.96	0.9110	125.3	11.2	-0.4	1.00	0.9369

<sup>a</sup> MSE = mean square error calculated in the analysis of variance of the nonlinear regression analysis.

<sup>b</sup> S.E. = standard error of the estimate.

<sup>c</sup> a, b and R<sup>2</sup> = intercept, slope and coefficient of determination of the equation y = a + bx, where y is the actual adsorbed quantity and x is the model predicted adsorbed quantity.

present a better fit to the Freundlich equation (Bolan et al., 1988, 1993; Marcano-Martinez and McBride, 1989). The experimental adsorption data and the adsorption curves drawn according to the Freundlich equation are presented in Fig. 1.

Although for most of our data, the Freundlich equation was the best model, the use of its parameter  $k$  for comparative purposes is not correct when the parameter  $n$  differs from 1. Chen et al. (1999) have questioned the suitability of Freundlich  $k$  as an adsorption index due to problems associated to the unit of this parameter. According to these authors, the comparison of  $k$  values among different adsorbents is not valid when the parameter  $n$  is  $\neq 1$  because the unit of  $k$  depends on the numerical value of  $n$  parameter. For this reason, Chen et al. (1999) have proposed for comparative purposes the use of the alternative variable:

$$k_u = \frac{k}{c^{(n-1)/n}} \quad (8)$$

where  $k_u$  = unified adsorption variable for the Freundlich equation,  $\text{ml } \mu\text{g}^{-1}$ ;  $c$  = equilibrium concentration of sulfate,  $\mu\text{g ml}^{-1}$ ; and  $k$  and  $n$  = parameters of the Freundlich equation.

Thus, the  $k_u$  values were calculated using Eq. (8) and the equilibrium concentration of  $30 \mu\text{g SO}_4^{2-} \text{ml}^{-1}$ , chosen due to its proximity to the highest one common for all isotherms ( $33.6 \mu\text{g SO}_4^{2-} \text{ml}^{-1}$ ). Table 5 presents the parameters fitted to the Freundlich equation and the  $k_u$  values.

### 3.3. Relationships between sulfate adsorption and soil properties

Table 6 presents simple linear correlation coefficients between sulfate adsorption indices and some soil properties.

Similar to observations by Serrano et al. (1999) on Spanish soils, the clay content was related to the sulfate adsorption. Although the silt content had a direct relationship with the adsorption, the sum of clay and silt contents did not promote significant increase of the correlation coefficients.

Most research about the influence of dithionite- and ammonium-oxalate-extractable iron and aluminum on sulfate adsorption is related to temperate climate soils. Although Johnson and Todd (1983) found that the difference  $\text{Fe}_d - \text{Fe}_o$  was better related to the sulfate adsorption by North American forest

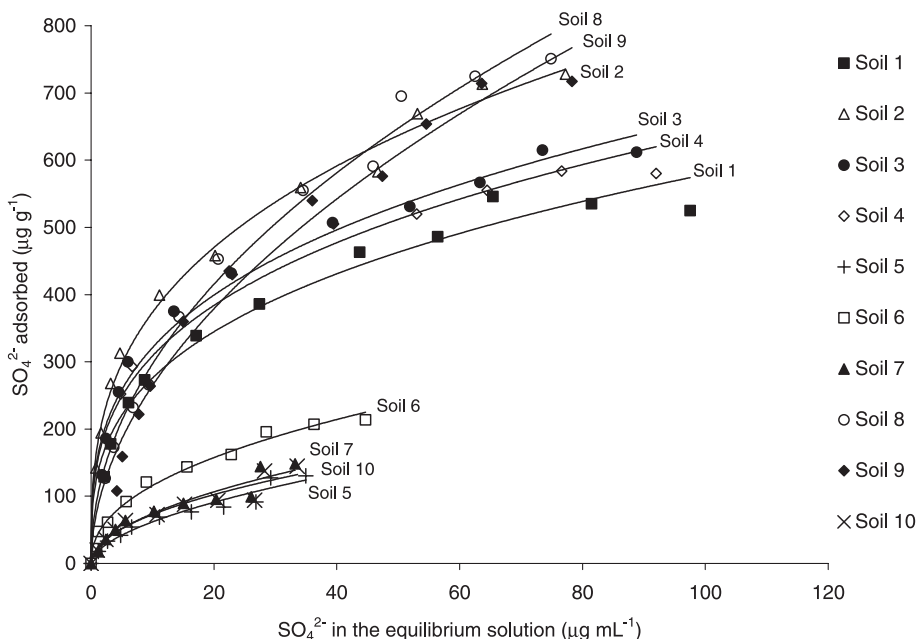


Fig. 1. Experimental data of sulfate adsorption and adsorption curves drawn according to the Freundlich equation.

