Revista Brasileira de Ciência do Solo

Division – Soil Use and Management | Commission – Soil Fertility and Plant Nutrition

New methods for estimating lime requirement to attain desirable pH values in Brazilian soils

Welldy Gonçalves Teixeira[(1)]* iD, **Víctor Hugo Alvarez V.**[(2)] iD and **Júlio César Lima Neves**[(2)] iD

[(1)] Universidade Federal de Goiás, Escola de Agronomia, Setor de Solos, Programa de Pós-Graduação em Agronomia, Goiânia, Goiás, Brasil.
[(2)] Universidade Federal de Viçosa, Departamento de Solos, Viçosa, Minas Gerais, Brasil.

ABSTRACT: In Brazil, empirical models are traditionally used to determine lime requirement (LR), but their reliability is doubtful in most cases, since they can lead to under- or overestimation of LR for different soil types. In this study, the most critical characteristics influencing LR were selected to develop reliable models for predicting LR that raise soil pH to optimum values for crop production in Brazil. Soil samples (n = 22) with varying proportions of clay (5-88 %) and organic matter (OM) levels (3.78-79.35 g kg^{-1}) were used to develop the models. Organic matter and potential acidity (HAl) combined with ΔpH [target pH(H$_2$O) - initial pH(H$_2$O)] were the best predictor variables for estimating LR. Four models were developed (OMpH$_{5.8}$, OMpH$_{6.0}$, HAlpH$_{5.8}$, and HAlpH$_{6.0}$) for estimating LR to attain target pH values of 5.8 or 6.0 with reasonably high prediction performance (0.758$\leq$ R^2 $\leq$0.886). An algorithm was further developed for selecting the LR to be recommended among those estimated by the models. The proposed algorithm enables to select the minimum LR that ensure the adequate supply of Ca and Mg to plants and does not exceed the levels of soil HAl, thus preventing excessive pH increase. The new predictive models were less sensitive to predict LR high enough to meet Ca^{2+} and Mg^{2+} requirements of plants in soils containing levels of HAl lower than 5 cmol$_c$ dm^{-3} and OM lower than 40 g kg^{-1}. However, they ensured an adequate supply of Ca^{2+} and Mg^{2+} to plants and avoided the overestimation of LR for most soils used in this research. Validation via an independent dataset (n = 100 samples) confirmed the good predictive performance of the models across a wide range of soil types. In summary, the proposed models can be used as good alternatives to traditional methods for predicting LR for a great variety of Brazilian soils. Further, they are versatile and may be easily deployed in soil testing laboratories, since soil pH, OM, and HAl are characteristics determined in routine analysis.

Keywords: lime requirement prediction, organic matter, potential acidity, algorithm.

INTRODUCTION

Acidic soils comprise nearly 30 % of the world's land area, occurring mostly in tropical and subtropical regions (von Uexkül and Murtert, 1995). Liming stands out as the most effective practice to overcome the adverse impacts of soil acidity (Fageria and Baligar, 2001). Liming increases soil pH, Ca^{2+}, and Mg^{2+} levels, and soil base saturation percentage (BSP), and consequently decreases Al and Mn toxicities, resulting in improved crop yield (Goedert, 1983; Oliveira et al., 1997; Sumner and Noble, 2003; Fageria and Nascente, 2014).

The lime requirement (LR) of a soil is defined as the amount of liming material needed to increase the soil pH from an initial acidic condition to a value that is suitable for plant growth (McLean, 1973). The LR has also been regarded as the amount of lime required to attain the maximum economic yield of crops grown on acid soils, which corresponds to the lime rate estimated to achieve about 90 % of maximum yield (Fageria and Baligar, 2008). Various studies have shown the importance of applying adequate LR on Brazilian acidic soils for successful crop production (Oliveira et al., 1997; Ernani et al., 1998; Caires et al., 2000; Campanharo et al., 2007). Empirical models have long been used to determine LR of acidic soils. Among these models, the base saturation method (van Raij et al., 1996) and the method based on the exchangeable acidity (M^{x+}) neutralization along with the increase of exchangeable Ca^{2+} and Mg^{2+} (Alvarez V and Ribeiro, 1999) are used most often in Brazil. However, they have been criticized for under- or overestimating the LR for different soil types.

The base saturation method aims to increase BSP for pre-determined values according to the crop nutrient requirement, taking into account the linear relationship between soil pH and BSP within the typical pH range of acid soils (Catani and Gallo, 1955; Quaggio, 1986). Nevertheless, this relationship is non-linear for some soils, mainly at BSP values close to 80-90 % (Nicolodi et al., 2008; Silva et al., 2008). As a result, the BSP achieved with liming is frequently lower than the predicted BSP, even with high lime rates (Oliveira et al., 1997; Weirich Neto et al., 2000; Alleoni et al., 2005; Soratto and Crusciol, 2008; Araújo et al., 2009). On the other hand, the method aiming to neutralize M^{x+} and increase Ca^{2+} and Mg^{2+} has underestimated LR for soils with high cation exchange capacity at pH 7.0 (T >12 $cmol_c$ dm^{-3}) and overestimated LR for soils with low T (<4 $cmol_c$ dm^{-3}), which may lead to very high pH values (Sousa et al., 1989). Where lime is applied in excess, micronutrient deficiencies are induced and may limit crop growth (Fageria and Baligar, 2003).

Due to the limitations of the above-mentioned approaches, new methods are needed for quantifying the actual LR for the wide range of soils occurring in Brazil. Adding appropriate rates of lime can cause a desired pH change in the soil thus leading to the maximum economic crop yields. In addition, more than two decades have elapsed since the last method for estimating LR was developed. Given the ongoing intensification of agricultural practices and resultant changes in soil pH buffering capacity (pHBC) caused by acid inputs, methods developed in past decades may not be efficient for assessing the current status of acidity and fertility of agricultural soils.

Predictions of the actual LR of soils require knowledge on the pHBC, which is strongly dependent on the proportion and type of clay minerals and organic matter (OM) levels, as these characteristics govern the cation exchange capacity (Thomas and Hargrove, 1984; Wong et al., 2013; Wang et al., 2015). The levels of potential acidity (HAl) also influence the soil pHBC. As OM and HAl reflect the soil pHBC, we hypothesize that they are reliable predictor variables for estimating LR. As such, the objectives of this study were to: i) select critical soil characteristics that most influence LR predictions; and ii) develop reliable models for predicting LR to raise soil pH to optimum values for crop production in Brazil.

