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POLLIANA SILVA FRANCO FERREIRA

**DOES POTENTIAL ACIDITY OF SAVANNA SOILS HAVE BEEN
DETERMINED WITH ACCURACY?**

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Dissertation presented to the Federal
University of Uberlândia, as a partial
requirement for obtaining the title of
Master in Agronomy

Advisor: PhD. Professor. Wedisson
Oliveira Santos

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*Bondade e misericórdia
certamente me seguirão todos os
dias da minha vida; e habitarei na
casa do Senhor para todo o
sempre.*

Salmos 23:6

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RESUMO

FERREIRA, Polliana Silva Franco. **Does potential acidity of savanna soils have been determined with accuracy?** 2024. 38p. Dissertação (Mestrado em Agronomia – Produção Vegetal) – Instituto de Ciências Agrárias. Universidade Federal de Uberlândia. 2024.

A acidez potencial do solo é composta principalmente pela acidez não trocável, que corresponde ao H ligado covalentemente à grupamentos funcionais de carga variável nos coloides do solo e que é neutralizada a determinado valor de pH. Trata-se do poder tampão de acidez de um solo. Portanto, a determinação acurada da acidez potencial do solo é essencial para um correto diagnóstico da fertilidade do solo, especialmente na determinação da saturação por bases, afetando consequentemente na necessidade de calagem quando o método de saturação por bases é o escolhido. Diferentes métodos são utilizados para a determinação da acidez potencial, incluindo o método de incubação do solo com CaCO_3 , que é considerado o mais exato, porém é incompatível com a rotina laboratorial. Métodos baseados em acetato de cálcio 0,5 mol/L pH 7.0 e no tampão SMP pH 7.5, de rotina, podem apresentar inexatidão devido ao baixo tamponamento do acetato de cálcio e à baixa universalidade das equações SMP calibradas para domínios restritos de solo. Inexatidões dos métodos tradicionais motivaram o presente estudo que teve por objetivo avaliar a exatidão de equações SMP e avaliar o efeito de concentrações e pH do acetato de cálcio na determinação da acidez potencial em solos do Triângulo Mineiro. Foram coletados 14 solos dentre os mais representativos agronomicamente (Utisols, Oxisols, Ultisols e Entisols), sendo no método do tampão SMP também avaliada a exatidão em solução modificada, sem o dicromato de potássio, componente do tampão de elevada toxicidade. No método do acetato de cálcio foram avaliadas variações na concentração do extrator (0,25; 0,5; 1 e 1,5 mol/L) e no pH (7,0 e 8,0). O delineamento utilizado foi em blocos casualizados com três repetições. Houve grande diferença de exatidão entre equações SMP na estimativa da acidez potencial dos solos, em sua grande maioria com tendências inaceitáveis. Nenhuma equação SMP avaliada foi considerada adequada para todos os solos. A ausência do dicromato de potássio no tampão SMP gerou valores de $\text{H}+\text{Al}$ menos exatos. O aumento na concentração do acetato de cálcio e do pH elevaram significativamente a extração da acidez potencial nos diferentes solos, exceto para dois Entisolss devido as suas baixas capacidades de tamponamento de acidez. Apesar do aumento da predição das equações SMP quando ajustadas aos dados com o agrupamento dos solos em Entisols-Utisols e Oxisols-Ultisols, não foi suficiente para garantir exatidão aceitável para todos os solos. Apesar de o acetato de cálcio 1,5 mol/L a pH 8,0 extrair teores de $\text{H}+\text{Al}$ mais próximos ao teor de referência, não é exato para todos os solos.

Palavra-chave: acetato de cálcio, acidez do solo, métodos, $\text{H}+\text{Al}$, SMP

ABSTRACT

The potential soil acidity is mainly composed of non-exchangeable acidity, which corresponds to the H covalently bonded to functional groups of variable charge in soil colloids and which is neutralized at a certain pH value. It is the acidity buffering power of a soil. Therefore, the accurate determination of potential soil acidity is essential for a correct diagnosis of soil fertility, especially in the determination of base saturation, consequently affecting the need for liming when the base saturation method is chosen. Different methods are used to determine potential acidity, including the CaCO_3 soil incubation method, which is considered the most accurate, but is incompatible with laboratory routine. Methods based on 0.5 mol/L calcium acetate pH 7.0 and routine SMP pH 7.5 buffer may present inaccuracy due to the low buffering of calcium acetate and the low universality of the SMP equations calibrated for restricted soil domains. Inaccuracies of traditional methods motivated the present study, which aimed to evaluate the accuracy of SMP equations and to evaluate the effect of calcium acetate concentrations and pH on the determination of potential acidity in soils of the Triângulo Mineiro region. A total of fourteen soils were collected among the most agronomically representative soils (Cambisol, Latosol, Argisol and Neosol), and the SMP buffer method also evaluated the accuracy in modified solution, without potassium dichromate, a highly toxic component of the buffer. In the calcium acetate method, variations in the concentration of the extractor (0.25; 0.5; 1 and 1.5 mol/L) and in pH (7.0 and 8.0) were evaluated. The experimental design was randomized blocks with three replications. There was a large difference in accuracy between SMP equations in the estimation of potential soil acidity, most of them with unacceptable trends. None of the SMP equations evaluated were considered adequate for all soils. The absence of potassium dichromate in the SMP buffer generated less accurate H^+Al values. The increase in calcium acetate concentration and pH significantly increased the extraction of potential acidity in the different soils, except for two Neosols due to their low acidity buffering capacities. Despite the increase in the prediction of the SMP equations when adjusted to the data by grouping the soils into Neosols-Cambisols and Latosols-Argisols, it was not enough to guarantee acceptable accuracy for all soils. Although calcium acetate 1.5 mol/L at pH 8.0 extracts H^+Al contents closer to the reference content, it is not accurate for all soils.

Keyword: calcium acetate, soil acidity, methods, H^+Al , SMP

INTRODUCTION

The potential soil acidity (H+Al) is composed of the exchangeable acidity fraction, which arises from the hydrolysis of cations such as Al^{3+} , Fe^{3+} , Mn^{2+} , Zn^{2+} , and Cu^{2+} . Among them, Al^{3+} is the most representative in tropical conditions. This fraction is typically extracted through ion exchange using unbuffered neutral salts (KAMINSKI et al., 2002). Non-exchangeable acidity, which generally constitutes the largest portion of potential soil acidity, corresponds to ionizable hydrogen (H^+) resulted from covalent bonds in functional groups of soil colloids. The relative proportion between the exchangeable and non-exchangeable acidity varies depending on soil characteristics, such as pH, the content and types of mineral clays, also organic matter content. The measurement of non-exchangeable acidity depends on the deprotonation of functional groups at a specific pH value, typically 7.0 (QUAGGIO; RAIJ, 2001).

The accuracy in determining H+Al content significantly impacts the diagnosis of the soil's base saturation index (V) and, consequently, the recommendations for liming when using V-based methods. Several routines analytical procedures are available to measure soil H+Al content, including methods based on a 0.5 mol/L acetate buffer solution at pH 7.0 with acid-base titration (EMPRESA BRASILEIRA DE PESQUISA AGROPECUÁRIA - EMBRAPA, 2017) and the SMP buffer solution at pH 7.5, which estimates H+Al indirectly through equilibrium pH and calibrated equations (SHOEMAKER; McLEAN; PRATT, 1961). H+Al content can also be measured through soil incubation trials with varying rates of CaCO_3 . Thus considering the stoichiometry of the neutralization reaction ($\text{CaCO}_3 + 2\text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$), the molar weight of CaCO_3 (100 g/mol), and the pH values achieved, it is possible to estimate H+Al content for any pH within the observed range. Although been highly accurate, the incubation method is impractical for routine laboratory use due to its lengthy duration, often requiring several weeks for the neutralization reaction to complete. Whereas, methods based on calcium acetate or SMP indices, while more practical, may suffer from low analytical accuracy (KAMINSKI et al., 2002; SILVA, 2005; TOLEDO et al., 2012; SILVA et al., 2008).

The calcium acetate method faces several challenges, including difficulty in identifying the titration endpoint, particularly when the extraction solution is cloudy. Additionally, the daily preparation of the buffer solution and the variable quality of commercially available reagents further complicate its use (GAMA et al., 2002). This

method may also underestimate potential acidity in highly buffered soils due to incomplete ionization of functional groups at pH 7.0, resulting from shifts in the buffer-soil equilibrium pH (SILVA, 2005).

The SMP buffer solution, developed by Shoemaker, McClean, and Pratt in 1961, is composed of p-nitrophenol, triethanolamine, potassium chromate, and calcium acetate. Initially designed to estimate liming requirements in southern Brazil due to its practicality (ALMEIDA JÚNIOR; NASCIMENTO; BARROS, 2015), it was later adapted to estimate H+Al content in soils (CQFS-RS/SC, 1989). The method depends on regional calibration equations that correlate H+Al values (determined by a reference method) with the equilibrium pH of soil/SMP buffer suspensions. Over time, SMP equations have been calibrated for various regions, including the semiarid northeast (SILVA, 2005), Minas Gerais (CORRÊA et al., 1985), northwest Paraná (SAMBATTI et al., 2003), Pernambuco (NASCIMENTO, 2000), the Brejo Paraibano microregion (CHAVES et al., 2007), western Paraguay (FORNASARE et al., 2023), Rio Grande do Sul and Santa Catarina (SIQUEIRA et al., 1987), and Paraíba (ALMEIDA JÚNIOR; NASCIMENTO; BARROS, 2015), among others. Despite its operational advantages, the SMP method exhibits inaccuracies due to regional soil variation compared to the soils used for calibration, limiting its applicability to specific regions or biomes. However, soil analysis laboratories can extend their scope beyond regional limits by recalibrating the method for local soil conditions (SILVA, 2005). Thus, there is a necessity to establish region-specific calibration curves to account for Brazil's diverse soil properties (KAMINSKI et al., 2002; PEREIRA et al., 2020).