Table 5  
Sulfate adsorbed by clays, parameters  $k$  and  $n$  of the Freundlich equation and unified adsorption variable ( $k_u$ )

Soil	SO <sub>4</sub> <sup>2-</sup> adsorbed* (μg SO <sub>4</sub> <sup>2-</sup> g <sup>-1</sup> clay)	Freundlich parameters		$k_u$ (ml g <sup>-1</sup> )
		$k$ (μg <sup>(1-1/m)</sup> g <sup>-1</sup> ml <sup>1/m</sup> )	$n$	
1	514e	131.5 (118.2–144.7)	3.1076 (2.8583–3.3568)	13.1
2	505e	174.3 (164.0–184.7)	3.0199 (2.8744–3.1654)	17.9
3	1200b	155.9 (143.8–168.0)	3.1859 (2.9805–3.3912)	15.1
4	1420a	149.8 (133.5–166.1)	3.1837 (2.8969–3.4705)	14.5
5	505e	17.2 (12.6–21.7)	1.7962 (1.5225–2.0701)	3.8
6	320f	41.7 (37.4–46.1)	2.2563 (2.0929–2.4196)	6.3
7	180g	22.3 (17.1–27.6)	1.9181 (1.6352–2.2010)	4.4
8	1155c	97.3 (87.3–107.2)	2.0634 (1.9491–2.1778)	16.9
9	895d	80.5 (68.7–92.2)	1.9337 (1.7917–2.0756)	15.6
10	478e	23.3 (18.0–28.7)	2.0250 (1.7204–2.3297)	4.2

Values in parentheses are the lower and upper limits of 95% confidence intervals.

\* Means followed by the same letter are not different at the 0.01 probability level according to Tukey's test (minimum significant difference = 42.7 μg SO<sub>4</sub><sup>2-</sup> g<sup>-1</sup>; coefficient of variation = 1.17%).

soils, the studies of Harrison et al. (1989) and McDonald and Hart (1990) with North American soils, Courchesne and Hendershot (1989) and Bhatti et al. (1997) with Canadian soils and Dolui and Chakrabarti (1998) with soils from India showed that the Al<sub>o</sub> was the extractable form better correlated with sulfate adsorption. In the present study, no remarkable difference among the correlations of Fe<sub>d</sub>, Fe<sub>o</sub>, Fe<sub>d</sub> – Fe<sub>o</sub>, Al<sub>d</sub> and Al<sub>o</sub> and sulfate adsorption was verified.

The direct relationship between sulfate adsorption and soil organic carbon can be due to an increase in reactive surfaces caused by either formation of Al–

and Fe–humus complexes (Shoji and Fujiwara, 1984) or delaying effect of organic matter on crystallization of Al and Fe oxides (Huang and Violante, 1986; Schwertmann, 1985). The correlations between organic carbon and Fe<sub>o</sub> (0.88\*\*) and Al<sub>o</sub> (0.82\*\*) reinforce these assumptions.

Although both pH CaCl<sub>2</sub> (3.7–5.6) and pH<sub>NaF</sub> (8.8–10.7) presented equal amplitudes (1.9), only the pH<sub>NaF</sub> was related to the unified adsorption index. The positive correlation of pH CaCl<sub>2</sub> and the affinity parameter  $n$  was not compatible with the well-known inverse relationship existent between pH and sulfate adsorption. However, the relationship between soil pH and sulfate adsorption found for a range of soils cannot be compared to that obtained when a single soil is artificially acidified. In the latter case, there is an increase in sorption capacity related to the increased positive surface charge that variable-charge soils acquire as pH decreases. On the other hand, when including soils from different sites, not only pH, but also nature and amount of organic matter, type and amount of minerals and even the crystallographic properties of a same mineral will differ, and may be interrelated, giving rise to different relationships.