MATERIALS AND METHODS

Soil sampling and characterization

A total of 22 soil samples (calibration dataset) were collected from the topsoil layer (0.00-0.20 m) across the Minas Gerais State from native areas under forest and tropical savanna (Cerrado) that had never been limed. These samples were selected to cover a wide range of soil types with different physical and chemical characteristics, which are representative of Brazilian agricultural areas. Soils were classified according to the Brazilian System of Soil Classification (Santos et al., 2013) up to the 4th category level (sub-group) and their Soil Taxonomy (Soil Survey Staff, 2014) nearest equivalent. They belong to four major orders, which comprised *Latossolos* (Oxisols, n = 17), *Argissolos* (Ultisols, n = 2), *Cambissolo* (Inceptisol, n = 1), and *Neossolos* (Entisols, n = 2) (Figure 1).

All samples were air-dried, ground, and passed through a 2-mm sieve and analyzed for selected physical and chemical characteristics. Soil particle size distribution was
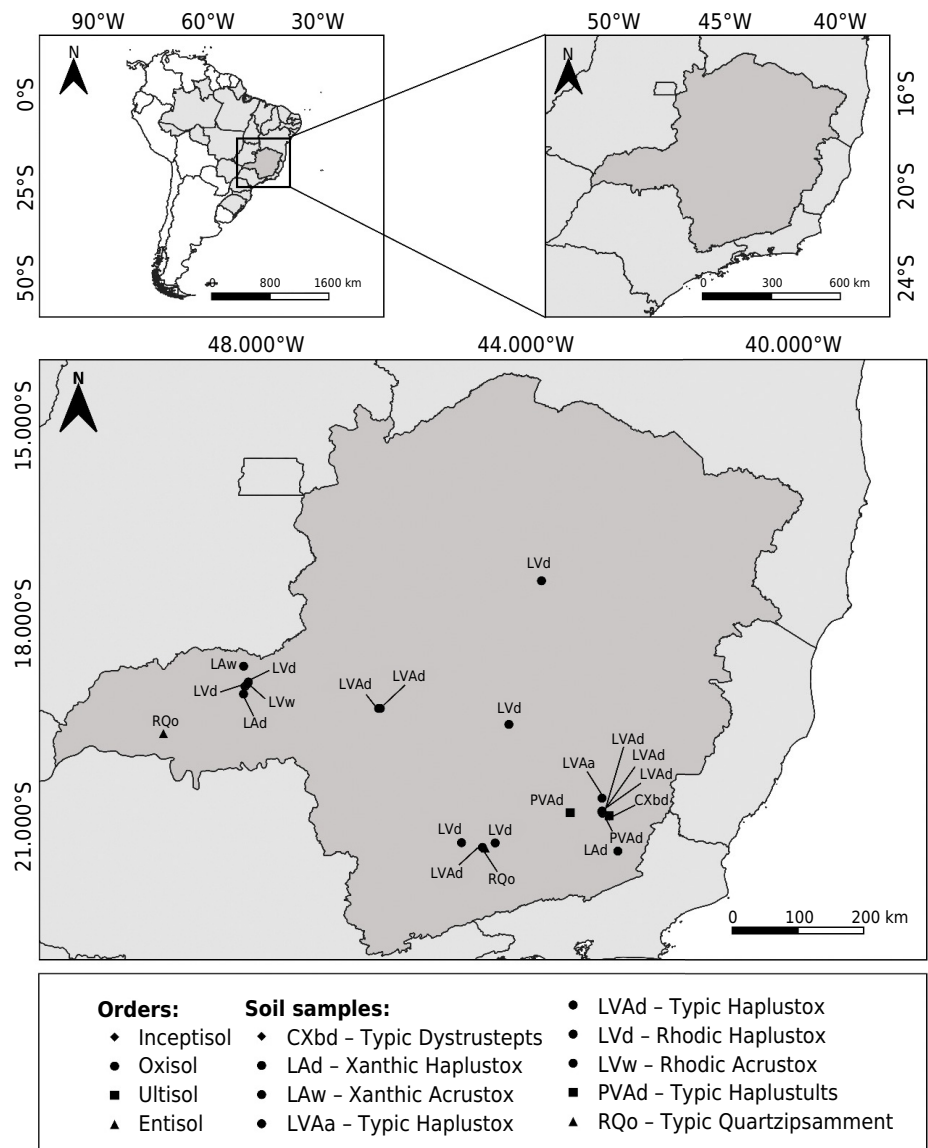
Figure 1. Study area and sampling locations at the Minas Gerais State, Brazil. The soil abbreviations were based on the Brazilian System of Soil Classification (Santos et al., 2013), followed by their Soil Taxonomy (Soil Survey Staff, 2014) nearest equivalent.

determined by the pipette method using NaOH 0.1 mol L^{-1} as a dispersing agent and the silt + clay determination as an additional step (Ruiz, 2005). Soil chemical analyses were determined using methods described by Defelipo and Ribeiro (1997) and comprised pH(H$_2$O), determined in a 1:2.5 (v:v) ratio; exchangeable Ca^{2+}, Mg^{2+}, and exchangeable acidity (M^{x+}), extracted with KCl 1 mol L^{-1}; available K$^+$, extracted with Mehlich-1; and potential acidity (HAl = H + Al), extracted with Ca(OAc)$_2$ 0.5 mol L^{-1} buffered at pH 7.0. Exchangeable Ca and Mg were determined by atomic absorption spectrometry, and M^{x+} was determined by titration with NaOH 0.025 mol L^{-1}. Available K$^+$ was determined by flame emission spectrometry.

The sum of exchangeable basic cations (SB = Ca^{2+} + Mg^{2+} + K$^+$), cation exchange capacity at pH 7.0 (T = SB + HAl), effective cation exchange capacity at the original soil pH (t = SB + M^{x+}), base saturation [V = (SB/T) × 100], and exchangeable acidity saturation [m = (M^{x+}/t) × 100] were then estimated. Remaining P was determined in solution after stirring 60 mg L^{-1} of P in CaCl$_2$ 10 mmol L^{-1} for 1 h in a soil:solution ratio of 1:10 (Alvarez V et al., 2000). Organic matter (OM) was calculated from the total carbon of organic compounds determined by oxidation with potassium dichromate using the Walkley-Black procedure (Nelson and Sommers, 1996). Soil buffer pH(SMP) was determined in a 10:25:5 (w:v:v) soil: CaCl$_2$ 10 mmol L^{-1}: buffer solution ratio, as proposed by van Raij et al. (1979).