Several SMP equations have been set (CORRÊA et al., 1985; QUAGGIO et al., 1985; SOUSA et al., 1989; ESCOSTEGUY; BISSANI, 1999; SILVA et al., 2000; SILVA et al., 2002) using the calcium acetate method (RAIJ et al., 1979) as a reference. However, as previously noted, the calcium acetate method itself may lack accuracy due to its limited extraction power. Additionally, the SMP buffer contains potassium dichromate, a highly toxic component that poses significant risks to human health and the environment. Potassium dichromate is associated with carcinogenicity, aquatic toxicity, and mutagenicity (TOLEDO et al., 2012; ROCHA et al., 2015).

In view of these limitations, this study aims to evaluate the accuracy of methods for determining potential acidity based on SMP pH and calcium acetate, comparing them to the reference method of soil incubation with CaCO₃ in soils from the Triângulo Mineiro region.

MATERIAL AND METHODS

The study was conducted at the Soil and Plant Tissue Analysis Laboratory (LABAS) of the Federal University of Uberlândia, located on the Umuarama campus in Minas Gerais State, Brazil. Topsoil samples (0–0.2 m depth) from fourteen soils representing major pedogenetic classes—Oxisols (Oxisols), Ultisols (Ultisols), Utisols (Inceptisols), and Entisols (Entisols)—were collected in the Triângulo Mineiro region. These soil classes are highly relevant for agricultural and forestry crops in Brazil. Detailed information on the sampled soils is presented in Table 1 and Figure 1.

Table 1. Location and description of soils collected in the top layer (0-0.20 m) in the Triângulo Mineiro region, Minas Gerais state, Brazil

Soil	Geographic Coordinates		Classification (SBCS)*
C1	18°55'17.31"S	49°37'50.91"W	CXbe1
C2	18°43'52.72"S	48°12'7.43"W	CXbe2
C3	18°55'20.93"S	49°37'54.31"W	CXbe3
A6	18°33'1.21"S	48° 2'52.05"W	PVAe1
A7	18°46'47.79"S	48°14'8.41"W	PVAe2
A8	10°06.297' S	48°21.040' W	PVAe3
N9	19°03.859' S	48°20.933' W	RQo1
N10	18°58.678' S	48°18.543' W	RQo2
N11	18°56'57.98"S	48°12'35.64"W	RQo3
N12	19° 9'5.29"S	48°10'1.38"W	RQo4
L13	19° 1'35.62"S	48°12'13.67"W	LVw1
L14	18°56'44.43"S	48°12'54.88"W	LVw2
L15	18°56'.43"S	48° 12'56"W	LVAd3
L16	19°09'04.6"S	48°10'00.6"W	LAd4

*Soil classification according to the Brazilian soil classification system (SBCS) - **LVAd**: OxisolsOxisols Vermelho-Amarelo Distrófico; **LVw**: Oxisols Vermelho Ácrico; **PVAe**: Ultisols Vermelho-Amarelo Eutrófico; **Cxbe**: Utisols Háplico Tb Eutroférico; **RQo**: Entisols Quartzarênico Órtico; **LVAd**: Oxisols Vermelho-Amarelo Distrófico; **LAd**: Oxisols Amarelo distrófico; **SBCS**: Brazilian Soil Classification System.

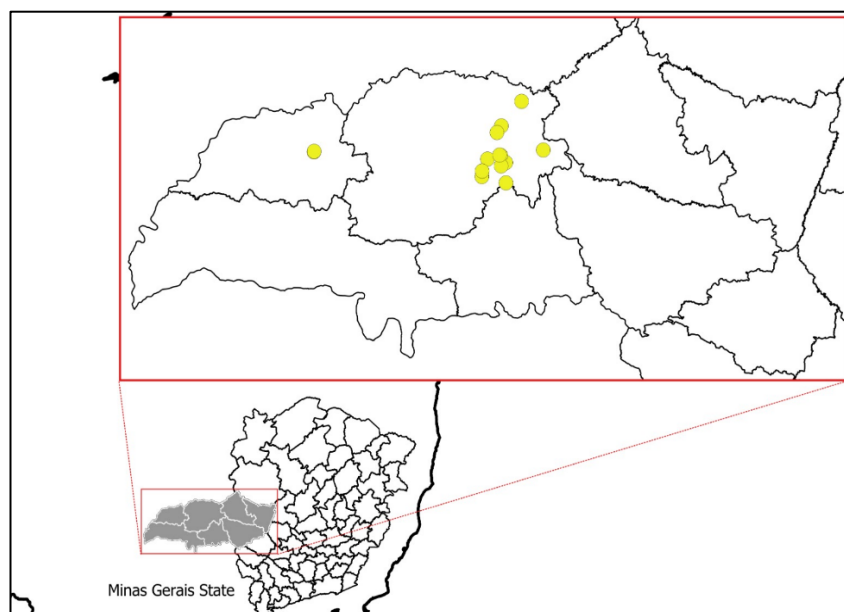


Figure 1. Soil collection points location in Triângulo Mineiro region, Minas Gerais state, Brazil

The tables 2 and 3 present the chemical and physical characteristics of the soils, respectively. These tables provide detailed information on key soil properties, enabling a comprehensive understanding of the sampled soils' composition.

Table 2. Chemical characterization of soil samples collected from the top layer (0.0-0.20 m) in Triângulo Mineiro region, Minas Gerais state, Brazil

Soil	pH	P	K	Ca	Mg	Al	H+Al	H	rem-P	MO
		 mg dm ⁻³				 cmol _c dm ⁻³			mg L ⁻¹	dag kg ⁻¹
C1	5.4	1.0	285.7	3.9	2.1	0.1	4.1	4.0	21.0	1.9
C2	5.2	1.7	129.0	7.4	2.5	0.1	4.7	4.6	11.6	2.1
C3	6.0	1.2	234.3	4.2	2.2	0.0	3.5	3.5	12.3	2.1
A6	4.4	0.8	51.9	0.9	0.4	0.5	3.4	2.9	18.3	1.6
A7	4.8	2.1	101.3	1.9	0.8	0.3	2.5	2.2	32.8	1.2
A8	4.9	10.0	47.9	1.0	0.4	0.2	1.7	1.5	55.6	0.9
N9	4.8	0.9	26.2	0.1	0.1	0.4	1.7	1.3	48.7	0.9
N10	4.6	0.6	6.4	0.4	0.1	0.3	2.0	1.7	35.7	0.9
N11	4.8	0.7	14.3	0.5	0.1	0.4	1.9	1.5	42.5	1.0
N12	4.7	0.9	22.2	0.8	0.2	0.1	1.4	1.3	51.1	0.9
L13	5.1	5.4	77.6	2.0	0.4	0.0	2.4	2.4	25.7	1.5
L14	4.7	3.3	115.2	2.8	1.1	0.0	2.8	2.8	20.9	1.6
L15	5.8	16.4	79.6	3.9	0.9	0.0	1.6	1.6	37.0	2.2
L16	4.1	0.9	75.6	0.4	0.1	0.1	4.1	4.0	3.5	2.0

pH in water, ratio v/v 1/2.5; P, K- Mehlich-1 extractor; Ca²⁺, Mg²⁺ and Al³⁺ (1.0 mol/L KCl extractor); H+Al in 0.5 mol/L calcium acetate, pH 7.0; MO (Organic Matter) - Colorimetric Method; S= Monocalcium Phosphate; rem-P= remaining P concentration of a 60 mg/L P solution in 0.01 mol/L CaCl₂.

Table 3. Physical characterization of soil samples collected from the top layer (0.0-0.20 m) in Triângulo Mineiro region, Minas Gerais state, Brazil

Soil*	Coarse Sand	Fine Sand	Silt	Clay	Texture
.....g/kg.....					
C1	44	131	320	505	clayey
C2	29	80	319	752	clayey
C3	43	119	283	555	clayey
A6	108	293	264	335	medium
A7	345	283	135	237	medium
A8	267	509	44	180	medium
N9	257	557	33	153	sandy
N10	316	480	58	146	sandy
N11	330	459	59	152	medium
N12	270	534	76	120	sandy
L13	356	235	138	271	medium
L14	118	67	179	636	very clayey
L15	32	127	453	388	clayey
L16	223	95	281	401	clayey

*C1 (CXbe1); C2 (CXbe2); C3 (CXbe3); A6 (PVAe1); A7 (PVAe2); A8 (PVAe3); N9 (RQo1); N10 (RQo2); N11 (RQo3); N12 (RQo4); L13 (LVw1); L14 (LVw2); L15 (LVAd3); L16 (LAd4).

Potential acidity reference

To measure the reference potential acidity of the soils, 150 g of each soil sample were incubated with varying rates of CaCO_3 PA, corresponding to 0, 25, 50, 100, 150, 200, and 250 % of the H+Al content of each soil. The 100% rate was established based on the H+Al content obtained using the 0.5 mol L⁻¹ calcium acetate method at pH 7.0. Upon homogenizing the soil-amendment mixture in plastic bags, distilled water was added to achieve approximately 80 % of the soil's field capacity. Every three days, the bags were opened to allow the release of CO₂ generated by the acidity neutralization reaction. The trial was concluded when the soil pH stabilized over time.

The reference potential acidity for pH 7.0 was estimated considering the equations presented in Table 5, which correlate the CaCO_3 rates (x) with the soil pH (y).

Estimating of potential acidity in SMP

The potential acidity of the soils was estimated using two methods: the traditional SMP method, as described by RAIJ et al. (2001), which is integrated with the routine for measuring pH in water (DEFELLIPO; RIBEIRO, 1997), and the modified SMP method, without the potassium dichromate ($K_2Cr_2O_7$) reagent. For both SMP methods, the 14 soils described in Tables 1 and 2 were used, with analyses performed in triplicate. The preparation of the SMP buffer, including the modified version, followed the official methodology of Pratt et al. (1961). The procedure involved transferring 10 cm³ of air-dried soil (≤ 2 mm) into a 50 mL flask, to which 25 mL of 0.01 mol/L $CaCl_2$ solution and 5 mL of SMP solution were added. The soil-buffer suspension was shaken for 15 minutes on a horizontal orbital shaker at 180 rpm. After shaking, the suspension was left to rest for 1 hour, after which the pH was measured. The H+Al content was estimated using the equations described in the Table 4.