The direct relationship observed between the sulfate adsorption and the AEC suggests the occurrence of electrostatic adsorption of sulfate on –OH<sub>2</sub><sup>+</sup> surface groups as proposed by Marsh et al. (1987). On the other hand, the correlation to pH<sub>NaF</sub> could indicate that the sulfate adsorption can occur through the exchange between sulfate ions and –OH surface

Table 6  
Correlation coefficients between soil properties, unified adsorption variable ( $k_u$ ) and parameter  $n$  of the Freundlich equation

Soil property <sup>a</sup>	$k_u$ (ml g <sup>-1</sup> )	$n$
Silt (g kg <sup>-1</sup> )	0.72*	0.58 <sup>ns</sup>
Clay (g kg <sup>-1</sup> )	0.82**	0.48 <sup>ns</sup>
Silt + clay (g kg <sup>-1</sup> )	0.85**	0.56 <sup>ns</sup>
OC (g kg <sup>-1</sup> )	0.62*	0.68*
pH CaCl <sub>2</sub>	0.46 <sup>ns</sup>	0.61*
pH <sub>NaF</sub>	0.82**	0.86**
AEC (cmol <sub>c</sub> kg <sup>-1</sup> )	0.81**	0.75**
Fe <sub>d</sub> (g kg <sup>-1</sup> )	0.73*	0.76**
Fe <sub>o</sub> (g kg <sup>-1</sup> )	0.78**	0.52 <sup>ns</sup>
Fe <sub>d</sub> – Fe <sub>o</sub> (g kg <sup>-1</sup> )	0.72*	0.78**
Al <sub>d</sub> (g kg <sup>-1</sup> )	0.79**	0.43 <sup>ns</sup>
Al <sub>o</sub> (g kg <sup>-1</sup> )	0.75*	0.69*

<sup>a</sup> Fe<sub>d</sub>, Fe<sub>o</sub>, Al<sub>d</sub> and Al<sub>o</sub> clay contents corrected for whole soil.

\* Significant at the 0.05 probability level ( $t$  test).

\*\* Significant at the 0.01 probability level ( $t$  test).

<sup>ns</sup> Not significant.

groups (Parfitt and Smart, 1978; Rajan, 1978). However, the direct correlation also verified between AEC and  $\text{pH}_{\text{NaF}}$  ( $r = 0.93^{**}$ ) shows that these properties are probably related to the same sulfate adsorption sites.

### 3.4. Effects of clay content and clay composition on sulfate adsorption

The influence of the composition of the clay fraction on sulfate adsorption was evaluated through direct measurements of adsorption performed on the clay. The adsorbed values ranged from 180 to 1420  $\mu\text{g SO}_4^{2-} \text{ g}^{-1}$  clay (Table 5) and the highest one was observed for the Xanthic Acrustox (soil 4), probably due to its highest goethite content. The lowest adsorption of the clay fraction of the Typic Hapludult (soil 7) can be attributed to its highest kaolinite content (nearly 80%) because this mineral has a very low capacity of sulfate adsorption (Aylmore et al., 1967). The significance of the clay composition for the soil sulfate adsorption can be noted comparing soils 3 and 4 that, although having very different clay contents (647 and 324  $\text{g kg}^{-1}$ , respectively), present similar  $k_u$  values (Table 5).

Regression analyses were carried out to evaluate the influence of clay content and clay composition on the sulfate adsorption. The slopes of the regression equations (Table 7) showed that the  $\text{Fe}_o$  and  $\text{Al}_o$  exerted major impacts on the sulfate adsorption while the clay content had the lowest influence.

Table 7

Results of linear regression analyses relating unified adsorption variable ( $k_u$ ) to soil contents of clay (%) and clay components (% whole soil) ( $n = 10$ )