Soil-lime incubations

The air-dried soils were incubated under greenhouse conditions with incremental amounts of a liming material for a period of 60 d. The liming material consisted of a mixture of reagent-grade CaCO$_3$ (100 % CaCO$_3$ equivalent) and dolomitic limestone with 92 % of total relative neutralizing power (TRNP) to have a 4:1 molar ratio of Ca:Mg.

The treatments were laid out in factorial arrangement [22 × (1 + 7 + 2)]. They consisted of 22 soil samples and 10 rates of lime, which comprised one control treatment (without lime), seven rates estimated by different traditional LR methods, and two additional rates chosen to get the rates more equally spaced. The traditional LR methods used in this study are described in table 1. The experiment was carried out in a randomized complete block design, with four replications.

The predictions of LR by the MG$_1$ and MG$_2$ methods (Table 1) were based on the nutritional requirements of corn (*Zea mays* L.): desired optimum base saturation (V$_2$ = 50 %),

Table 1. Traditional methods to determine the lime requirement (LR) used in the 60 d incubation study

Method	LR[1] equations	Reference
M^{x+}[2]	LR = 1.5 M^{x+}	Cate and Nelson (1965)
BSAT[3]	LR = (V$_2$ - V$_1$) T/100	van Raij et al. (1996)
MG$_1$[4]	LR = Y M^{x+} + [X - (Ca + Mg)]	Lopes and Guimarães (1989)
MG$_2$[5]	LR = Y [M^{x+} - (m$_t$ t/100)] + [X - (Ca + Mg)]	Alvarez V and Ribeiro (1999)
SMP[6]	LR to raise the soil pH(H$_2$O) to 6.0 using the SMP buffer	van Raij et al. (1979)
HAl[7]	LR = -0.086 + 0.7557 HAl	Teixeira et al. (2014)
pHOM[8]	LR = 0.16 (6 - pH) OM	Defelipo et al. (1972)

[1] LR expressed as t ha^{-1} of pure CaCO$_3$ or limestone with total relative neutralizing power (TRNP) 100 %; [2] M^{x+}: exchangeable acidity, in cmol$_c$ dm^{-3}; [3] BSAT: base saturation; V$_2$: desired optimum base saturation, in %; V$_1$: existing base saturation, in %; T: cation exchange capacity at pH 7.0, in cmol$_c$ dm^{-3}; [4] MG$_1$: Minas Gerais State-method 1; Y: variable as a function of the soil pH buffering capacity; X: variable as a function of Ca^{2+} and Mg^{2+} requirements of the crop; [5] MG$_2$: Minas Gerais State-method 2; m$_t$: maximum M^{x+} saturation tolerated by the crop, in %; [6] SMP: Shoemaker-McLean-Pratt buffer slightly altered from the one first proposed by Shoemaker et al. (1961) in which the ratio soil:CaCl$_2$ 10 mmol L^{-1}: buffer solution of 10:25:5 (w:v:v) was used; [7] HAl: potential acidity, in cmol$_c$ dm^{-3}; [8] pH(H$_2$O) at 1:2.5 (v:v) ratio; OM: organic matter (Walkley-Black method), in g kg^{-1}.

Ca^{2+} and Mg^{2+} requirements (X = 2 $cmol_c$ dm^{-3}), and maximum exchangeable acidity saturation tolerated by the crop (m_t = 15 %) (Alvarez V and Ribeiro, 1999). Nutrient requirements for the corn crop were used to estimate LR because this species was grown after the incubation period to verify the effects of LR predictions on yield responses in a subsequent experiment.

The experimental units consisted of 2 dm^3-plastic bags containing 0.5 dm^3 of the fine earth fraction (<2 mm) of each soil. The liming material was carefully mixed with the whole soil volume into the plastic bags. The treated soils were then moistened to 80 % of their field capacity with distilled water, as previously estimated by the moisture equivalent method (Ruiz et al., 2003). During the 60-d incubation period at room temperature, the soil moisture was kept near 80 % of the field capacity by adding distilled water at regular intervals, and the soils were thoroughly mixed. The plastic bags were opened for a few hours each day to facilitate gas exchange.

Soil pH at a 1:2.5 soil:water ratio was measured in five different treatments, including the control (0 lime) at 15, 30, and 45 d after beginning the incubation period to ensure the equilibrium pH was reached. At 60 d of incubation, when the pH of all soils reached a relatively steady state, soil samples of all treatments were air-dried, ground to pass a 2-mm sieve, and reanalyzed for soil pH, M^{x+}, HAl, and Ca^{2+} and Mg^{2+} using the procedures mentioned earlier.

Lime requirement from incubation

The soil-lime incubation was used as the standard method to determine the actual LR for attaining target pH values. As such, soil pH values (ŷ) measured at the end of the incubation period were plotted as a function of the 10 lime rates (x, t ha^{-1}) to obtain soil acidity neutralization curves using linear and curvilinear regression equations. The LR needed to raise the initial soil pH to target values of 5.8 ($LR_{5.8}$) and 6.0 ($LR_{6.0}$) were then obtained from the soil acidity neutralization curves. These pH values were selected based on the optimal range of pH (5.7 to 6.0) reported in the literature for most crops in Brazil (Sousa et al., 2007).

Model development and validation

The new models for predicting LR were calibrated to target pH values of 5.8 and 6.0 using LR predicted from incubation. First, $LR_{5.8}$ or $LR_{6.0}$ were plotted against relevant soil acidity-related characteristics of unlimed soils (analyzed before incubation) using nonlinear regression analyses. The resultant nonlinear regression functions consisted of the proposed models to predict LR.

The model performances were evaluated based on the coefficient of determination (R^2). Thereafter, to ascertain whether LRs predicted by the models (Y_j) were equivalent to the incubation LRs (Y_1), the identity test proposed by Leite and Oliveira (2002) was used. The null hypothesis that the LR estimated by the models (alternative methods) and the incubation procedure (standard method) are not statistically different (H_0: β = [0 1]) was evaluated.