Table 4. Equations used to estimate H+Al content (cmol_c dm⁻³) from the equilibrium pH of both SMP and modified SMP buffer solutions

N	Reference	Equation
1	Quaggio et al. (1985)	$\ln (H + Al) = 7.76 - 1.053 \text{ pH}_{SMP}$
2	Correa et al. (1985)	$\ln (H + Al) = 8.06 - 1.11 \text{ pH}_{SMP}$
3	Sousa et al. (1989)	$\ln (H + Al) = 7.719 - 1.068 \text{ pH}_{SMP}$
4*	Ecosteguy; Bissani, (1999)	$\log (H+Al) = (3.914 - 0.391 \text{ pH}_{SMP})/10$
5*	Silva et al. (2000)	$H+Al = [31.521 (\text{pH}_{SMP})^2 - 451.61 \text{ pH}_{SMP} + 1625.3]/10$
6	Silva et al. (2002)	$H+Al = 0.00359 + 1,556.5806 e^{-\text{pH}_{SMP}}$
7	Ferreira et al. (2004)	$H + Al = 35.57 - 4.81 \text{ pH}_{SMP}$
8	PROFERT (2005)	$\ln (H+Al) = 8.0629 - 1.110 \text{ pH}_{SMP}$
9	Kaminski et al. (2002)	$\log (H + Al) = 3.020 - 0.371 \text{ pH}_{SMP}$
10	Embrapa (2022)	$H + Al = - 0.6896 (\text{pH}_{SMP})^2 + 5.6458 (\text{pH}_{SMP}) - 3.7178$
11	Gama et al. (2013)	$\text{Ln} (H+Al) = 8.06 - 1.111 \text{ pH}_{SMP}$
12	Moline et al. (2011)	$H+Al = 31.22 - 8.20 \text{ pH}_{SMP} + 0.59 \text{ pH}_{SMP}^2$
13	Júnior et al. (2015)	$H+Al = 57.108 - 13.338 \text{ pH}_{SMP} + 0.7637 \text{ pH}_{SMP}^2$
14	Araujo et al. (2014)	$H + Al = 62.08 - 14.394 \text{ pH}_{SMP} + 0.8263 \text{ pH}_{SMP}^2$
15	Silva (2005)	$\text{Ln} (H+Al) = 8.93 - 1.255 \text{ pH}_{SMP}$

...Continued

... Continued

16	Vilela (2020)	$H+Al = 53.105 - 26.54 \ln (pH_{SMP})$
17*	Silva et al. (2000)	$H + Al = [31.521 (pH_{SMP})^2 - 451.61 pH_{SMP} + 1625.3]/10$
18	Fornasari et al. (2023)	$H + Al = 10743.6198 e^{(-1.2479 pH_{SMP})}$
19	Prado et. Al. (2020)	$H + Al = 51.189 - 25.70 \ln (pH_{SMP})$
20	Gama et al. (2013)	$H + Al = 77.77 + 20.61 pH_{SMP} - 1.435 pH_{SMP}^2$

*SMP equations 4, 5 and 17 were modified (/10) for the H+Al content to be expressed in $cmol_c.dm^{-3}$

The approximation degree or deviation of estimated H+Al content by the SMP buffer equations (obtained H+Al), in the presence or absence of $K_2Cr_2O_7$, in relation to the reference method (reference H+Al) was investigated by calculating the relative trend as a percentage of deviation, following Eq. 1.

$$Relative\ Trend\ (\%) = \frac{(Obtained\ H+Al - Reference\ H+Al) \times 100}{Reference\ H+Al} \quad Eq. 1$$

Soil acidity potential in Calcium Acetate

Eight contrasting soils in terms of H+Al content were selected within each pedogenetic class (soils 1, 2, 7, 8, 11, 12, 14 and 16 - Table 2), in order to assess the impact of varying calcium acetate concentrations at pH 7.0 or 8.0 on H+Al content. The trial followed a factorial scheme of 8 x 4 x 2, with eight soils (two soils from each pedogenic class), four calcium acetate concentrations (0.25; 0.5; 1 and 1.5 mol/L) and two pH (7.0 and 8.0). The treatments were distributed in randomized blocks, with three replicates. The extraction and acidity measurement methodology of Defellipo; Ribeiro (1997) was followed.

After the soil/extractor suspension had rested for 16 h, before acid-base titration, the equilibrium pH was measured in order to evaluate soil and extractor concentration effect on initial pH displacement and, consequently, such effects on H+Al content. Subsequently, 25 mL aliquots of the supernatant of each sample were taken, in which the acidity was measured by acid-base titration with $0.025\ mol\ L^{-1}$ NaOH solution, using phenolphthalein as an indicator.

For statistical data analysis, a randomized block design (RBD) was considered, since due the high number of samples, the dosage was made following the repetitions. Initially, the errors normality and variance homogeneity were verified. The trends were

evaluated by t-test. Models used to estimate soil H⁺Al content as a function of SMP pH were adjusted from the validation by means of correlation analysis between the reference H⁺Al contents and those estimated by the models under test. Regression analysis was conducted to study the effect of calcium acetate concentrations on the potential soil acidity extraction. The probability of error α for all analyses was 5 %.

RESULTS AND DISCUSSION

Potential acidity reference

The soils potential acidity reference at pH 7.0 was obtained from regression equations described in the Table 5. Considering the determination coefficient value (R^2), the quadratic model best adjusted to the data. The equations parameters were not tested because pH and H+Al variables are independent, being suitable for correlation analysis, which was highly significative for all soils. However, since the correlation model is linear, it is not very predictive, limiting the phenomenon description, the model that best fit the data based on the R^2 value was chosen for presentation. Since a pH equal to or greater than 7.0 was reached for all soils, the models were considered suitable for estimating the H+Al content at pH 7.0.

Soils presented a wide variation in H+Al contents, between 2.14 and 8.44 $\text{cmol}_c\text{dm}^{-3}$ (Table 5). This variability is expected due to different soils studied, once they present expressive differences in terms of chemical (organic matter content, exchangeable acidity, rem-P), physical (clay content) or pedogenic attributes (different classes) (Tables 2 and 3). Therefore, this variation makes the scope of the study broader regarding the buffering range of soil acidity.

Table 5: Regression equations relating the pH reached (y) with CaCO_3 rates, in neutralizing equivalent of H+ Al as $\text{cmol}_c \text{dm}^{-3}$ (x), coefficient of determination (R^2), highest pH and estimated H+Al content for pH 7.0

Soil*	Equation	R^2	pH _{highest}	H+Al
C1	$\hat{y} = 5.434 + 0.4287x - 0.0206x^2$	0.99	7.69	4.73
C2	$\hat{y} = 5.2797 + 0.3551x - 0.0129x^2$	0.99	7.74	6.27
C3	$\hat{y} = 5.8415 + 0.3025x - 0.011x^2$	0.98	7.65	4.60
A6	$\hat{y} = 4.307 + 0.3849x - 0.0078x^2$	0.99	7.00	8.44
A7	$\hat{y} = 4.5394 + 0.6362x - 0.0337x^2$	0.99	7.24	5.43
A8	$\hat{y} = 4.8884 + 0.9778x - 0.07x^2$	0.99	7.83	2.67
N9	$\hat{y} = 4.4524 + 0.7768x + 0.0051x^2$	0.97	7.52	3.21
N10	$\hat{y} = 4.7752 + 1.0696x - 0.0886x^2$	0.99	7.98	2.67
N11	$\hat{y} = 3.7054 + 1.6158x - 0.1609x^2$	0.99	7.81	2.84
N12	$\hat{y} = 4.6915 + 1.402x - 0.15x^2$	0.99	7.86	2.14
L13	$\hat{y} = 5.1643 + 0.4458x - 0.0091x^2$	0.99	7.50	4.54
L14	$\hat{y} = 4.7132 + 0.369x - 0.005x^2$	0.99	7.09	6.83
L15	$\hat{y} = 5.8259 + 0.486x - 0.019x^2$	0.99	7.47	2.70
L16	$\hat{y} = 4.2838 + 0.5183x - 0.0216x^2$	0.99	7.39	7.73

*C1 (CXbe1); C2 (CXbe2); C3 (CXbe3); A6 (PVAe1); A7 (PVAe2); A8 (PVAe3); N9 (RQo1); N10 (RQo2); N11 (RQo3); N12 (RQo4); L13 (LVw1); L14 (LVw2); L15 (LVAd3); L16 (LAd4).

Potential acidity in standard and modified SMP.

No tested equation provided accuracy in estimating H+Al contents for all soils (Table 6). In most cases (72.5%), the equations underestimated the H+Al contents. Among the soils, the trends increased (absolute values) in the following order: Utisols, Entisols, Ultisols and Oxisol. Despite the lowest average trends for equations 19, 13 and 18, they provided accurate values for only 29% of the soils. Equations 4 and 3 did not present accurate data for any soil.

The SMP buffer modified method (Figure 7) generally increased the trends. In fact, there was an underestimation of the H+Al content for only 20% of the soils. Equations 3 and 6 were the most predictive.

Table 6: Relative trend for H+Al content obtained by SMP equations (Table 4) in relation to the reference method (soils incubation with CaCO₃).

