

## RELATIONSHIP BETWEEN ACIDITY AND CHEMICAL PROPERTIES OF BRAZILIAN SOILS

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**ABSTRACT:** In soils of tropical climate regions the high acidity and the presence of exchangeable aluminum ( $Al^{3+}$ ), associated to low fertility, are the main restraining factors for agricultural production. A laboratory experiment was conducted using 26 soils of different Brazilian regions, to investigate soil acidity components, giving emphasis to Al and their relations with chemical properties. The pH correlated positively with P, Ca, Mg, K, BS, CEC and V% values, and negatively with Al saturation. The  $Al^{3+}$  was the predominant exchangeable cation in 32% of the soils with pH below 5.6. The KCl titratable  $H^+$  represents the hydroxi- $Al(OH)_x$  complex with low stability and the Wolf-Morgan extracted Al corresponds to the exchangeable + non-exchangeable Al species. The  $Al^{3+}$  and low stability hydroxi-Al decreased quickly with increasing pH up to 5.5. The non-exchangeable Al increased up to pH 4.5, then decreased to pH 5.5 and had a small increment from 7.0 to 7.5.

**Key words:** total acidity, exchangeable acidity, pH, aluminum in soil

## RELAÇÕES ENTRE ACIDEZ E PROPRIEDADES QUÍMICAS DE SOLOS BRASILEIROS

**RESUMO:** Nos solos de regiões de clima tropical, a elevada acidez e a presença de alumínio trocável ( $Al^{3+}$ ), aliadas à baixa fertilidade, são os principais fatores a restringir a produção agrícola. Investigaram-se os componentes da acidez, com ênfase ao alumínio, e suas relações com as propriedades químicas de 26 solos de regiões brasileiras. O pH correlacionou positivamente com os valores de P, Ca, Mg, K, SB, CTC e V%, e negativamente com a saturação de Al. O  $Al^{3+}$  foi o cátion trocável predominante em 32 % dos solos com pH inferior a 5,6. O  $H^+$  titulável em KCl representa formas hydroxi- $Al(OH)_x$  de baixa estabilidade e o Al obtido pelo extrator de Wolf-Morgan corresponde ao Al trocável + não-trocável. As formas  $Al^{3+}$  e hydroxi-Al de baixa estabilidade diminuíram rapidamente com o pH até 5,5. O Al não-trocável aumentou até pH 4,5, diminuiu a seguir até pH 5,5 e aumentou lentamente com o pH de 7,0 a 7,5.

**Palavras-chave:** acidez total, acidez trocável, pH, alumínio no solo

### INTRODUCTION

For soils of tropical and humid subtropical climate regions, the high acidity and high exchangeable aluminum content, associated to low fertility, are the main constraints for agricultural production (McLean, 1965; Pavan, 1983; Nachtigall & Vahl, 1989). Soil acidity is characterized by its intensity and quantity aspects (Kinjo, 1983). The intensity factor is given by the soil solution hydrogen ( $H^+$ ) ion activity, and the quantity factor, by the amount of H, bound to the exchange complex, which the soil can liberate to solution. There is also the soil acidity capacity factor, which is the resistance to the variation of pH resulting from the addition of acids or bases, *i.e.*, the soil buffering capacity.

The characterization of soil acidity components is given by the active acidity (intensity factor), usually expressed as soil pH ( $-\log[H^+]$  in solution), and by the

potential acidity (quantity factor), of which more actual terminology, and hereafter used, is the total acidity (at pH 7) (Raij et al., 2001). The total acidity, by its turn, is the sum of exchangeable acidity and non-exchangeable acidity. The exchangeable acidity is given by the aluminum ion electrostatically retained by colloid surfaces with pH dependent negative charges, also called exchangeable aluminum ( $Al^{3+}$ ). The non-exchangeable is related to the content of H covalently bound to colloids, and monomers and polymers of aluminum in soil (Kinjo, 1983; Thomas & Hargrove, 1984; Raij et al., 1987; Nachtigall & Vahl, 1989; Raij et al., 2001).

The detrimental effects of acidity on plant growth depend on the  $H^+$  and  $Al^{3+}$  ions activities in the soil solution, which may be related to the activities and exchangeable contents of calcium ( $Ca^{2+}$ ), magnesium ( $Mg^{2+}$ ) and potassium ( $K^+$ ) cations, of orthophosphate ( $H_2PO_4^-$ ), nitrate ( $NO_3^-$ ) and sulphate ( $SO_4^{2-}$ ) anions, and with organic

matter (MO) content (Pavan, 1983; Thomas & Hargrove, 1984). With the neutralization of part of the soil total acidity by lime application, negative charges of the soil exchange complex are released, and then occupied by  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^{+}$  (Oates & Kamprath, 1983), improving the soil fertility and the conditions for agricultural production.