The identity test is based in a combination of the following parameters: (i) statistic F [F(H_0)] as modified from Graybill (1976), which tests both hypotheses H_0: $β_0$ = 0 and H_1: $β_1$ = 1 simultaneously in the adjusted linear regression equation $Y_j = β_0 + β_1 Y_1 + e_i$; (ii) t-test for mean error (tē), which quantifies the accuracy (i.e., the bias) of LR predictions estimated by the new predictive models in relation to the standard incubation method by measuring the average mean error; and (iii) linear correlation coefficient (r_{Y1Yj}). Hence, after fitting the linear regression equation, the identity between Y_j and Y_1 is verified when: (i) F(H_0) is not significant: F(H_0) < $F_α$ (2, n-2 d.f.); (ii) the mean error is statistically equal to zero: ē = 0 (non-significant); and (iii) the linear correlation coefficient is significant and greater than (1 - |ē|): r_{Y1Yj} > (1 - |ē|).

An independent dataset consisting of 100 soil samples with pH(H_2O) values (1:2.5 soil:water) lower than 6.0 was used to validate the models. These samples were originated from the soil library of the Minas Gerais State and were chosen for their variability in physical and chemical characteristics.

Algorithm to select the recommended lime requirement

Among the LRs predicted by the proposed models, the lowest LR was considered here as the recommended LR as long as it is higher than the Ca^{2+} and Mg^{2+} requirements of the plant (X) and lower than the levels of soil potential acidity (HAl). For selecting the LR to be recommended (LR_R), an algorithm was developed in this study, which comprised the following steps (Figure 2):

a. The LR is estimated (LR_E) from the predictive models.

b. The lowest LR (LR_{LOW}) is selected among the values of LR_E.

c. The LR_{LOW} is compared with the Ca^{2+} and Mg^{2+} requirements of the plant (X).

If $LR_{LOW} \geq X$, LR_{LOW} will be compared with the level of HAl: if $LR_{LOW} < HAl$, LR_{LOW} will be the LR_R; otherwise, HAl will be the LR_R.

If $LR_{LOW} < X$, the second lowest LR_E (2nd LR_{LOW}) is compared with X.

d. The procedure described in "c" with the 2nd LR_{LOW} is repeated until finding among the LR_E values the one that is equal or higher than X; otherwise, X will be the LR_R.

In summary, the levels of X and HAl are considered by the proposed algorithm as the minimum and maximum limits to the LR_R, respectively. Hence, it seeks to select the
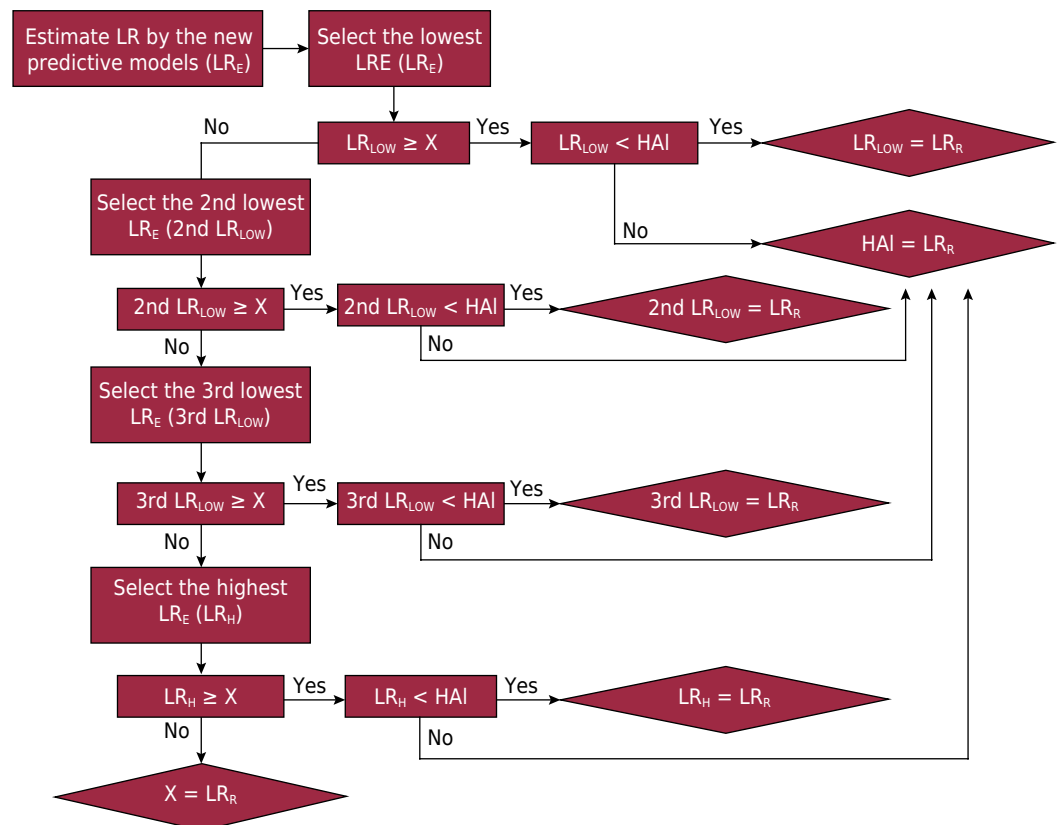

Figure 2. Flowchart of the proposed algorithm to select which estimated lime requirement (LR_E, t ha⁻¹) by the new predictive models should be recommended (LR_R). X, crop nutrient requirements for Ca^{2+} and Mg^{2+}; HAl, soil potential acidity, both in $cmol_c$ dm⁻³.

minimum LR to meet the Ca^{2+} and Mg^{2+} requirements of plants while concurrently preventing LR_E from exceeding the levels of HAl and causing an excessive increase of soil pH, which can create an imbalance with other nutrients and affect crop production.

The values of LR_R were then used to estimate soil pH, exchangeable acidity (M^{x+}), potential acidity (HAl), and the levels of Ca^{2+} and Mg^{2+} that would be reached in soils from the calibration dataset. This was done by substituting the LR_R in the regression equations relating each of these characteristics ($\hat{y}$) as a function of the lime rates (x, t ha^{-1}). The same was not carried out for the validation dataset as these soils were not incubated with increasing lime rates and, hence, did not have regression equations relating soil characteristics with the lime rates applied.

Further, the recommendation frequency of LR, which is the frequency at which the models estimated LR following different criteria according to the proposed algorithm, was calculated for both calibration (n = 22) and validation (n = 100) datasets.