Regression equation	$R^2$	$F$ value	$p > F$
$k_u = 2.0 + 0.2\text{clay}$	0.683	17.235	0.0032*
$k_u = 6.7 + 0.27\text{kaolinite}$	0.184	1.800	0.2165 <sup>ns</sup>
$k_u = 9.1 + 0.23\text{gibbsite}$	0.268	2.933	0.1251 <sup>ns</sup>
$k_u = 9.0 + 0.52\text{hematite}$	0.283	3.149	0.1139 <sup>ns</sup>
$k_u = 7.7 + 1.20\text{goethite}$	0.248	2.633	0.1433 <sup>ns</sup>
$k_u = 5.6 + 0.78$ (hematite + goethite)	0.584	11.237	0.0100*
$k_u = 6.3 + 0.08\text{Fe}_d$	0.534	9.176	0.0163*
$k_u = 5.6 + 1.34\text{Fe}_o$	0.590	11.491	0.0095*
$k_u = 6.4 + 0.08(\text{Fe}_d - \text{Fe}_o)$	0.525	8.829	0.0178*
$k_u = 5.4 + 1.41\text{Al}_o$	0.572	10.673	0.0114*

\* Significant at  $p < 0.05$ .

<sup>ns</sup> Not significant.

The low sulfate adsorption of kaolinite and the presence of more effective adsorbers such as iron and aluminum oxides probably accounted for the nonsignificant effect of this mineral on sulfate adsorption.

Although the importance of crystalline iron oxides as sulfate adsorbers is widely recognized (Parfitt and Smart, 1978; Turner and Kramer, 1991), the present study did not reveal significant relationships between sulfate adsorption and the individual contents of hematite and goethite. Fontes and Weed (1996) obtained similar results for phosphate adsorption by clay fractions of Brazilian Oxisols. It is probable that hematite and goethite characteristics such as crystallite size, specific surface area, crystallinity degree, exposed face for adsorption, etc., can be more important than their contents for the sulfate adsorption. The significant effect of the sum of hematite and goethite on the sulfate adsorption seems reinforce this assumption. The comparison of slopes for the sum of hematite and goethite and for  $\text{Fe}_d - \text{Fe}_o$  indicates that the conversion of  $\text{Fe}_d - \text{Fe}_o$  into hematite and goethite increased the impact of the crystalline iron on the sulfate adsorption.

Probably, the nonsignificant effect of gibbsite on sulfate adsorption observed in this study can be also due to variations in its intrinsic properties as those mentioned for hematite and goethite. Jones (1981) showed the importance of crystallite size on the P adsorption due to goethite, hematite and gibbsite in a group of 11 Puerto Rican soils, which probably can also be extended to sulfate adsorption.

Sakurai et al. (1989) verified that  $\text{Al}_o$  was the main property directly related to the point of zero charge (PZC) of Japanese and Thai soils, most probably due to high PZC values presented by the poorly ordered Al oxides as related by Parks (1965) (7.5–8.0) and Perrott (1977) (9.3). Thus, under the pH values of our soils (3.7–5.6), the  $\text{Al}_o$  compounds have a great number of protonated surface hydroxyls ( $\text{OH}_2^+$ ), which, according to Zhang and Yu (1997), are the easiest surface reactive groups exchangeable by sulfate ions. Both high PZC and high specific surface areas of the oxalate-soluble Al compounds can confer to them a high reactive surface toward sulfate adsorption, which can account for their major effect sulfate retention as verified in the present study.

Schwertmann and Fechter (1982) found PZC values from 5.3 to 6.3 for natural ferrihydrites, whereas

Parks (1965) found values of 7–8.8 for synthetic amorphous iron oxides. Even if the PZC values of the oxalate-extractable Fe compounds are not so high as those of  $Al_o$ , their high surface areas also contribute for their accentuate impact on the sulfate adsorption. As shown by Cornell and Schwertmann (1996), the specific surface area of ferrihydrite ranges from 100 to 400  $m^2 g^{-1}$ , while this range goes from 2 to 90  $m^2 g^{-1}$  for hematite and from 8 to 200  $m^2 g^{-1}$  for goethite.

### 3.5. Use of $pH_{NaF}$ for estimating sulfate adsorption

Regressions were carried out to assess the influence of the clay content and clay composition on  $pH_{NaF}$  values. Equation slopes showed that the  $Fe_o$  and  $Al_o$  exerted the major impact on  $pH_{NaF}$ , while clay content had a minor effect (Table 8). These results are in line with the higher reactivity of poorly ordered minerals toward NaF solution (Perrott et al., 1976).