The objective of this work was to evaluate the acidity components and their relationship with chemical properties, for improving crop management in soils from different regions of Brazil.

## MATERIAL AND METHODS

The experiment was carried out in Piracicaba (SP), Brazil, using samples collected from the surface layer (0 – 0.2 m depth) of 26 soils from different Brazilian regions (Table 1). Soil samples with reaction close to neutrality were also included with the objective of evaluating the extraction of non-exchangeable forms of aluminum and to obtain low total acidity values.

Air dried samples of each soil were homogenized, divided in three subsamples, identified, ground in a porcelain crucible and passed through 0.5 mm mesh sieve and packed. For the chemical characterization of soil

samples (Table 2), methods described in Rajj et al. (1987; 2001) were used, except for the exchangeable sodium which was extracted with  $0.05 \text{ mol L}^{-1} \text{ HCl} + 0.0125 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  solution in 1:5 (v/v) soil/extractant ratio and determined in flame photometer.

Soil acidity components were characterized as follows: the active acidity was determined in  $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$  solution, 1:2.5 (v/v) soil/solution ratio, through pH measurement; the total acidity ( $\text{H} + \text{Al}^{3+}$ ) directly through the extraction with  $1 \text{ mol L}^{-1}$  ammonium acetate solution at pH 7, followed by titration, and indirectly by SMP method (Rajj et al., 1987; 2001). The exchangeable acidity ( $\text{Al}^{3+} + \text{H}^{+}_{\text{tit}}$ ) and the exchangeable aluminum ( $\text{Al}^{3+}$ ) were extracted by  $1 \text{ mol L}^{-1} \text{ KCl}$  solution, 1:10 (v/v) soil/solution ratio, and determined by titration of 25 mL KCl extract with  $25 \text{ mmol L}^{-1} \text{ NaOH}$ , using  $1 \text{ g L}^{-1}$  phenolphthalein as indicator, and by back-titration, after acidification with  $40 \text{ g L}^{-1} \text{ NaF}$ , with  $25 \text{ mmol L}^{-1} \text{ HCl}$ , respectively (routine methodology of Soil Fertility Lab., USP/CENA, adapted from McLean, 1965). The difference between titratable exchangeable acidity and titratable aluminum gave the so-called titratable hydrogen ( $\text{H}^{+}_{\text{tit}}$ ) content. The soluble Al (WM-Al) was extracted with Wolf-Morgan solution ( $0.73 \text{ mol L}^{-1}$  sodium acetate and  $0.0001 \text{ mol L}^{-1}$  DTPA, pH 4.8) and

Table 1 - Legend, classification, and origin of the soil samples used in the experiment.

Legend	Soil classification (Soil Survey, 1999; FAO, 1994; Embrapa, 1999; respectively)	Municipality	State
GX	Typic Umbraquult/Dystric Gleisol/Gleissolo Háplico Tb distrófico	Irاندوبا	AM
RQ-1	Typic Quartzipsamment/Haplic Arenosol/Neossolo Quartzarênico distrófico	Paraipabas	CE
LA-1	Typic Acrudox/Geric Ferralsol/Latossolo Amarelo acriférrico	Viçosa	MG
LV-1	Typic Hapludox/Rhodic Ferralsol/Latossolo Vermelho distroférrico	Três Lagoas	MS
LV-2	Typic Acrudox/Geric Ferralsol/Latossolo Vermelho acriférrico	Cuiabá	MT
LA-2	Typic Hapludox/Xantic Ferralsol/Latossolo Amarelo distrófico	Capitão Poço	PA
PVA-1	Typic Hapludult/Haplic Acrisol/Argissolo Vermelho-Amarelo distrófico	Capitão Poço	PA
LA-3	Typic Hapludox/Xantic Ferralsol/Latossolo Amarelo distrófico	Ipixuna	PA
LA-4	Typic Hapludox/Xantic Ferralsol/Latossolo Amarelo distrófico	Ipixuna	PA
NV-1	Typic Kandiodult/Rhodic Ferralsol/Nitossolo Vermelho distroférrico	Maringá	PR
LA-5	Xantic Hapludox/Haplic Acrisol/Latossolo Amarelo distrófico argissólico	Ariquemes	RO
PVA-2	Typic Hapludult/Haplic Acrisol/Argissolo Vermelho-Amarelo distrófico	Ariquemes	RO
LA-6	Xantic Eutrudox/Xantic Ferralsol/Latossolo Amarelo eutrófico argissólico	Not identified	SC
PVA-3	Typic Hapludult/Haplic Acrisol/Argissolo Vermelho-Amarelo distrófico	Capão Bonito	SP
LV-3	Typic Acrudox/Geric Ferralsol/Latossolo Vermelho acriférrico	Guataparά	SP
LV-4	Typic Hapludox/Rhodic Ferralsol/Latossolo Vermelho distrófico	Piracicaba	SP
PV	Typic Hapludult/Haplic Acrisol/Argissolo Vermelho distrófico	Piracicaba	SP
PVA-4	Typic Hapludult/Haplic Acrisol/Argissolo Vermelho-Amarelo distrófico	Piracicaba	SP
NV-2	Typic Kandiodult/Rhodic Ferralsol/Nitossolo Vermelho distrófico	Piracicaba	SP
RQ-2	Typic Quartzipsamment/Haplic Arenosol/Neossolo Quartzarênico distrófico	São Pedro	SP
LVA-1	Typic Hapludox/Xantic Ferralsol/Latossolo Vermelho-Amarelo distrófico	Três Barras	SP
CX-1	Typic Eutrochrept/Eutric Cambisol/Cambissolo Háplico Ta eutrófico	Irecê	BA
CX-2	Vertic Eutrochrept/Eutric Cambisol/Cambissolo Háplico Ta eutrófico vértico	Irecê	BA
LA-7	Typic Eustrudox/Xantic Ferralsol/Latossolo Amarelo eutrófico	Irecê	BA
LVA-2	Typic Eustrudox/Xantic Ferralsol/Latossolo Vermelho-Amarelo eutrófico	Irecê	BA
SS	Typic Natraqualf/Gleyic Solonckak/Salino-Sódico	Souza	PB