RESULTS

Soil characteristics and incubation lime requirement

Descriptive statistics for soil analytical results of the calibration and validation datasets are summarized in table 2. The soils used for calibrating (n = 22) the predictive models of LR showed a broad range of textures varying from sandy to loamy and clayey classes according to the soil particle size distribution. These soils were predominantly acidic [pH(H$_2$O) = 4.12-5.26], with low base saturation (V up to 35 %), high exchangeable acidity saturation (m up to 96 %), and medium to high organic matter level (OM up to 79.3 g kg^{-1}) as per the classes to interpret soil acidity and fertility proposed by Alvarez V et al. (1999).

Table 2. Descriptive statistics for chemical and physical characteristics of the soils used to develop (calibration dataset) and validate (validation dataset) the new predictive models

Soil characteristic[1]	Calibration dataset[2]			Validation dataset[3]		
	Mean	Lowest	Highest	Mean	Lowest	Highest
pH(H$_2$O)	4.63	4.12	5.26	4.95	4.10	5.87
pH(SMP)	5.72	4.82	6.78	5.90	5.17	7.59
Ca^{2+} (cmol$_c$ dm^{-3})	0.45	0.02	1.66	0.61	0.00	3.15
Mg^{2+} (cmol$_c$ dm^{-3})	0.20	0.00	0.87	0.23	0.00	1.87
K$^+$ (cmol$_c$ dm^{-3})	0.10	0.02	0.24	0.12	0.00	0.49
M^{x+} (cmol$_c$ dm^{-3})	0.87	0.21	1.98	0.85	0.00	3.00
HAl (cmol$_c$ dm^{-3})	6.63	1.68	13.06	5.75	0.70	11.30
SB (cmol$_c$ dm^{-3})	0.77	0.04	2.04	1.09	0.07	6.55
T (cmol$_c$ dm^{-3})	7.40	1.72	14.06	6.84	1.68	11.90
t (cmol$_c$ dm^{-3})	1.64	0.50	3.02	1.93	0.07	6.55
V (%)	10.64	0.77	34.53	17.45	1.10	90.30
m (%)	57.41	9.60	95.77	51.39	0.00	94.90
P-rem (mg L^{-1})	18.51	5.44	60.00	26.63	0.70	57.20
OM (g kg^{-1})	41.87	3.78	79.35	30.17	1.30	89.00
Sand (g kg^{-1})	331	49	926	401	37	910
Silt (g kg^{-1})	74	6	230	170	10	590
Clay (g kg^{-1})	594	54	884	430	60	810

[1] pH(H$_2$O) at a 1:2.5 (v:v) soil:water ratio; pH(SMP) at a 10:25:5 (w:v:v) soil:CaCl$_2$ 10 mmol L^{-1}:buffer solution ratio; M^{x+}: exchangeable acidity extracted with KCl 1 mol L^{-1}; HAl: potential acidity extracted with Ca(OAc)$_2$ 0.5 mol L^{-1} buffered at pH 7.0; SB: sum of exchangeable basic cations; T: cation exchange capacity at pH 7.0; t: effective cation exchange capacity at the original soil pH; V: base saturation; m: exchangeable acidity saturation; P-rem: remaining P (Alvarez V et al., 2000); OM: organic matter (Walkley-Black method). [2] n = 22 soils. [3] n = 100 soils.

The validation dataset (n = 100) also exhibited a large variability of particle size distribution and chemical characteristics. In general, soil texture was classified as clayey for the majority (75 %) of the soils. The variations in soil pH (4.10-5.87), exchangeable acidity saturation (m up to 95 %) and OM level (up to 89.0 g kg^{-1}) were similar to those for calibration dataset, with the exception of the base saturation (V up to 90 %) that varied substantially across these soils.

Table 3 exhibits the LR predictions from the standard incubation method determined using soil acidity neutralization curves. The incubation LRs ranged from 0.57 to 6.62 t ha^{-1} to attain pH 5.8 (LR$_{5.8}$), or from 0.77 to 8.72 t ha^{-1} to attain pH 6.0 (LR$_{6.0}$). The highest LR values to reach pH 5.8 and 6.0 were more than 6 t ha^{-1} larger than the lowest, contributing to the high variation of LR (CV = 51 and 55 %) as determined from incubation across the 22 soils. Most of the high values of incubation LR were estimated for soils high in potential acidity and OM, characteristics associated with highly buffered soils.

Predictive models of lime requirement

Because soil pH is an important characteristic that provides a rapid and inexpensive indication of the soil acidity or alkalinity, it was prioritized as a predictor variable of LR. For that, the combined variable ΔpH (target pH - initial pH), which consisted of the desired target pH values of 5.8 or 6.0 minus the initial pH measured before liming, was calculated. Incubation LRs to attain either pH 5.8 or 6.0 were plotted against the variables (5.8 - pH) or (6.0 - pH) and fitted by nonlinear regressions. Statistically significant (p<0.05) nonlinear relationships were observed between incubation LRs (LR$_{5.8}$ and LR$_{6.0}$) and ΔpH, but the R^2 values were very low for both relationships (R^2 = 0.30) (Figure 3).

Based on the influence of OM and HAl in the soil pHBC, these soil characteristics were considered as predictor variables of LR. New combined variables consisting in the desired target pH (5.8 or 6.0) minus the initial pH multiplied either by the organic matter level ([(5.8 - pH) OM] and [(6.0 - pH) OM] = ΔpHOM) or the potential acidity level ([5.8 - pH) HAl] and [6.0 - pH) HAl] = ΔpHHAl) were then calculated. Incubation LRs to attain pH 5.8 or 6.0 were plotted against the new combined variables and fitted by nonlinear regressions. Five soils appeared to be outliers and so were excluded from the regression analysis. These soils contained medium to high levels of OM (26.5-63.3 g kg^{-1}) and HAl (3.6-7.9 cmol$_c$ dm^{-3}), but they were considerably deviated from the nonlinear regression line between incubation LR and the new combined variables as compared with the other soils.

In general, both combined predictor variables (ΔpHOM or ΔpHHAl) showed good relationships with incubation LRs, even though the relationships between ΔpHOM and incubation LR to raise soil pH to either 5.8 (R^2 = 0.863) or 6.0 (R^2 = 0.886) showed higher performance in comparison to those between ΔpHHAl and incubation LRs (R^2 = 0.758 and 0.836, respectively).