Equation	Soil														Mean	CV
	C1	C2	C3	A6	A7	A8	N9	N10	N11	N12	L13	L14	L15	L16		
	 %															
1	-12.4	-27.1	-11.8	-51.9	-38.4	-9.9*	-22.6	-12.3	1.9*	5.1*	-30.8	-52.4	-7.5	-37.7	23.0	74.0
2	-16.6	-30.2	-16.1	-54.3	-42.0	-16.7	-28.3	-19.1	-4.9*	-3.2*	-35.1	-55.3	-14.3	-40.2	26.9	62.2
3	-23.2	-36.0	-22.6	-57.9	-46.1	-21.6	-32.6	-23.7	-11.1	-8.6	-39.6	-58.4	-19.4	-45.2	31.9	50.0
4	-69.7	-77.0	-68.9	-83.1	-74.1	-48.8	-57.3	-48.9	-51.1	-36.5	-69.2	-79.5	-49.2	-81.2	63.9	23.4
5	3.5*	-10.7*	3.4*	-43.7	-34.3	-24.5	-33.3	-28.2	-1.2*	-17.0	-29.1	-50.1	-20.0	-22.5	23.0	65.0
6	-19.9	-33.7	-19.3	-56.0	-43.0	-15.3	-27.4	-17.5	-5.1*	-0.8*	-35.8	-55.9	-13.2	-43.5	27.6	63.7
7	39.8	12.6	41.7	-22.8	3.8*	54.6	33.1	49.8	75.3	78.7	17.8	-19.4	59.4	-5.5*	36.7	66.7
8	-15.9	-29.6	-15.3	-53.9	-41.5	-16.0	-27.7	-18.4	-4.0*	-2.3*	-34.5	-54.8	-13.5	-39.6	26.2	64.4
9	29.4	5.7*	30.8	-28.7	-5.2*	47.5	25.9	44.2	61.1	74.2	7.7*	-26.4	50.4	-10.5	32.0	66.6
10	11.6	-12.0	13.6	-38.1	-13.3	39.3	19.0	35.9	51.2	63.8	-0.2*	-32.2	42.4	-27.0	28.5	62.5
11	-16.6	-30.2	-16.1	-54.3	-42.0	-16.7	-28.3	-19.1	-4.9*	-3.2*	-35.1	-55.3	-14.3	-40.2	26.9	62.2
12	-31.5	-46.6	-30.1	-61.9	-44.0	6.0	-11.3	5.5	3.3*	30.9	-34.1	-55.8	5.5*	-55.9	30.2	69.3
13	-5.1*	-22.1	-4.2*	-47.8	-32.2	-4.3*	-17.2	-7.6*	11.6	9.6*	-23.9	-47.6	-0.8	-34.0	19.1	83.4
14	13.6	-7.6	14.9	-37.4	-17.0	23.5	6.2*	20.0	39.4	43.6	-6.1*	-35.6	27.0	-22.0	22.4	56.3
15	-16.3	-29.0	-16.0	-54.3	-43.5	-22.5	-33.0	-24.9	-9.1*	-10.7*	-37.3	-56.6	-19.8	-38.7	29.4	51.5
16	15.5	-6.2*	16.9	-36.3	-15.6	22.8	6.0*	18.8	41.0	41.2	-4.7*	-34.6	26.9	-21.0	22.0	57.1
17	3.5*	-10.7	3.4*	-43.7	-34.3	-24.5	-33.3	-28.2	-1.2*	-17.0	-29.1	-50.1	-20.0	-22.5	23.0	65.0
18	24.2	5.2*	24.6	-32.1	-16.0	15.5	-0.2*	11.8	35.2	33.1	-6.8*	-35.4	19.4	-9.2*	19.2	61.7
19	6.9	-13.0	8.1*	-41.1	-22.6	10.1*	-4.7*	6.2*	28.3	25.8	-12.9	-40.1	14.2	-26.6	18.6	65.7
Mean (%)	19.8	23.4	19.9	47.3	32.1	23.2	23.5	23.2	23.2	26.6	25.8	47.1	23.0	32.8		
CV (%)	78.2	76.0	77.5	29.2	54.1	62.4	58.3	57.9	102.3	92.4	65.2	29.8	70.0	54.3		

Relative trend = (Obtained H+Al - Reference H+Al) / (Reference H+Al) x 100. Mean and Coefficient of Variation (CV) were calculated with absolute trends. *Indicates non-significant trend at 5% probability by t-test.

Table 7: Relative trend for H+Al contents obtained by the SMP equations (Table 4), with the absence of potassium dichromate in the buffer solution, in relation to the reference method (incubation of soils with CaCO₃)

Equation	Soil														Mean	CV
	C1	C2	C3	A6	A7	A8	N9	N10	N11	N12	L13	L14	L15	L16		
	 %															
1	43.2	27.3	33.0	-8.9*	12.4	34.9	32.3	26.6	78.3	49.5	11.4	-30.7	30.5	11.2	30.7	59.8
2	40.0	25.7	29.3	-10.2*	9.3*	27.4	26.1	19.2	71.6	40.5	7.3*	-33.5	23.2	10.2	26.7	63.5
3	26.4	12.7	17.2	-19.4	-0.9*	18.0	16.1	10.7	56.8	30.6	-2.0*	-39.1	14.2	-1.5	19.0	81.2
4	-68.4	-75.8	-67.8	-82.1	-72.7	-47.0	-55.3	-47.3	-48.7	-34.6	-67.9	-78.8	-47.7	-80.3	62.5	24.5
5	89.2	69.3	73.8	21.0	46.8	49.5	57.7	35.7	124.8	55.2	40.5	-14.2	43.1	47.6	54.9	51.3
6	27.6	12.6	19.1	-19.3	0.7*	24.1	20.8	17.0	61.3	38.3	0.8*	-37.1	20.3	-2.1	21.5	76.3
7	87.3	53.3	82.5	11.8	54.3	123.1	109.0	112.9	165.1	149.1	65.8	5.8	117.6	28.7	83.3	59.1
8	41.2	26.7	30.4	-9.5*	10.2*	28.6	27.3	20.3	73.1	41.8	8.2*	-33.0	24.3	11.1	27.6	62.4
9	92.7	66.2	82.5	19.8	54.2	104.4	94.4	94.3	153.5	131.0	58.5	-0.2*	98.8	43.1	78.1	52.9
10	34.6	6.3	34.1	-21.8	13.4	83.4	65.9	77.5	102.7	110.0	26.8	-18.0	79.8	-12.2	49.0	73.5
11	40.0	25.7	29.3	-10.2	9.3*	27.4	26.1	19.2	71.6	40.5	7.3*	-33.5	23.2	10.2	26.7	63.5
12	-18.0	-33.8	-19.0	-51.6	-31.5	16.2	1.7	14.2	22.1	40.7	-23.6	-50.4	14.2	-44.6	27.3	55.5
13	39.3	17.5	33.2	-14.9	12.6	47.7	42.6	39.3	86.8	62.1	16.9	-26.4	43.4	0.0	34.5	65.3
14	61.3	35.0	55.0	-2.0*	31.1	79.3	70.4	70.3	120.0	100.0	37.6	-12.9	74.5	14.5	54.6	62.7
15	50.3	37.9	36.8	-2.0*	15.6	25.5	27.1	16.3	77.0	36.6	10.6	-32.1	20.9	22.1	29.3	63.4
16	60.8	33.4	55.4	-3.0*	31.3	82.4	73.0	73.2	122.4	102.2	39.1	-11.7	77.6	12.7	55.6	63.8
17	89.2	69.3	73.8	21.0	46.8	49.5	57.7	35.7	124.8	55.2	40.5	-14.2	43.1	47.6	54.9	51.3
18	122.3	103.8	102.6	44.9	71.1	86.4	88.5	72.9	162.3	103.0	63.9	0.7*	79.6	80.4	84.4	44.0
19	50.7	25.4	45.3	-8.9*	22.9	67.8	60.2	58.9	107.0	84.8	29.5	-18.0	63.3	6.1	46.3	63.8
Mean (%)	57.0	39.9	48.4	20.1	28.8	53.8	50.1	45.3	96.3	68.7	29.4	25.8	49.4	25.6		
CV (%)	48.8	65.1	52.3	98.4	79.1	58.5	58.1	67.2	41.3	53.2	76.6	73.1	62.5	97.4		

Relative trend = (Obtained H+Al - Reference H+Al) / (Reference H+Al) x 100. Mean and Coefficient of Variation (CV) were calculated with absolute trends. *Indicates non-significant trend at 5% probability by t-test.

Although some SMP equations have shown accuracy with respect to the reference method, the variation in trends between soils, including within the same class, clay content or P-rem concentration, makes them unacceptable as a reliable method for estimating H+Al soil content. This low accuracy is due to the different mechanisms of buffering soil acidity that interact with SMP buffering in defining the equilibrium pH, such as active acidity, non-exchangeable and exchangeable acidity contents (ESCOSTEGUY; BISSANI, 1999; SILVA, 2005; SILVA et al., 2002). In fact, in sandier Entisols, the deviation tended to be lower due to their lower acidity buffering capacity. Although regional calibration is a premise for adjusting these SMP equations (KAMINSKI et al., 2002), the soil variability makes widespread use unfeasible. Additionally, expanding the use of these equations to regions with soils that contrast with those used for calibration may increase inaccuracy.

The underestimation of the H+Al content with the standard SMP method, for some equations, may be associated with the use of the 0,5 mol/L calcium acetate method at pH 7.0, since this method is adopted as a reference for the calibration of the standard SMP method. Previous studies prove this characteristic of underestimation of the H+Al content of soils by the calcium acetate method (VETTORI, 1969; KAMINSKI 1974; ERNANI; ALMEIDA, 1986; SOUZA et al., 1989, SILVA, 2005).

The reduction in the buffering capacity of the SMP solution, resulting from the exclusion of potassium dichromate, leads to a decrease in the accuracy of the method. Potassium dichromate is an oxidizing agent, especially in more acidic conditions, it does not directly affect the solution acidity buffering power as it does not form weak acids but seems to interact with some solution component such as triethanolamine, imidazole or calcium acetate, increasing buffering acidity (SOUZA et al., 2014).

SMP equations were previously calibrated under highly diverse regional conditions, which partly explains the significant variability in their adjustments in relation to the actual H+Al content. Another critical factor is that soil analysis laboratories routinely handle soils with a wide range of physical and chemical characteristics, which can have an even greater influence on the accuracy of these equations than regional factors only (SILVA, 2005).