Table 2 - Chemical properties of soil samples of 0 - 0.2 m layer.

Soil	Organic mater	Resin P	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	<sup>(1)</sup> Na <sup>+</sup>	Sum of bases	CEC	Base saturation
	g dm <sup>-3</sup>	mg dm <sup>-3</sup>	----- mmol <sub>c</sub> dm <sup>-3</sup> -----						%
GX	12.7	11.0	1.45	27.2	6.8	1.1	36.4	72.6	50.1
RQ-1	21.7	4.0	1.13	15.9	6.8	0.3	24.2	37.0	65.4
LA-1	25.2	5.0	0.89	2.1	1.3	0.2	4.5	99.7	4.5
LV-1	22.2	4.9	2.84	26.4	14.6	0.3	44.1	65.4	67.4
LV-2	27.4	3.5	0.78	1.2	1.1	0.2	3.3	70.6	4.7
LA-2	22.9	5.0	0.71	4.8	2.2	0.5	8.4	59.2	14.2
PVA-1	25.0	3.3	0.74	8.1	2.5	0.8	12.1	52.7	23.1
LA-3	37.9	5.8	1.06	9.2	8.3	1.2	19.8	101.7	19.5
LA-4	32.6	3.9	1.92	21.2	6.0	0.5	29.7	58.3	50.9
NV-1	14.9	1.4	0.99	17.1	7.0	0.3	25.4	70.6	35.9
LA-5	19.9	6.9	2.62	15.5	3.6	0.4	22.1	52.4	42.2
PVA-2	22.4	4.9	1.32	7.9	3.6	0.2	13.1	37.7	34.8
LA-6	24.1	13.6	2.13	36.3	10.6	0.8	49.8	96.5	51.6
PVA-3	40.8	1.3	2.33	4.3	2.4	0.2	9.2	117.8	7.8
LV-3	30.1	4.3	1.07	13.4	8.7	0.2	23.3	64.7	36.0
LV-4	27.9	45.4	3.84	16.8	10.8	0.3	31.8	83.6	37.9
PV	27.9	2.8	0.70	22.3	8.1	0.2	31.4	71.8	43.7
PVA-4	25.1	3.6	0.74	10.3	3.5	0.3	14.8	53.1	27.8
NV-2	45.0	10.2	2.16	50.0	14.1	0.2	66.6	100.9	66.0
RQ-2	17.9	2.8	0.71	1.8	0.7	1.0	4.6	48.5	9.5
LVA-1	36.1	4.9	1.95	7.9	3.3	0.6	14.0	62.1	22.5
CX-1	24.0	46.5	2.47	139.8	22.5	0.2	165.1	186.8	88.4
<sup>(2)</sup> CX-2	32.5	5.5	1.33	412.0	20.5	1.2	435.2	445.1	97.8
LA-7	23.3	24.4	7.56	87.6	17.0	0.5	112.8	125.7	89.7
LVA-2	25.0	42.9	13.84	118.6	25.6	0.7	158.7	169.7	93.5
SS	24.5	13.4	2.34	166.8	40.6	43.6	262.8	270.8	97.1

<sup>(1)</sup>Sodium extracted with 0.05 mol L<sup>-1</sup> HCl + 0.0125 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, 1:5 (v/v) soil/solution ratio. Other chemical analyses as described in Raij et al. (1987; 2001). <sup>(2)</sup>Soil sample containing free carbonate.

determined through the aluminon method, (Wolf, 1982). The total Al content was determined in ICP-AES, after HClO<sub>4</sub> + HNO<sub>3</sub> + HF digestion. The non-exchangeable acidity was determined by the difference between the total acidity and exchangeable acidity obtained by titrimetric method.