Organic acids released from non-humified soil organic matter can lower the  $pH_{NaF}$  values, whereas the presence of carbonates can increase them (Perrott et al., 1976). Thus, both tillage practices that increase the soil organic matter and liming can affect the  $pH_{NaF}$  in surface agricultural soils in addition to mineralogy, which, in turn, is the main factor that defines the  $pH_{NaF}$  of weathered subsoils where the organic matter is more humified and less abundant and where there are small amounts of carbonates. In the present study, the direct relationship between the  $pH_{NaF}$  and organic carbon ( $r=0.73^*$ ) can be due to the reaction of NaF

solution with Al– and Fe–humus because both  $Al_o$  and  $Fe_o$  were also related to organic carbon, as mentioned earlier.

The high correlation between  $pH_{NaF}$  and sulfate adsorption (Table 6) and the very similar effect of soil properties on both indicate that  $pH_{NaF}$ , whose determination is cheap and not time consuming, can be used as a suitable estimator of sulfate adsorption capacity of weathered subsoils.

### 3.6. Practical implications

An adequate approach, when practical applications are aimed, consists of exploring the natural variability of soil properties such as pH, organic matter, clay content and clay mineralogy and its effects on some phenomenon in order to obtain results that can be of general application, at least to soils whose properties fall in the same ranges.

As this approach was used in the present research, some results allow to question the official method used in São Paulo State for the recommendation of gypsum requirement of agricultural soils. According to this method, the gypsum quantities to be applied are directly proportional to the subsurface soil clay content (de Sousa et al., 1992). It is desirable to optimize the gypsum quantities to be applied to the soil to minimize sulfate leaching and consequent cation losses. In this context, the current method not always permits this because it is possible that clayey soils may present kaolinite as a major clay constituent, a fact that can probably favor sulfate leaching after the application of great quantities of gypsum to these soils. Furthermore, for the studied soils, the clay content has a very little impact on the sulfate adsorption when compared to those of  $Fe_o$  and  $Al_o$ , which raises the possibility of using the  $pH_{NaF}$  as an additional criterion for optimizing gypsum requirements. This topic should be object of future research.

## 4. Conclusions

The kaolinite lowered the clay capacity of sulfate adsorption. However, no relationship was observed between the soil kaolinite content and sulfate adsorption by the whole soil. On the other hand, oxalate-soluble iron and aluminum play an important

Table 8  
Results of linear regression analyses relating  $pH_{NaF}$  to soil contents of clay (%) and clay components (% whole soil) ( $n=10$ )

Regression equation	$R^2$	$F$ value	$p>F$
$pH_{NaF}=8.8+0.025\text{clay}$	0.644	14.474	0.0052*
$pH_{NaF}=9.7+0.0066\text{kaolinite}$	0.009	0.069	0.7993 <sup>ns</sup>
$pH_{NaF}=9.4+0.0414\text{gibbsite}$	0.667	16.027	0.0039*
$pH_{NaF}=9.5+0.0792\text{hematite}$	0.527	8.901	0.0175*
$pH_{NaF}=9.5+0.0964\text{goethite}$	0.123	1.122	0.3204 <sup>ns</sup>
$pH_{NaF}=9.1+0.1041$ (hematite + goethite)	0.825	37.627	0.0003*
$pH_{NaF}=9.1+0.0103Fe_d$	0.765	26.034	0.0009*
$pH_{NaF}=9.2+0.1475Fe_o$	0.574	10.759	0.0112*
$pH_{NaF}=9.2+0.0110(Fe_d - Fe_o)$	0.770	26.769	0.0008*
$pH_{NaF}=9.0+0.1877Al_o$	0.789	29.653	0.0006*

\* Significant at  $p < 0.05$ .

<sup>ns</sup> Not significant.

role in sulfate adsorption by weathered subsoils. No consistent relationship was observed between individual contents of hematite and goethite and sulfate adsorption. However, the sum of soil hematite and goethite contents was directly related to sulfate adsorption.

The composition of the clay fraction is more important than the soil clay content for the definition of the soil sulfate adsorption capacity. For this reason, the present rules adopted in the São Paulo State for the gypsum requirements of agricultural soils should be revised. In this context, the use of  $\text{pH}_{\text{NaF}}$  as an ancillary criterion could be helpful because not only is it a good indicator of sulfate adsorption capacity of subsurface soil samples, but it is also dependent mainly on  $\text{Fe}_0$  and  $\text{Al}_0$ , as is the sulfate adsorption.

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