Potential acidity from SMP-pH

According to the significance correlation between estimated H+Al content ($H+Al_{Est}$) by the tested equations and measured by the incubation method ($H+Al_M$) -

graphs B of Figures 3, 4, 5, 6 and 7, the models for graphs A of the respective Figures were selected. Indeed, it is not possible to test the regression parameters, since the variables are independent, but is a study aim to establish predictive equations for soil H+Al content as a function of SMP-pH.

For all soils (Figure 2 A), considering the presence of potassium dichromate in the SMP buffer, the predictive capacity of the equation that best fitted the data was considered low, underestimating the soils H+Al content by an average of 24% (Figure 2 B).

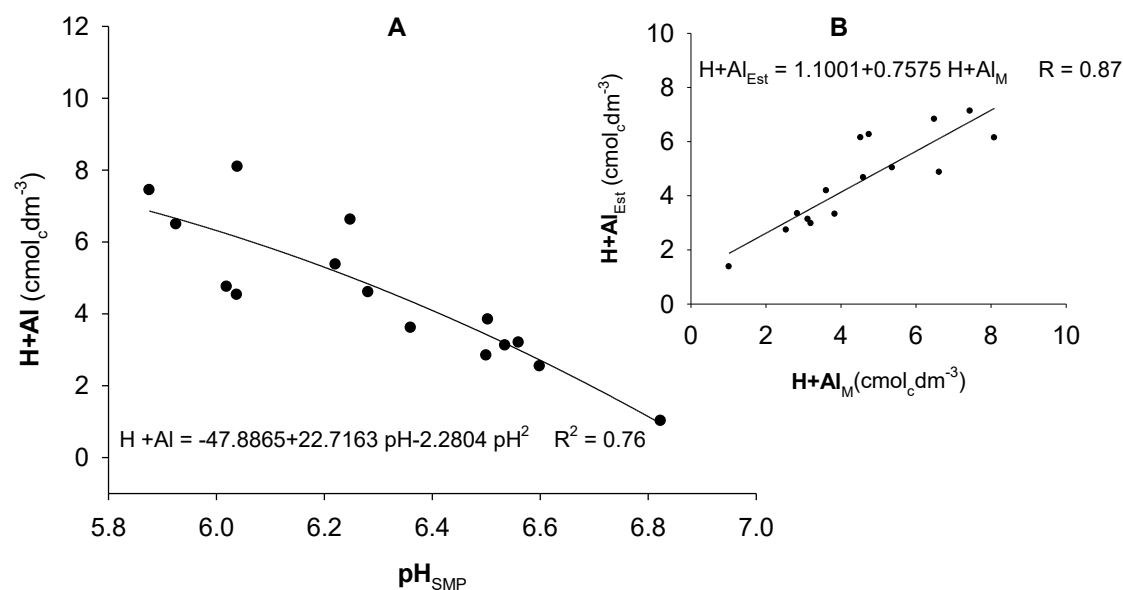


Figure 2. Relationship between reference potential acidity (H+Al) and SMP-pH in the presence of potassium dichromate (A). The inner graph (B) represents the correlation between reference ($H+Al_M$) and estimated contents of acidity ($H+Al_{Est}$) from the fit equation (A).

When the soils were grouped into the classes Latosols-Argisols (Figure 3) and Neosols-Cambisols (Figure 4), the predictive capacity of the equations increased significantly. For the Latosols-Argisols, the prediction accounted was 94% of the reference H+Al content, while for the Neosols-Cambisols, the prediction reached 98%. This improvement was attributed to the similarity in buffering characteristics within each soil class, which was considered when grouping the soils.

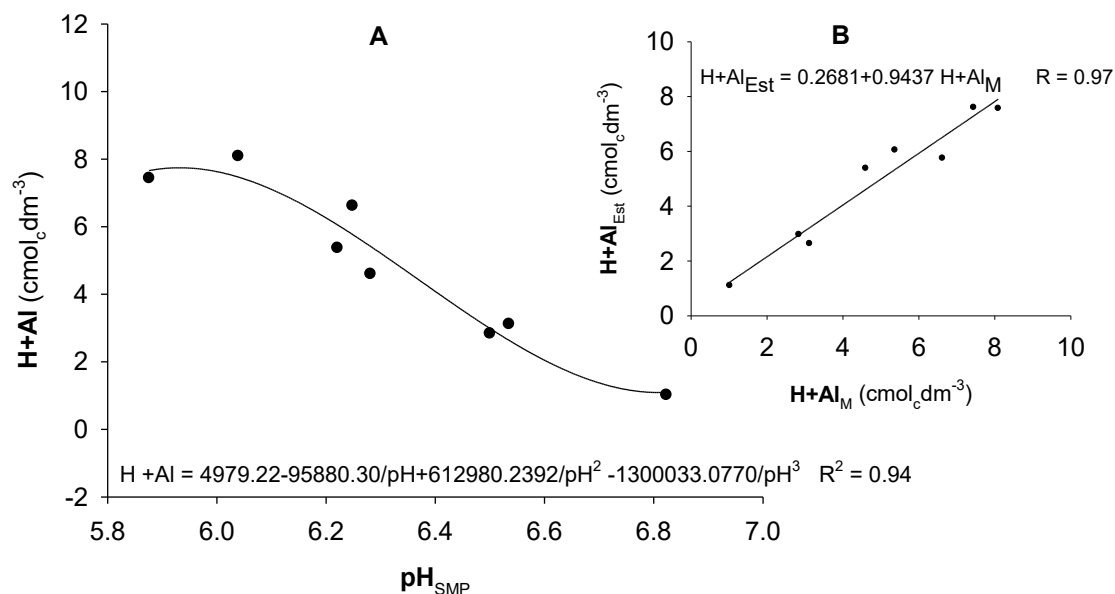


Figure 3. Relationship between potential acidity reference ($H+Al$) and SMP-pH in the presence of potassium dichromate (A) for *Oxisol-Ultisols classes. The internal graph (B) represents the correlation between reference ($H+Al_M$) and estimated contents of acidity ($H+Al_{Est}$) from the fit equation (A). *Soil classification according to the Brazilian soil classification system.

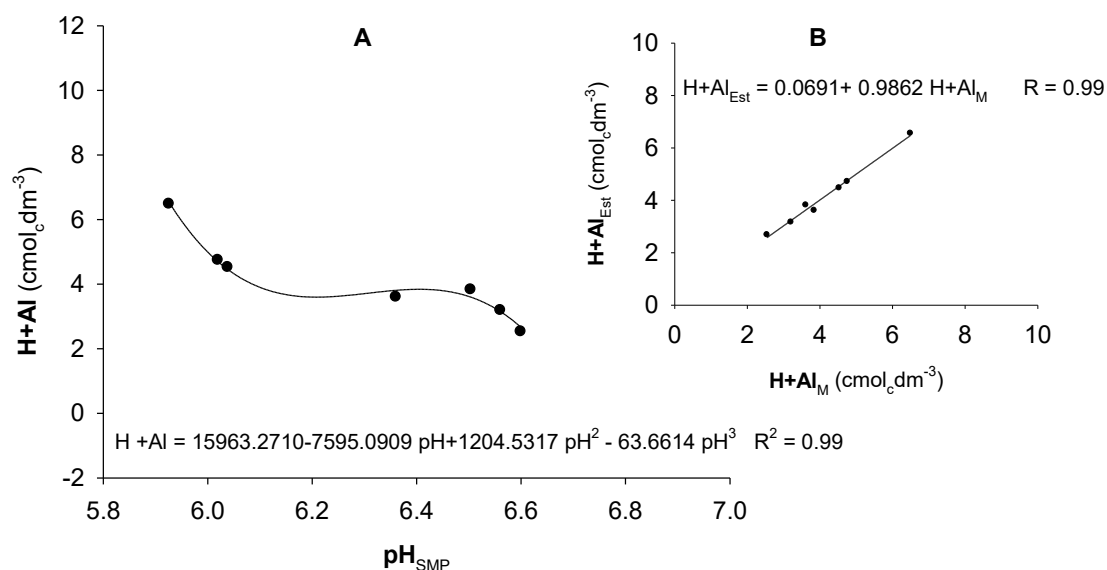


Figure 4. Relationship between reference potential acidity ($H+Al$) and SMP-pH in the presence of potassium dichromate (A) for *Entisolss-Utisols classes. The internal graph (B) represents the correlation between reference ($H+Al_M$) and estimated contents of acidity ($H+Al_{Est}$) from the fit equation (A). *Soil classification according to the Brazilian soil classification system.

In the absence of potassium dichromate in the SMP buffer composition, the prediction of $H+Al$ content improved, reaching 79 % of the reference content, compared to predictions made with potassium dichromate. However, this improvement was observed only when all soils were considered together (Figure 5).

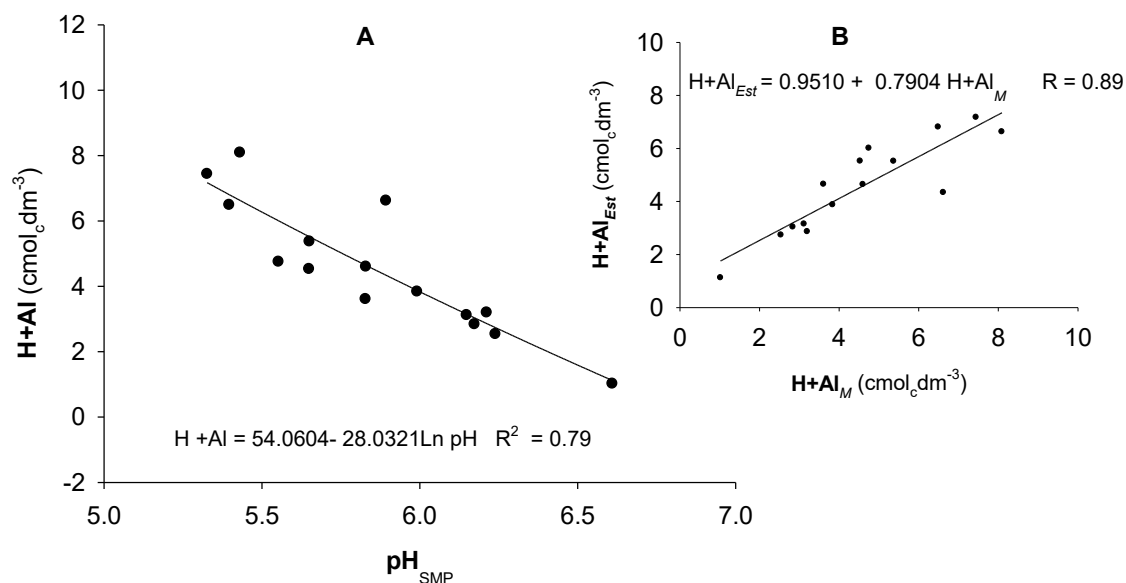


Figure 5. Relationship between reference potential acidity ($H+Al$) and SMP-pH in the absence of potassium dichromate (A). The inner graph (B) represents the correlation between reference ($H+Al_M$) and estimated contents of acidity ($H+Al_{Est}$) from the fit equation (A).