Results were submitted to descriptive statistics for estimations of mean, median, upper and lower quartiles, and correlation and regression analysis for selected variables.

## RESULTS AND DISCUSSION

The pH values in CaCl<sub>2</sub> (Table 3), varied from 3.78 to 7.86, with 4.58 as the most frequent value, and 75% of values between 4.25 and 5.52. According to the limits established by Raij et al. (1987) for soils of São Paulo State, Brazil, 31% of samples presented very high active acidity (pH<sub>CaCl2</sub> ≤ 4.3), 38% high (4.4 to 5.0), 4% medium (5.1 to 5.5), 8% low (5.6 to 6.0), and 19% very low (> 6.0).

For soil samples with medium to very high acidity (pH < 5.6), the sum of bases (SB), the cation exchange capacity (CEC) and base saturation (V%) (Table 2) varied from 3.3 to 66.7 mmol<sub>c</sub> dm<sup>-3</sup>, from 37.7 to 117.8 mmol<sub>c</sub> dm<sup>-3</sup> and from 4.5 to 66.0%, respectively. There were positive correlations between the values of P (resin), Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, SB, CEC and V% and soil pH (Table 4), and a negative correlation between aluminum saturation (m%), showing the importance of soil reaction on soil fertility and the conditions for crop production. The chemical properties values (Tables 2 and 3) were similar to those obtained by Pavan (1983) and Nachtigal & Vahl (1989) for soils in the same pH range.

The titratable exchangeable acidity (Al<sup>3+</sup> + H<sup>+</sup><sub>tit</sub>) varied between 0 to 18 mmol<sub>c</sub> dm<sup>-3</sup>, and the exchangeable aluminum (Al<sup>3+</sup>) between 0 to 15 mmol<sub>c</sub> dm<sup>-3</sup> (Table 3). This demonstrated that the exchangeable acidity was constituted mostly of Al<sup>3+</sup>. In samples with pH lower than 5.6, the contribution of H<sup>+</sup><sub>tit</sub> was highly significant, representing 50% or more of titrated exchangeable acidity in 35% of all samples.

Table 3 - Values of pH in CaCl<sub>2</sub> (active acidity) and SMP solutions, titratable exchangeable acidity, exchangeable aluminum, titratable hydrogen, soluble aluminum (Wolf-Morgan), direct (ammonium acetate at pH 7) and indirect (SMP pH) total acidity, non-exchangeable acidity, total aluminum, and aluminum saturation, for characterization of acidity components of soils from Brazilian regions.

Soil	pH		Titratable acidity				Soluble Al (WM)	Non-exchange Al	Total acidity		Non-exchange acidity	Total Al	Al saturation
	(CaCl <sub>2</sub> )	SMP	Al <sup>3+</sup> + H <sup>+</sup>	Al <sup>3+</sup>	H <sup>+</sup>	Ca(Oac) <sub>2</sub>			SMP pH				
	----- mmol <sub>c</sub> dm <sup>-3</sup> -----												
GX	4.56	6.05	5.8	3.7	2.1	6.9	3.19	37.1	36.2	30.4	52.8	9.2	
RQ-1	5.52	7.48	0.1	0.0	0.1	0.2	0.23	12.6	12.8	12.7	13.5	0.0	
LA-1	3.82	5.19	17.5	13.4	4.1	14.3	0.86	91.9	95.2	77.7	79.0	75.0	
LV-1	5.52	6.83	0.7	0.2	0.5	1.2	0.99	21.1	21.3	20.6	49.5	0.5	
LV-2	4.10	5.50	9.4	6.9	2.5	10.3	3.33	66.2	67.3	57.8	98.3	67.9	
LA-2	3.78	6.02	12.3	7.6	4.7	10.6	2.93	48.7	50.8	38.4	42.6	47.7	
PVA-1	3.98	6.18	8.0	5.0	3.0	8.8	3.85	40.0	40.5	32.6	48.9	29.1	
LA-3	3.91	5.36	13.4	9.1	4.3	8.0	-1.05	80.4	81.9	68.6	90.0	31.5	
LA-4	4.72	6.56	2.2	0.7	1.5	8.2	7.44	29.0	28.6	26.4	34.8	2.4	
NV-1	4.64	6.02	5.3	3.7	1.6	9.3	5.60	44.6	45.2	40.0	101.8	12.7	
LA-5	4.52	6.50	2.9	1.5	1.4	2.4	0.86	30.0	30.3	27.3	52.7	6.5	
PVA-2	4.54	6.73	1.7	0.8	0.9	1.8	0.99	24.4	24.6	22.9	34.2	6.0	
LA-6	4.58	5.91	6.7	4.2	2.5	8.1	3.85	45.6	46.7	39.9	49.8	7.8	
PVA-3	4.25	4.94	17.7	14.7	3.0	21.8	7.11	98.3	108.6	90.9	90.8	61.6	
LV-3	4.63	6.02	0.6	0.3	0.3	7.1	6.79	40.9	41.4	40.8	105.3	1.2	
LV-4	4.57	5.88	4.1	2.2	1.9	2.1	-0.10	51.4	51.8	47.7	78.3	6.6	
PV	4.72	6.13	2.0	0.8	1.2	2.3	1.45	40.4	40.4	38.4	66.2	2.5	
PVA-4	4.28	6.32	7.6	5.4	2.2	9.9	4.47	38.2	38.3	30.7	38.3	27.0	
NV-2	5.28	6.30	0.3	0.1	0.2	1.7	1.59	33.0	34.3	34.0	66.3	0.2	
RQ-2	3.96	6.33	11.1	8.4	2.7	17.4	9.01	41.6	43.9	32.9	13.5	64.6	
LVA-1	4.43	6.10	7.5	5.0	2.5	16.8	11.73	47.8	48.1	40.6	26.7	26.6	
CX-1	6.06	6.75	0.8	0.1	0.7	1.3	1.23	22.9	21.7	21.0	66.2	0.1	
CX-2	7.58	7.52	0.0	0.0	0.0	1.9	1.91	11.2	9.8	9.8	59.1	0.0	
LA-7	6.74	7.31	0.0	0.0	0.0	0.5	0.45	13.2	12.9	12.9	55.3	0.0	
LVA-2	7.29	7.42	0.0	0.0	0.0	0.8	0.77	11.9	11.0	11.0	58.8	0.0	
SS	7.86	7.77	0.2	0.0	0.2	1.2	1.25	8.6	7.9	7.8	61.5	0.0	