The four power regression equations relating incubation LRs (LR$_{5.8}$ or LR$_{6.0}$) with ΔpHOM or ΔpHHAl that are shown in figure 4 consisted of the new predictive models of LR developed in this study. As such, LR can be predicted by the new models, here referred to as OMpH$_{5.8}$, HAlpH$_{5.8}$, OMpH$_{6.0}$, and HAlpH$_{6.0}$, according to equations 1, 2, 3, and 4.

$$OMpH_{5.8} = 0.0699 \times [(5.8 - pH)\ OM]^{0.9225**} \qquad R^2 = 0.863 \qquad \text{Eq. 1}$$

$$HAlpH_{5.8} = 0.3750 \times [(5.8 - pH)\ HAl]^{0.9127**} \qquad R^2 = 0.758 \qquad \text{Eq. 2}$$

$$OMpH_{6.0} = 0.1059 \times [(6.0 - pH)\ OM]^{0.8729**} \qquad R^2 = 0.886 \qquad \text{Eq. 3}$$

$$HAlpH_{6.0} = 0.4558 \times [6.0 - pH)\ HAl]^{0.9162**} \qquad R^2 = 0.836 \qquad \text{Eq. 4}$$

Table 3. Lime requirement estimated from the standard incubation method and from the new predictive models using organic matter (OMpH) and potential acidity (HAlpH) to attain pH 5.8 or 6.0 for the soils used to develop and validate the new predictive models

Soil	Lime requirement[1]						X[2]	HAI[3]
	Incubation		OMpH		HAlpH			
	pH 5.8	pH 6.0	pH 5.8	pH 6.0	pH 5.8	pH 6.0		
	———————————————— t ha⁻¹ ————————————————							
	Calibration dataset[4]							
LVAd₁	4.03	5.28	3.06	**4.46**	*2.55*	3.72		
LVd₁	3.97	4.70	1.24	***2.12***	0.83	1.35		
Law	3.08	3.95	2.95	**4.14**	*2.74*	3.82		
LVAd₂	4.32	6.15	*2.00*	2.88	2.57	**3.60**		
LVAa	6.62	8.72	6.38	8.36	*6.28*	**8.55**		
LVAd₃	0.84	1.61	0.71	1.13	1.11	1.63	*2*	
LVd₂	4.52	5.94	2.27	**3.47**	*2.01*	3.02		
LVAd₄	4.54	6.99	*4.53*	6.07	5.24	**7.16**		
LVAd₅	3.11	4.21	4.11	**5.64**	*3.71*	5.17		
LVd₃	5.89	7.31	5.48	**7.33**	*4.35*	6.00		
LVd₄	2.54	4.50	3.47	**4.93**	*3.15*	4.49		
PVAd₁	0.75	1.31	1.61	**2.50**	1.41	*2.10*		
CXbd	3.18	4.14	*2.24*	3.11	2.83	**3.84**		
LVd₅	2.45	3.68	4.84	**6.48**	*3.52*	4.81		
LVw	2.91	3.65	2.92	**4.04**	*2.75*	3.78		
PVAd₂	2.40	3.42	1.39	***2.36***	1.18	1.92		
LVAd₆	3.38	4.14	0.89	1.51	0.76	1.21	*2*	
LAd₁	1.87	2.54	*2.19*	3.07	2.36	**3.24**		
LVd₆	1.08	1.64	1.16	1.73	1.59	***2.24***		
LAd₂	1.59	2.62	*2.37*	3.27	3.35	**4.55**		
RQo₁	1.60	2.39	1.21	1.85	1.24	1.78	*2*	
RQo₂	0.57	0.77	0.19	0.33	0.48	0.72		*1.68*
Lowest	0.57	0.77	0.19	0.33	0.48	0.72		
Highest	6.62	8.72	6.38	8.36	6.28	8.55		
Mean	2.97	4.07	2.60	3.67	2.55	3.58		
CV (%)	54.81	50.54	62.89	56.96	58.45	55.35		
	Validation dataset[5]							
Lowest			0.00	0.04	0.00	0.07		
Highest			5.20	7.15	4.57	6.25		
Mean			1.46	2.20	1.70	2.48		
CV (%)			76.06	67.69	66.45	61.79		

[1] Values in italic refer to the lowest LR, which is considered the recommended LR since it is higher than the Ca^{2+} and Mg^{2+} requirements of the plant (X) and lower than the levels of potential acidity of each soil sample; and bold values refer to the highest LR. [2] X = 2 $cmol_c$ dm^{-3} for corn crop. [3] Potential acidity. [4] n = 22 soils. [5] n = 100 soils.

in which: LR is the lime requirement of the soil expressed as t ha⁻¹ of pure $CaCO_3$ or limestone with TRNP of 100 %, pH is the initial pH of the acidic soil, OM is the organic matter level expressed as g kg⁻¹, and HAI is the potential acidity level expressed in $cmol_c$ dm^{-3}.
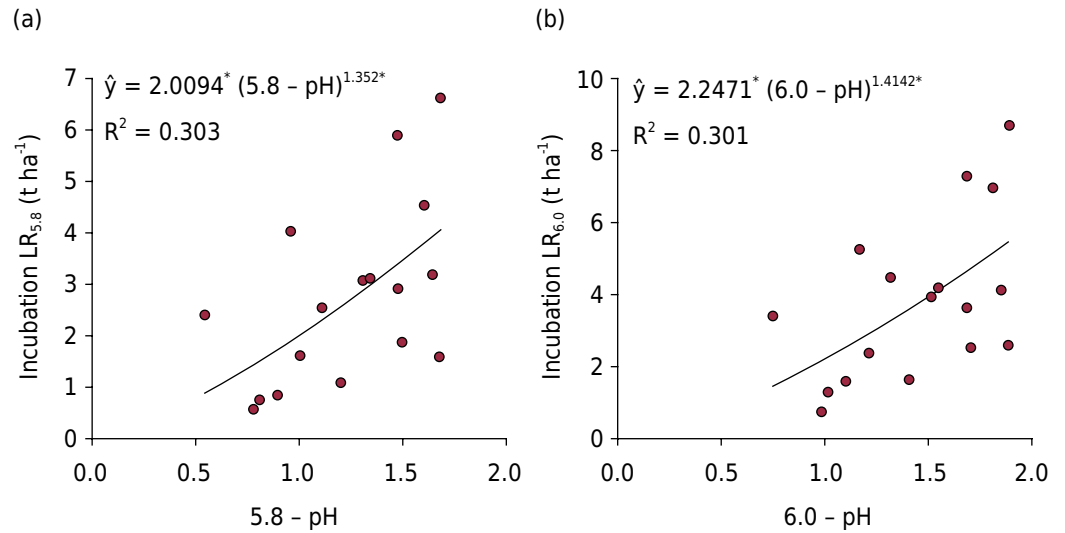
(a)