As observed in the presence of potassium dichromate, in its absence it also showed that grouping soils increased the predictive capacity of the equations. The prediction accuracy rose to 87 % for Latosols-Argisols (Figure 6) and 91 % for Neosols-Cambisols (Figure 7). This improvement highlights the importance of soil grouping based on similar buffering characteristics, even when potassium dichromate is excluded from the SMP buffer composition.

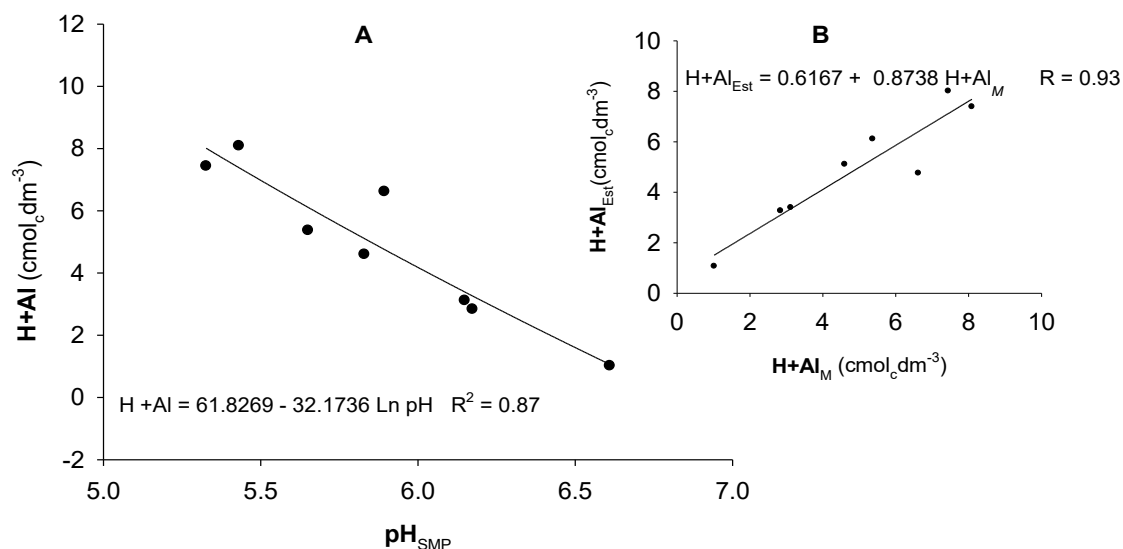


Figure 6. Relationship between reference potential acidity ($H+Al$) and SMP-pH in the absence of potassium dichromate (A) for *Oxisols - Ultisols classes. The internal graph (B) represents the correlation between reference ($H+Al_M$) and estimated contents of acidity ($H+Al_{Est}$) from the fit equation (A). *Soil classification according to the Soil Taxonomy system.

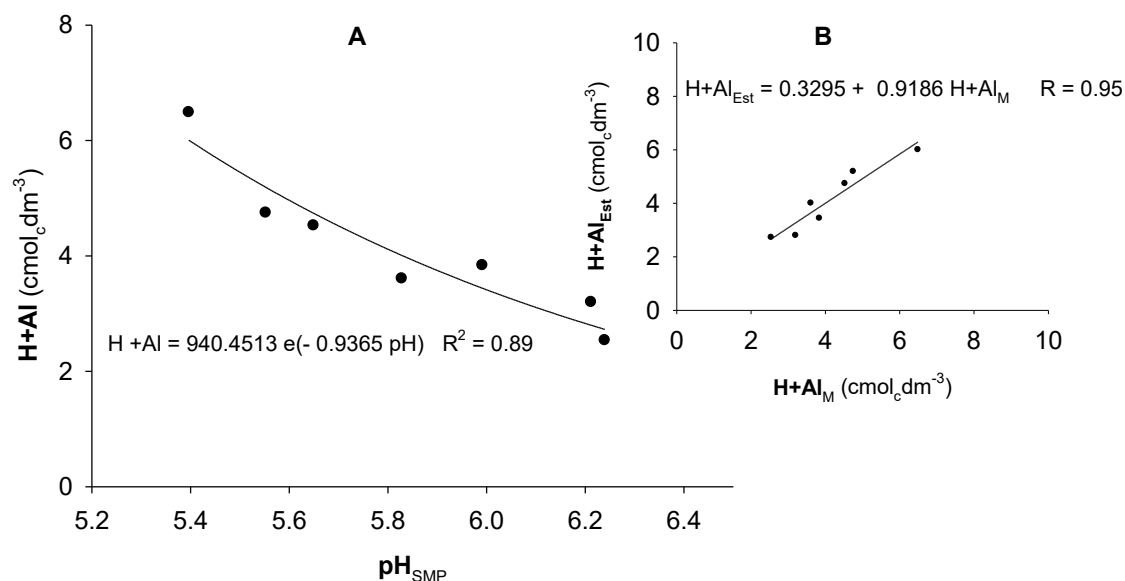


Figure 7. Relationship between reference potential acidity ($H+Al$) and SMP-pH in the absence of potassium dichromate (A) for *Entisols-Inceptisols classes. The internal graph (B) represents the correlation between reference ($H+Al_M$) and estimated contents of acidity ($H+Al_{Est}$) from the fit equation (A). *Soil classification according to the Brazilian soil classification system.

The prediction improvement of soils potential acidity, when they were grouped into Oxisols-Ultisols and Entisols-Utisols, is attributed to the similarity of buffering mechanisms between them, especially in relation to non-exchangeable acidity (pKa of functional groups), which was predominant in the soils. The clay contents, organic matter, exchangeable acidity, non-exchangeable acidity, potential acidity or remaining P (see Tables 2 and 3) content did not explain the similarities. Indeed, while the Entisols presented remaining P contents higher than 35 mg/L, low organic matter content and clay contents ranging from 120 to 152 g/kg, the Utisols varied from clayey to very clayey, with low remaining P contents (maximum of 21 mg/L) and with organic matter contents close to twice that of the Entisols. They were also contrasting in terms of different types of acidity content. Investigating the second group, between Oxisols and Ultisols, the Oxisols texture ranged from medium to very clayey, while Ultisols had a medium texture. Furthermore, regarding organic matter content, there was a variation of 1.5 to 2.2 dag/kg for the Oxisols and 0.9 to 1.6 dag/kg for the Ultisols. Regarding the remaining P contents, there was a great variation between the soils, from 18 to 56 mg/L for Ultisols and from 3.5 to 37 mg/L for Oxisols. In addition, regarding content of exchangeable, non-exchangeable and potential acidity, they were not convergent.

Despite the increase in accuracy within the soil groups, even if it is proposed to use correction factors in the equation underestimations and the need for prior classification of soils to better allocation equations, there is no guarantee that accuracy will be satisfactory.

Potential acidity in calcium acetate

Significant effects of the variation in calcium acetate concentration and buffer pH across different soils enabled the analysis of these factors within each soil type (Figure 8). At pH 8, the extraction of potential acidity was generally greater. A non-significant effect of calcium acetate concentration was observed only for Entisols (N), except for N12 at pH 7. For soils N 12, C2, A7 with extractor at pH 8.0 and C2 and L16 with extractor at pH 7.0, the linear models best fitted the data. For other treatments, first-order inverse models satisfactorily described the effect of buffer concentration on potential acidity contents.

The data regards calcium acetate concentrations at pH 7 or 8 effect on soil/extractor suspension equilibrium pH did not satisfy the assumptions of errors normality and variance homogeneity required for variance analysis. Thus, Figure 9 only presents the models trends considering the highest value of determination coefficient (R^2).

Overall, increasing the buffer capacity of the extractor by raising the concentration of calcium acetate and/or the pH resulted in higher equilibrium pH values. For soils N11, N12 and A8 with buffer at pH 8, an equilibrium pH equal to or greater than 7.0 was reached. For other combinations soil and pH, the equilibrium pH 7.0 was not reached, including the highest concentrations of calcium acetate at pH 8 (Figure 9).