Aluminum (Al<sup>3+</sup>) was the predominant exchangeable cation (m% > 30) in 23% of the analyzed soils, and in 32% of those with pH lower than 5.6. This result differs from that verified by Pavan (1983) in acid soils of Paraná, and explains that even in soil with high acidity, the Al<sup>3+</sup> may not be present and Al<sup>3+</sup> is a function of parent material and of soil mineralogy. The high Ca<sup>2+</sup> and Mg<sup>2+</sup> content (Table 2) and the negative correlation between these cations with Al<sup>3+</sup> (Table 4) may indicate that a significant fraction of soluble Al could have been neutralized by the liming.

In acid mineral soils, the H<sup>+</sup><sub>tit</sub> present in the KCl soil extract is not derived from Al<sup>3+</sup><sub>tit</sub> displaced from exchange sites; it is rather the result of pH dependent hydrolysis reactions that involve the hydroxi-Al(OH)<sub>x</sub> forms, the organic matter, and the Al and Fe oxides (Kissel et al., 1971; Thomas & Hargrove, 1984). Hiradate et al. (1998), using the nuclear magnetic resonance technique

for the Al speciation of acid soil samples in KCl solution, verified that 92 to 96% of Al<sup>3+</sup> were made of electrically symmetric octahedral Al (monomer and dimer of hydroxi-Al) and of organically complexed Al, respectively. However, the behavior of hydrogen bound to exchange complex depends on the nature of soil colloids. When associated to constant negative charge of 2:1 clay minerals, with planar surface, the H<sup>+</sup> ion is retained by electrostatic forces, *i.e.*, as exchangeable cation; when associated to variable negative charge of organic matter, kaolinite, allophane and iron and aluminum oxides, the hydrogen is retained by covalent bond, *i.e.*, non-exchangeable cation (Kinjo, 1983). Therefore, in acid mineral soils, the H<sup>+</sup><sub>tit</sub> present in non-buffered KCl soil solution extract does not represent the soil exchangeable acidity, but the low stability hydroxi-Al forms, except in soils with high organic matter content (Oates & Kamprath, 1983; Rajj et al., 1987; 2001).

Table 4 - Correlation coefficient between attributes related to acidity and fertility of soils from Brazilian regions.