(b)

Figure 3. Relationships between lime requirement (LR) determined from the 60 d incubation to target pH values of 5.8 (a) or 6.0 (b) and changes in soil pH (target pH - initial pH). *: p<0.05.
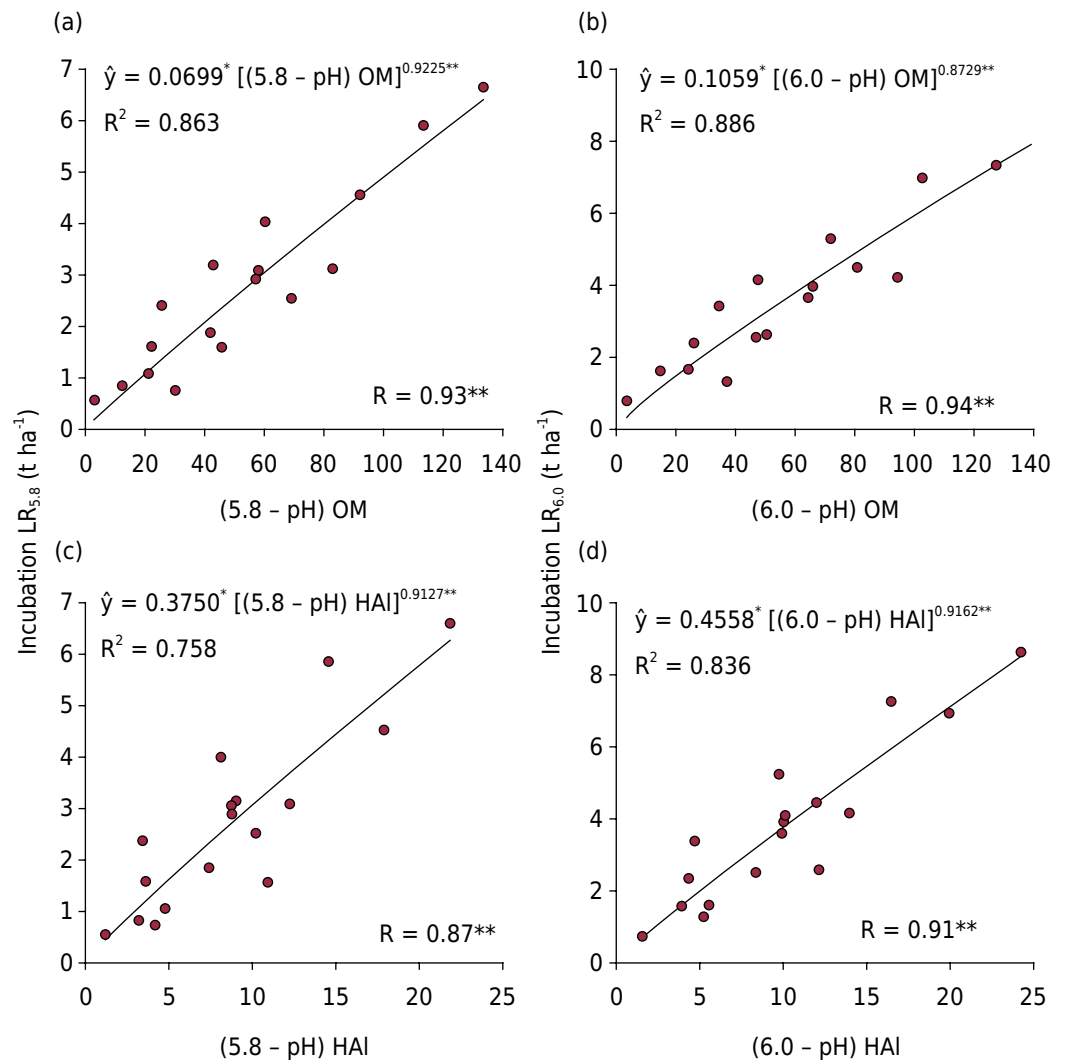
(a)

(b)

(c)

(d)

Figure 4. Relationships between lime requirement (LR) determined from the 60 d incubation to target pH values of 5.8 (a and c) or 6.0 (b and d) and combined variables consisted of changes in soil pH (target pH - initial pH) multiplied either by the level of organic matter (OM) or potential acidity (HAl). *: 0.05> p ≥0.01; **: p<0.01.

Predictive ability of the models

The models developed showed satisfying performances for predicting LR ($R^2 \geq 0.758$). Also, LR predicted from incubation and LR predicted by the models were highly related ($p<0.01$) (Figure 4). As can be seen in the magnitude of the correlation coefficient (R) values, there is a strong relationship between LR predicted from the fitted models and LR predicted from incubation. Among the four predictive models, the OMpH was more closely related to the standard incubation method than the HAlpH. As such, the predictive models to attain either pH 5.8 or 6.0 using OM had the highest relationships to the standard incubation method ($R = 0.93^{**}$ and 0.94^{**}), while those using HAl had the lowest ($R = 0.87^{**}$ and 0.91^{**}).

For determining if there is a perfect agreement between the new predictive models and the standard incubation method, the identity between models was verified (Leite and Oliveira, 2002). According to the fitting parameters of the identity test (Table 4), the $F(H_0)$ values were not significant ($p>0.05$), indicating that the intercept (β_0) and the slope (β_1) in the adjusted linear regression model $Y_j = \beta_0 + \beta_1 Y_1 + e_i$ were not statistically different from 0 and 1, respectively. Therefore, the hypothesis $H_0: \beta = [0\ 1]$ was not rejected.

In the t-test for mean error ($t\bar{e}$), the mean error values were not significant ($p>0.05$), indicating that the hypothesis $H_0: \bar{e} = 0$ was not rejected. Hence, the differences between Y_j and Y_1 are casual, revealing the absence of a systematic error in LR estimated by the predictive models compared with LR estimated from incubation.