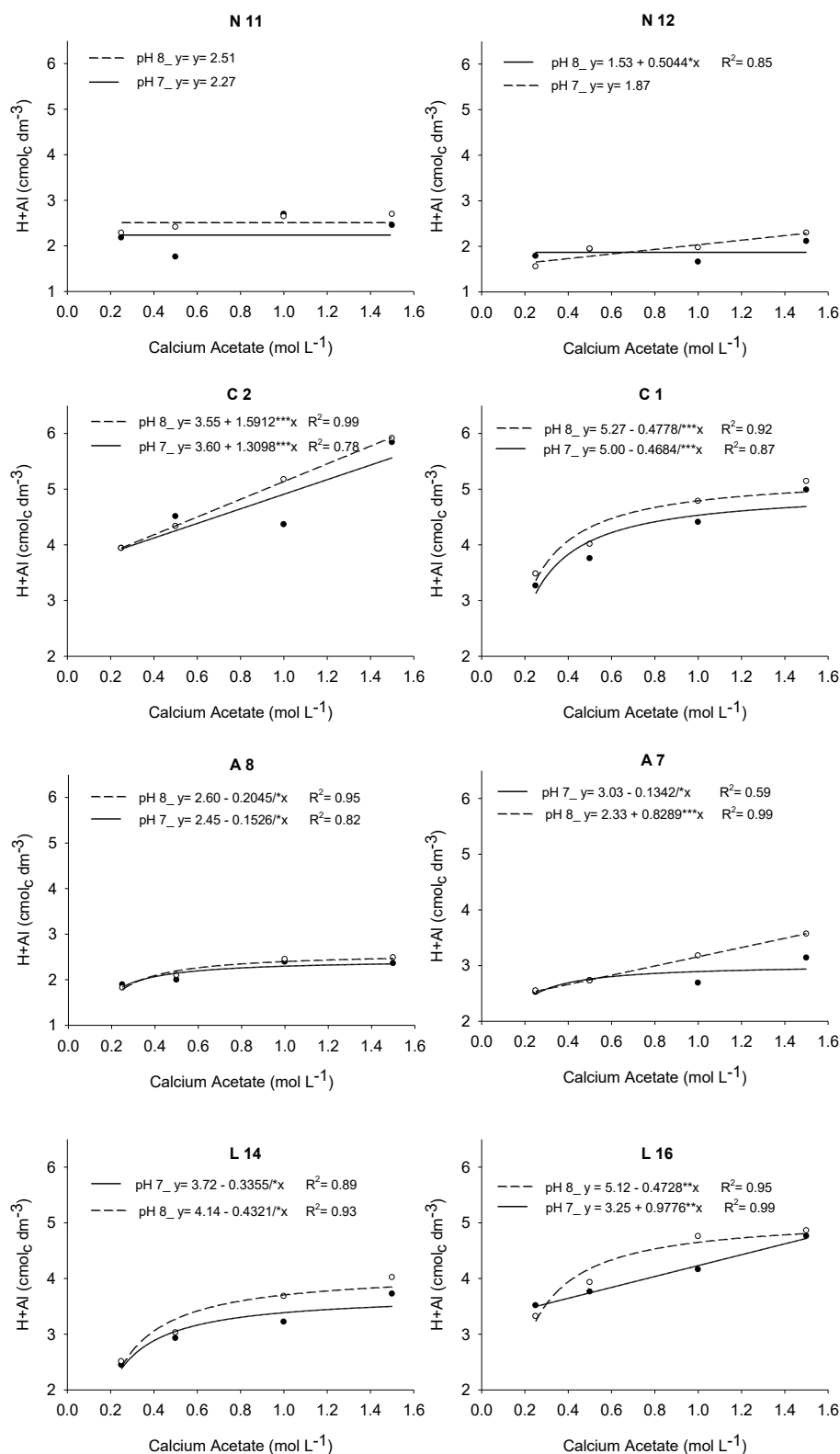


Figure 8. Regression models describing the relationship between calcium acetate concentration at pH 8 or 7 on soils potential acidity content in Triângulo Mineiro region, Minas Gerais, Brazil. *N11- Entisols Quartizarênico, N12-Entisols C2- Utisols, C1-Utisols, A8-Ultisols, A7-Ultisols, L14-Oxisols, L16- Oxisols Amarelo. * Soil classification according to the Brazilian soil classification system.

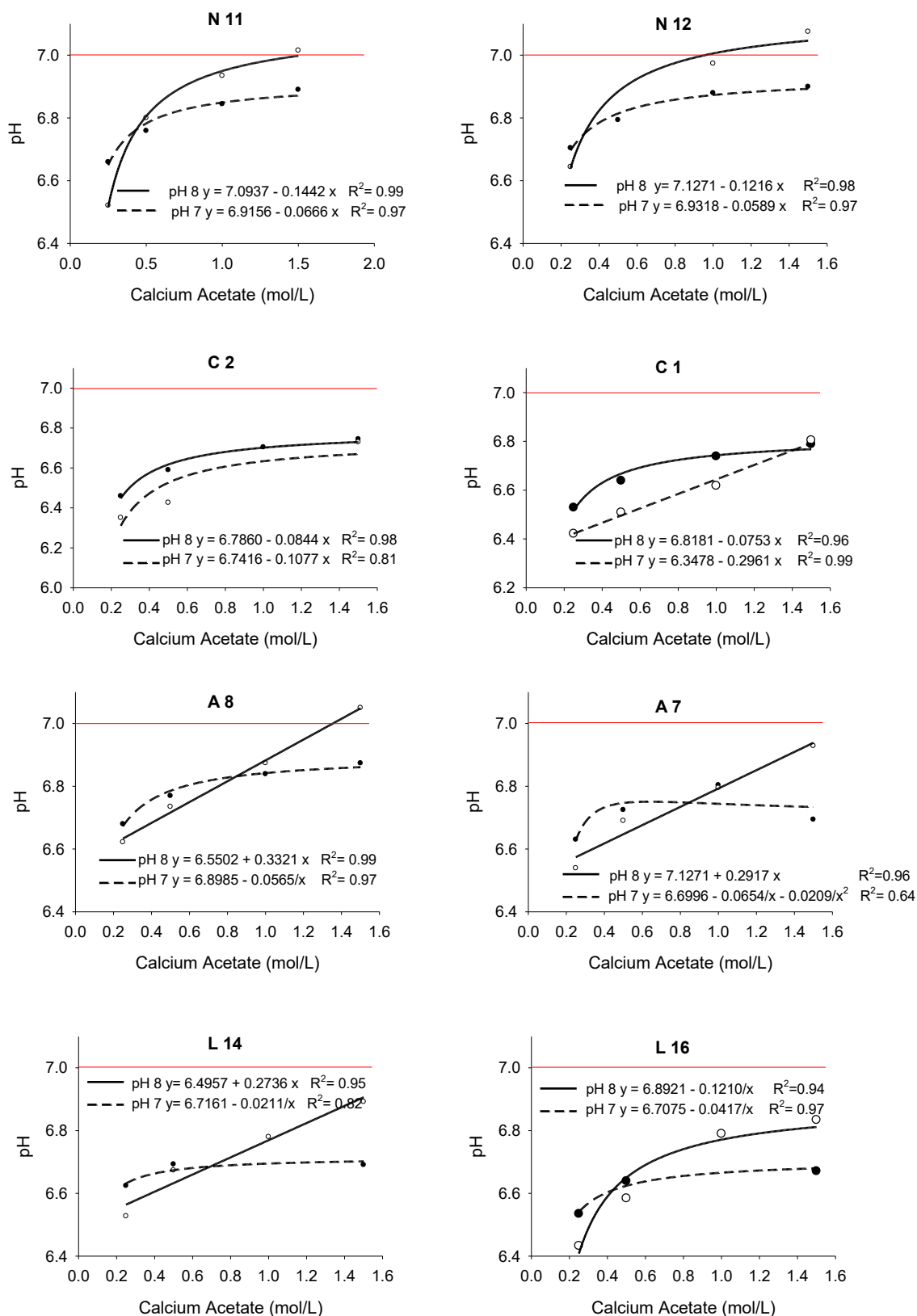


Figure 9. Relationship between calcium acetate concentration solution at pH 7 or 8 on the equilibrium pH before titrimetric dosing of the soil's potential acidity. *N11- Neossolo Quartzarênico, N12-Neossolo C2- Utisols, C1-Utisols, A8-Argissolo, A7-Argissolo, L14-Oxisols, L16- Oxisols yelow. *Soil classification according to the Brazilian soil classification system.

The magnitude of initial pH shifts of calcium acetate buffer to pH 7 or 8 is associated with soils acidity content and the buffering mechanisms, which include the content and type of mineral and organic clays (SAMBATTI et al., 2003). For exchangeable cations from acid hydrolysis, especially Al^{3+} , the buffering range typically take place until to pH 5.5 (KAMINSKI et al., 2002). The buffering of non-exchangeable acidity is associated with the acidity and abundance of different functional groups of variable charge (pKa) in soil colloids (RAIJ; KUPPER, 1966). Silva et al. (2006) and Kamiski et al. (2002) highlighted the importance of organic matter in the acidity of tropical soils.

Since non-exchangeable acidity constitutes the majority of potential soil acidity, the change in pH of calcium acetate buffer at equilibrium of soil/extractor suspension will negatively affect the method extraction capacity. Indeed, non-exchangeable acidity is accessed through ionization of protonated functional groups. As also observed by Zozimo (2005), the potential acidity estimated by incubation curves is generally higher than that estimated by calcium acetate, which is justified by the weak extractant buffering (VETTORI, 1969; RAIJ; KUPPER, 1966; SILVA et al., 2005).

The extraction of potential acidity determined by calcium acetate buffer would be complete if the soil/extractor suspension could reach a pH close to 7, since with pH shift to values below this, the calcium acetate solution is unable to access all the potential acidity and part of the non-exchangeable acidity is not accessed. Thus, it is highly expected, as confirmed in this study, that less buffered soils have easier access to this acidity content, unlike soils with high clay contents, including organic matter. However, the results demonstrate that even at the highest concentration of calcium acetate (1.5 mol L^{-1}) and pH 8, for most soils the equilibrium pH was not lower than 7.0. According to Silva (2005) the potential acidity determined in 0.5 mol/L calcium acetate pH 7.0 is equivalent to the acidity for pH 5.7 when compared to incubation method with CaCO_3 .

Comparing the performance of calcium acetate extractor in relation to the reference method, an underestimation of $\text{H}^+\text{+Al}$ content by calcium acetate method is observed, due to the displacement of soil/extractor suspension pH to values below 7, affecting the deprotonation of acidic groups in the soil. As a consequence, the present work results demonstrate that calcium acetate method use to estimate $\text{H}^+\text{+Al}$ values would not be ideal for adjusting other methods, such as SMP buffer, Sikora buffer and Santa Maria buffer (SMB) (PRADO et al. 2020), requiring correction factors use to adjust the

values, as recommended by Vettori (1969) who suggests adding 10% to the result obtained by titration with calcium acetate.