Soil properties	Titratable		Soluble Al	Non-exchange Al	Non-exchange acidity	Total acidity at pH 7	Total Al	pH (CaCl <sub>2</sub> )
	Al <sup>3+</sup>	H <sup>+</sup>						
<i>All soils (N = 26)</i>								
pH (CaCl <sub>2</sub> )	-0.637***	-0.775***	-0.633***	-0.345	-0.691***	-0.709***	-0.053	--
Organic mater	0.164	0.047	0.184	0.128	0.388*	0.344	0.253	-0.005
P (resin)	-0.349	-0.315	-0.453*	-0.389*	-0.269	-0.294	0.094	0.449*
Ca <sup>2+</sup>	-0.401*	-0.495*	-0.409*	-0.236	-0.491*	-0.492*	0.015	0.801***
Mg <sup>2+</sup>	-0.562**	-0.629***	-0.606**	-0.391*	-0.562**	-0.584**	0.094	0.907***
K <sup>+</sup>	-0.310	-0.409*	-0.355	-0.257	-0.329	-0.341	0.001	0.560**
SB	-0.435*	-0.533**	-0.449*	-0.265	-0.527**	-0.529**	0.023	0.864***
CEC	-0.224	-0.368	-0.281	-0.231	-0.302	-0.303	0.163	0.764***
V%	-0.788***	-0.821***	-0.779***	-0.418*	-0.782***	-0.811***	-0.137	0.932***
m%	0.917***	0.784***	0.820***	0.322	0.727***	0.785***	0.131	-0.607**
<i>Soil with pH(CaCl<sub>2</sub>) &lt; 5.6 (N = 21)</i>								
pH (CaCl <sub>2</sub> )	-0.752***	-0.879***	-0.657***	-0.197	-0.565**	-0.614***	-0.178	--
Organic mater	0.165	0.036	0.183	0.111	0.458*	0.401	0.262	0.028
P (resin)	-0.189	-0.049	-0.319	-0.323	0.021	-0.020	0.110	0.102
Ca <sup>2+</sup>	-0.592**	-0.541*	-0.558**	-0.226	-0.381	-0.444*	-0.027	0.693***
Mg <sup>2+</sup>	-0.591**	-0.546*	-0.634***	-0.362	-0.270	-0.356	0.168	0.731***
K <sup>+</sup>	-0.247	-0.295	-0.256	-0.135	-0.011	-0.070	0.038	0.437*
SB	-0.607**	-0.554**	-0.590**	-0.265	-0.360	-0.431	0.015	0.725***
CEC	0.512*	0.341	0.308	-0.114	0.793***	0.751***	0.626**	-0.152
V%	-0.828***	-0.769***	-0.771***	-0.299	-0.682***	-0.743***	-0.258	0.908***
m%	0.903***	0.747***	0.787***	0.232	0.676***	0.750***	0.151	-0.765***

\*significant  $P < 0.05$ . \*\* significant  $P < 0.01$ . \*\*\*significant  $P < 0.001$ .

The concentration of low stability hydroxi-Al forms in soil samples from different regions of Brazil ( $H^+_{tit}$  contained in non-buffered KCl solution) varied from 0 to 4.7 mmol<sub>c</sub> dm<sup>-3</sup> (Table 3) and was dependent on Al<sup>3+</sup> content (Figure 1) and of sample pH (Table 4). In acid soils, there are predominance of Al<sup>3+</sup> over the Al(OH)<sup>2+</sup> and Al(OH)<sup>+</sup>, however with increasing pH, there gradually occurs the increment of OH/Al relation and of polymerization of hydroxi-Al forms. The formed polymers, of variable size and charges, neutralize negative charges but are not displaced in non-buffered saline solutions (Thomas & Hargrove, 1984). Therefore, in acid mineral soil containing 1:1 clay minerals and Al, Fe oxides, the lower the hydroxi-Al forms content, the higher is the proportion of their hydrolysable forms, resulting from lower polymerization (stability) of these Al forms, which produces H<sup>+</sup> in KCl extract (Kissel et al., 1971).

The soluble Al content obtained by Wolf-Morgan extractant (WM-Al) varied from 0.2 to 21.8 mmol<sub>c</sub> dm<sup>-3</sup> (Table 3), with most frequent value of 7.0 mmol<sub>c</sub> dm<sup>-3</sup> (8.2 mmol<sub>c</sub> dm<sup>-3</sup> in samples with pH < 5.6) and were superior or near the Al<sup>3+</sup> content in KCl neutral solution,

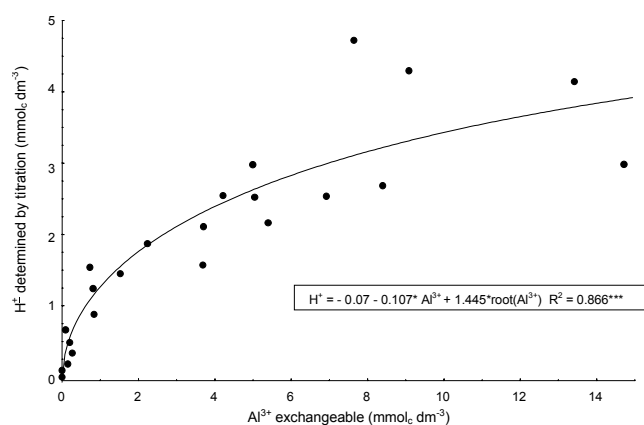


Figure 1 - Relation between the exchangeable aluminum (Al<sup>3+</sup>) and the so-called exchangeable hydrogen ( $H^+_{tit}$ ) determined by titration, in 1 mol L<sup>-1</sup> KCl extract, for soil samples from Brazilian regions. In acid mineral soil, this  $H^+_{tit}$  may indeed represent low stability hydroxi-Al.

except in LA-3 sample. Similar values of Al extracted with 1 mol L<sup>-1</sup> NH<sub>4</sub>AO<sub>c</sub> (pH 4.8), to obtain the exchangeable + non-exchangeable Al, was reported by Pavan (1983) in soil samples from Paraná with the same range

of  $\text{Al}^{3+}$  of this work. This indicates that the Wolf-Morgan solution extracts exchangeable Al and non-exchangeable Al as well, which may be toxic to plants (Noble et al., 1988; Hiradate et al., 1998). Therefore, the Al obtained by difference between WM-Al and  $\text{Al}^{3+}$  constitute the non-exchangeable Al (Table 3), and those values varied from 0 to  $11.7 \text{ mmol}_c \text{ dm}^{-3}$ . Similar results were observed by Pavan (1983) in soil samples with the same variation in  $\text{Al}^{3+}$ .

The Al contents of exchangeable and of low polymerization degree hydroxi forms diminish rapidly with the sample pH increment up to 5.5 value; through the non-exchangeable form increased up to pH 4.5, decreased thereafter up to pH 5.5, and increased slowly with the pH of 7.0 to 7.5 (Figure 2), according to the stage of polymerization of hydroxi-Al forms which are functions of pH and of organic matter (McLean, 1965; Kissel et al., 1971; Pavan, 1983; Thomas & Hargrove, 1984).

The determined total acidity was 8.6 to  $91.9 \text{ mmol}_c \text{ dm}^{-3}$  and those obtained by SMP pH, 7.9 to  $95.2 \text{ mmol}_c \text{ dm}^{-3}$ , with most frequent values of 39.1 to  $39.4 \text{ mmol}_c \text{ dm}^{-3}$ , respectively. The indirect determination of total acidity (Raij et al., 1987) is based on SMP pH (buffered at pH 7.5) variations in consequence of  $\text{H}^+$ ,  $\text{Al}^{3+}$  and  $\text{OH}^-$  ions released by soil colloids and organic matter, which allows to establish the relationship between the pH of SMP solution and the  $\text{H}^+ + \text{Al}^{3+}$  content in the soil sample.

The analysis of the relationship between exchangeable aluminum with total acidity and base saturation of the soils (Figure 3) revealed that a small increase in  $\text{Al}^{3+}$  content (0 to  $0.2 \text{ mmol}_c \text{ dm}^{-3}$ ) results in a quick evolution of total acidity ( $8.6$  to  $21.1 \text{ mmol}_c \text{ dm}^{-3}$ ). This generated acidity, for soils with  $\text{pH} \geq 5.6$ , is exclusively attributed to  $\text{H}^+$  ions (Table 3). Thereafter, when  $\text{Al}^{3+} > 0.2 \text{ mmol}_c \text{ dm}^{-3}$ , the total acidity increased  $5.1 \text{ mmol}_c \text{ dm}^{-3}$ , on average, for each released  $\text{mmol}_c \text{ dm}^{-3}$  of  $\text{Al}^{3+}$ . Simultaneously, the base saturation reduced drastically with increasing  $\text{Al}^{3+}$  content from 0 to  $4 \text{ mmol}_c \text{ dm}^{-3}$ ; above this boundary value, the effect of increasing  $\text{Al}^{3+}$  was much smaller in reducing soil V%.

There was a very narrow relationship between the total acidity obtained directly and indirectly (Figure 4a) and the obtained exponential relationship between SMP pH and the determined total acidity (Figure 4b) was much similar to that used by laboratories of soil analyses, mainly in the State of São Paulo (Raij et al., 1987; 2001). This indicates that the SMP pH method can be used for the evaluation of total acidity of soils practically from all Brazilian regions. Recently, Nascimento (2000) and Silva et al. (2000) established second degree equations for the calculation of  $\text{H}^+ + \text{Al}^{3+}$  by SMP pH method in soils of Pernambuco and of Semi-Arido of Brazilian Northeast, respectively.

Although, unlike Pavan's (1983) paper, significant correlations have not been verified among the variables associated to the soil acidity and the organic matter content (Table 4), except for non-exchangeable acidity, it is known that in acid soils the organic matter can play an important role in  $\text{Al}^{3+}$  complexation (McLean, 1965; Pavan, 1983; Oates & Kamprath, 1984; Hiradate et al., 1998), reducing the toxic effect of aluminum to plants. This fact may have an important role in agricultural systems with management of crop residues or of organic fertilizers, for which the liming would be reduced without affecting productivity, increasing the cost/benefit relationship. The relationship with organic matter explains also the  $\text{Al}^{3+}$  content reduction along the acid soil profile (McLean, 1965).