Although grouping soils by pedogenetic classes increases SMP equations accuracy, variations in acidity buffering mechanisms even within the same class can make the use of prediction equations unfeasible.

Given the uncertainties raised for both SMP equations development or acetate method optimization, it is suggested to consider methods for direct determination of soil H^+Al content or from direct determination of potential CEC and sum of bases..

CONCLUSION

The SMP and calcium acetate methods do not accurately determine the potential acidity of soils, often leading to underestimation or overestimation.

The SMP equations that best fitted the data were equations 13, 18, and 19 when in the presence of potassium dichromate.

The exclusion of potassium dichromate from the SMP buffer reduces the accuracy of the method.

The grouping soil classes- Oxisols with Ultisols and Entisols with Inceptisols- significantly increases the predictive capacity of the method.

The extraction capacity of potential soil acidity by the calcium acetate method was most effective at a concentration of 1.5 mol L^{-1} and a pH of 8.

The SMP equations evaluated in the study do not satisfactorily address the variation in Cerrado soils and may either underestimate or overestimate the H^+Al content.

Increasing the pH and calcium acetate concentration enhances its capacity to extract potential soil acidity.

REFERENCES

- ALVAREZ, V. V. H.; RIBEIRO, A. C. Calagem. Cap. 8, In: RIBEIRO, A. C.; GUIMARÃES, P. T. G.; ALVAREZ V. V. H. **Recomendações para o uso de corretivos e fertilizantes em Minas Gerais: 5ª Aproximação**. Viçosa: CFSEMG, 1999, p.43-61.
- ARAUJO, D. D. F.; CASTRO, G. S. A.; DAMASCENO, L. F. MONTAGNER, A. E. A. D.; GUEDES, M. C.; MELÉM JÚNIOR, N. J. Potential acidity of soils in the Amapá State estimated by the potentiometric SMP method. **Acta Iguazu**, v. 3, n. 3, p. 57-65, 2014. Disponível em: <https://www.cabidigitallibrary.org/doi/epdf/10.5555/20153242848>.
- DEFELLIPO, B. V.; RIBEIRO, A. C. **Análise Química do solo**. Viçosa, MG. UFV, 1981. 17p. (Boletim de Extensão).
- EMPRESA BRASILEIRA DE PESQUISA AGROPECUÁRIA - EMBRAPA. Centro Nacional de Pesquisa de Solos. **Manual de métodos de análise do solo**. 2ª.ed. Rio de Janeiro, 1997.
- ESCOSTEGUY, P. A. V.; BISSANI, C. A. Estimativa de H + Al pelo pH SMP em solos do Rio Grande do Sul e de Santa Catarina. **Revista Brasileira de Ciência do Solo**, v. 23, n. 1, p. 175-179, 1999. Disponível em: <https://doi.org/10.1590/S0100-06831999000100021>
- FINKLER, R. **Ciências do Solo e Fertilidade**. 1. ed. Porto Alegre: Sagra, 2018.
- FORNASARI, C. H.; GARCIA, Y. J. A.; DAMASCENO, F. M.; ZANÃO JÚNIOR, L. A. Estimate of Potential Acidity Using the pH SMP Method in Soils in the West Paraguay. *Communications in Soil Science and Plant Analysis*, v. 55, n. 2, p. 208-216, 2024. Disponível em: <https://doi.org/10.1080/00103624.2023.2265429>
- GAMA, M. A. P.; MATOS, G. S. B. D.; SILVA, G. R. D.; BRASIL, E. C.; NUNES, O. F. Potential acidity estimated by SMP pH in soils of the state of Pará. **Revista Brasileira de Ciência do Solo**, v. 37, n. 1, p.199-203, 2013. Disponível em: <https://doi.org/10.1590/S0100-06832013000100020>
- ALMEIDA JÚNIOR, A. B. A.; NASCIMENTO, C. W. A.; BARROS, F. M. R. Acidez Potencial Estimada pelo Método do pH SMP em Solos do Estado da Paraíba. **Revista Brasileira de Ciência do Solo**. V. 39, p. 767-773, 2015. Disponível em: <https://doi.org/10.1590/01000683rbs20140307>
- KAMINSKI, J.; GATIBONI, L. C.; RHEINHEIMER, D. S.; MARTINS, J. R.; SANTOS, E. J. S.; TISSOT, C. A. Estimativa da acidez potencial em solos e sua implicação no cálculo da necessidade de calcário. **Revista Brasileira de Ciência do Solo**, v. 26, p. 1107-1113, 2002. Disponível em: <https://doi.org/10.1590/S0100-06832002000400029>
- LIU, X.; LU, X.; SPRIK, M.; CHENG, J.; MEIJER, E. J.; WANG, R. Acidity of edge surface sites of montmorillonite and kaolinite. **Geochimica et Cosmochimica Acta**, v. 117, p. 180-190, 2013. Disponível em: <https://doi.org/10.1016/j.gca.2013.04.008>
- MAEDA, S.; KURIHARA, C.; HERNANI, L.; FABRICIO, A.; SILVA, W.; KURIHARA, C. H. Estimativa da acidez potencial, pelo método do SMP pH, em solos do Mato Grosso do Sul. EMBRAPA, Dourados, **Boletim de Pesquisa**, n.3, 1997. 25p.

PAVAN, M. A.; OLIVEIRA, E. L.; MIYAZAWA, M. Determinação indireta da acidez extraível do solo ($H + Al$) por potenciometria com a solução-tampão SMP. **Arquivos de Biologia e Tecnologia**, v. 39, p. 307-312, 1996.

PEREIRA, M. G.; ARAÚJO, A. L. S.; DORTZBACH, D.; TAVARES, O. C. H.; NETO, E. C. S. Estimativa da acidez potencial através do método do pH SMP em solos de altitude de Santa Catarina. **Agropecuária Catarinense**, v. 33, n. 1, 2020. Disponível em: <https://doi.org/10.52945/rac.v33i1.531>

PRADO, M. R. V.; MORAES, M. F. D.; RAMOS, F. T.; SANTOS, C. L. R. D.; CAMPOS, D. V. B. D.; BARROS, G. T. Use of buffer methods to estimate the potential acidity of Mato Grosso soils. **Ciência e Agrotecnologia**, v. 44, 2020. Disponível em: <https://doi.org/10.1590/1413-7054202044026019>

QUAGGIO, A. J.; RAIJ, B. Determinação do pH em cloreto de cálcio e da acidez total. In: RAIJ, B.; ANDRADE, J. C.; CANTARELLA, H.; QUAGGIO, J. A. **Análise química para avaliação da fertilidade de solos tropicais**. Campinas: Instituto Agrônômico de Campinas, p.181-188, 2001.

RAIJ, B.; CANTARELLA, H.; ZULLO, M. A. T. O método tampão SMP para determinação da necessidade de calagem de solos do estado de São Paulo. **Bragantia**, v. 38, p. 57-69, 1979. Disponível em: <https://doi.org/10.1590/S0006-87051979000100007>

RAIJ, B.; KUPPER, A. Capacidade de troca de cátions em solos: estudo comparativo de alguns métodos. **Bragantia**, v. 25, p. 327-336, 1966. Disponível em: <https://doi.org/10.1590/S0006-87051966000200005>

ROCHA, C.; CARDOSO, P.; CUNHA, L.; GOMES, C.; RIBEIRO JÚNIOR, R.; PINHEIRO, R. H.; COSTA, M. N. BURBANO, R. Mutagenic effects of potassium dichromate as evaluated by means of animal and plant bioindicators. **in vivo**, v. 29, n. 6, p. 729-735, 2015. Disponível em: <https://iv.iijournals.org/content/invivo/29/6/729.full.pdf>.

SAMBATTI, J. A.; SOUZA JUNIOR, I. G.; COSTA, A. C. S.; TORMENA, C. A. Estimativa da acidez potencial pelo método do pH SMP em solos da Formação Caiuá, noroeste do estado do Paraná. **Revista Brasileira de Ciência do Solo**, v. 27, n. 2, p. 257-264, 2003. Disponível em: <https://doi.org/10.1590/S0100-06832003000200006>

SHOEMAKER, H. E.; MCLEAN, E. O.; PRATT, P. F. Buffer methods for determining lime requirements of soils with appreciable amount of extractable aluminum. **Soil Science Society of America Journal**, [S.L.], v. 25, n. 4, p. 274-277, jul. 1961. Wiley. Disponível em: <https://doi.org/10.2136/sssaj1961.03615995002500040014x>

SILVA, M. Z. **A acidez potencial do solo não é determinada a pH 7,0**. 47 f. Tese (Mestrado em Agronomia) – Universidade Federal de Viçosa, Viçosa: UFV, 2005. Disponível em: <https://locus.ufv.br/server/api/core/bitstreams/66fbff80-008f-4a63-82f3-a41a5394ea04/content>.

SIQUEIRA, O. J. F.; SCHERER, E. E.; TASSINARI, G.; ANGHINONI, I.; PATELLA, J. F.; TEDESCO, M. J.; MILAN, P. A.; ERNANI, P. R. **Recomendações de adubação e calagem para os estados do Rio Grande do Sul e Santa Catarina**. Passo Fundo: EMBRAPA-CNPT, 1987. 100 p.

TEIXEIRA, P. C. et al. **Manual de Métodos de Análise de Solo**. 3ª edição. Brasília, Embrapa, 2017. 573p.

TOLEDO, J. D. A.; KAMINSKI, J.; SANTANNA, M. A.; SANTOS, D. R. D. Tampão Santa Maria (TSM) como Alternativa ao Tampão SMP para Medição da Acidez Potencial de Solos Ácidos. **Revista Brasileira de Ciência do Solo**, Santa Maria, v. 36, n. 2, p. 427-435, fev. 2012. Disponível em: <https://doi.org/10.1590/S0100-06832012000200012>