There were correlations ( $P < 0.001$ ) between the soil Al saturation (m%) and other acidity associated variables (Table 4), except for total Al. The total Al only correlated with the CEC of soil with pH below 5.6, evidencing different mineralogy among the studied soil samples.

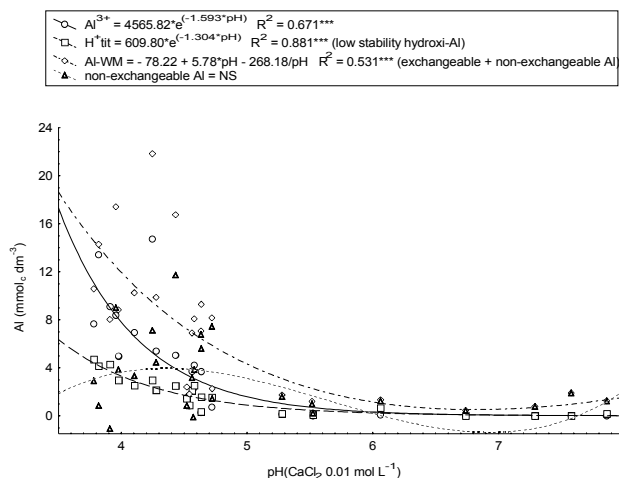


Figure 2 - Relationships between pH, in  $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$ , and exchangeable aluminum ( $\text{Al}^{3+}$ ), low stability hydroxi-Al ( $\text{H}^+_{\text{tit}}$ ), exchangeable plus non-exchangeable aluminum (Wolf-Morgan Al), and non-exchangeable aluminum for soil samples from Brazilian regions.

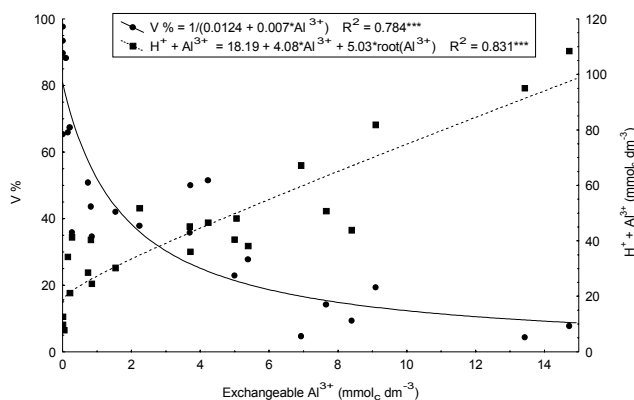


Figure 3 - Relationships between the exchangeable aluminum ( $\text{Al}^{3+}$ ) and base saturation (V%) and total acidity at pH 7 ( $\text{H}^+ + \text{Al}^{3+}$ ) for soil samples from Brazilian regions.

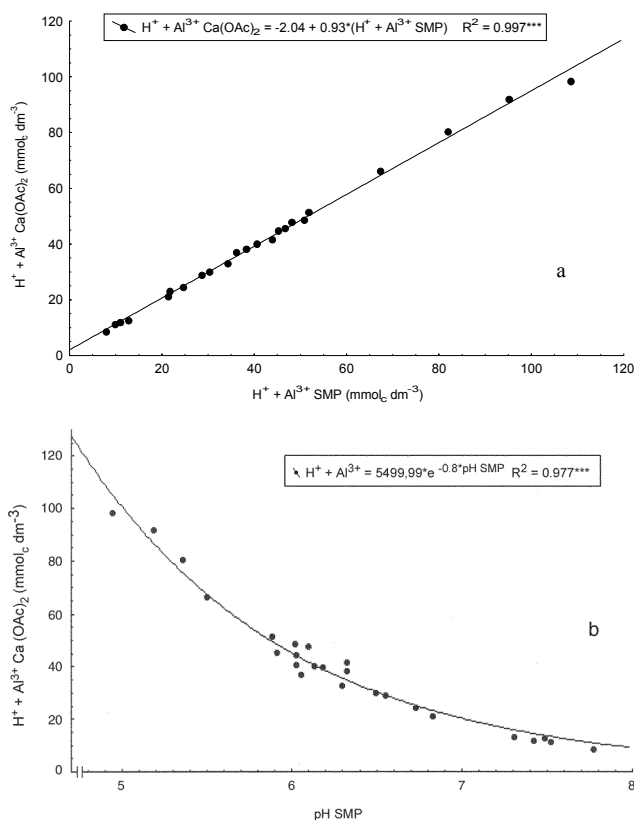


Figure 4 - Relationships between the total acidity ( $H^+ + Al^{3+}$ ) determined by SMP buffer pH and by ammonium acetate at pH 7 (a), and between the pH of SMP buffer solution and the total acidity with ammonium acetate at pH 7 (b) for soil samples from Brazilian regions.

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