The linear correlation coefficients (r_{Y1Yj}) indicated a relatively low dispersion of the data between LRs estimated by the predictive models and the incubation method, since the r_{Y1Yj} values were equal or greater than 0.87^{**}. Thus, the parameter $r_{Y1Yj} \geq (1 - |\bar{e}|)$ was not satisfied, which led to the conclusion that none of the LR predictive models estimated equivalent amounts of lime to the standard incubation method. Hence, the alternative LR methods were not identical, but very close to the standard incubation method.

Predictions of lime requirement

The estimated LR using the new predictive models are presented in table 3, along with LR from the standard incubation method. As evidenced for the soils from the calibration dataset, the ranges of LR to attain pH 5.8 predicted from the models based on OM (OMpH$_{5.8}$: 0.19-6.38 t ha^{-1}) and HAl (HAlpH$_{5.8}$: 0.48-6.28 t ha^{-1}) were very close to the range of incubation LR to attain the same pH value (0.57-6.62 t ha^{-1}). Likewise, the ranges of LR to achieve pH 6.0 predicted by the models based on OM (OMpH$_{6.0}$: 0.33-8.36 t ha^{-1}) and HAl (HAlpH$_{6.0}$: 0.72-8.55 t ha^{-1}) were very close the range of incubation LR to attain such pH value (0.77-8.72 t ha^{-1}).

The ranges of LR on the validation dataset were also close to each other when comparing different predictive models to achieve the same pH value (Table 3). Thus, to attain pH 5.8, the OMpH model predicted LR ranging from 0 to 5.20 t ha^{-1}, whereas the LR

Table 4. Results of the identity test between the standard incubation method (Y_1) and the new predictive models (Y_j) of lime requirement

Method		target pH	β_0	β_1	R^2	$F(H_0)$	$t\bar{e}$	$r_{Y1Yj} \geq (1 - |\bar{e}|)$	Conclusion[2]
Standard	Alternative[1]								
Incubation	OMpH	5.8	0.24^{ns}	0.8988^{ns}	0.865	0.64^{ns}	0.24^{ns}	No	$Y_j \neq Y_1$
		6.0	0.26^{ns}	0.9202^{ns}	0.887	0.47^{ns}	0.03^{ns}	No	$Y_j \neq Y_1$
Incubation	HAlpH	5.8	0.60^{ns}	0.7738^{ns}	0.759	2.02^{ns}	1.02^{ns}	No	$Y_j \neq Y_1$
		6.0	0.55^{ns}	0.8514^{ns}	0.836	1.17^{ns}	0.73^{ns}	No	$Y_j \neq Y_1$

[1] Considering 17 out of the 22 soil samples used to develop the new predictive models. [2] According to the statistical procedure proposed by Leite and Oliveira (2002). ns: not significant until 5 %.

predicted by the HAlpH model ranged from 0 to 4.57 t ha^{-1}. On the other hand, the LR predictions by the OMpH and HAlpH models to attain pH 6.0 ranged from 0.04 to 7.15 t ha^{-1} and from 0.07 to 6.25 t ha^{-1}, respectively.

The results in table 3 show the recommended LR (LR$_R$) depicted as values in italic, as well as the highest LR (LR$_H$), highlighted as bold values. Looking at the 22 soils from the calibration dataset, the HAlpH$_{5.8}$ model predicted the LR$_R$ to the largest number of soils (9 soils), followed by OMpH$_{5.8}$ (5 soils), HAlpH$_{6.0}$, and OMpH$_{6.0}$ (2 soils). For the independent set of 100 soil samples, the LR$_R$ was predicted to the largest number of soils by the HAlpH$_{6.0}$ (20 soils), followed by the OMpH$_{5.8}$ and OMpH$_{6.0}$ (19 soils), and the HAlpH$_{5.8}$ (7 soils). With regard the LR$_H$, both OMpH$_{6.0}$ and HAlpH$_{6.0}$ models predicted such values to most soils used to develop (n = 11) and validate (n = 48) the new predictive models, respectively. A large difference (>1.40 t ha^{-1}) between LR$_R$ and LR$_H$ was observed for 13 out of the 22 soils used in the incubation study. As a result, the magnitude of the difference varied greatly (LR$_H$/LR$_R$ = 0-92 %) across all 22 soil samples and was higher for the strongly buffered soils (Table 5).

Table 5. Recommended (LR$_R$) and highest (LR$_H$) lime requirement and selected soil characteristics associated with LR$_R$ for the soils used to develop the new predictive models

Soil	LR$_R$	LR$_H$	LR$_H$/LR$_R$	pH	M^{x+}	HAl	Ca^{2+}	Mg^{2+}
	——— t ha^{-1} ———		%		——————— cmol$_c$ dm^{-3} ———————			
				Calibration dataset[1]				
LVAd$_1$	2.55	4.46	175	5.52	0.09	5.59	1.62	0.68
LVd$_1$	2.12	2.12	100	5.46	0.04	4.33	1.24	0.43
Law	2.74	4.14	151	5.72	0.03	4.40	1.39	0.43
LVAd$_2$	2.00	3.60	180	5.47	0.19	5.98	1.33	0.40
LVAa	6.28	8.55	136	5.77	0.06	7.35	3.56	1.17
LVAd$_3$	2.00	2.00	100	6.12	0.02	1.94	1.33	0.34
LVd$_2$	2.01	3.47	172	5.59	0.04	4.96	2.73	1.08
LVAd$_4$	4.53	7.16	158	5.80	0.18	7.73	2.72	0.79
LVAd$_5$	3.71	5.17	139	5.91	0.02	5.60	2.07	0.75
LVd$_3$	4.35	7.33	168	5.56	0.22	8.03	2.40	1.01
LVd$_4$	3.15	4.93	157	5.86	0.09	6.11	2.62	0.58
PVAd$_1$	2.10	2.50	119	6.27	0.01	2.46	1.39	0.73
CXbd	2.24	3.84	172	5.58	0.08	3.09	1.32	0.39
LVd$_5$	3.52	6.48	184	5.97	0.09	7.04	1.77	0.66
LVw	2.75	4.04	147	5.75	0.03	3.52	1.44	0.43
PVAd$_2$	2.36	2.36	100	5.79	0.00	3.64	2.45	1.60
LVAd$_6$	2.00	2.00	100	5.43	0.09	3.50	1.53	0.57
LAd$_1$	2.19	3.24	148	5.90	0.06	2.65	1.25	0.41
LVd$_6$	2.24	2.24	100	6.21	0.01	1.78	0.95	0.39
LAd$_2$	2.37	4.55	192	5.95	0.03	3.87	1.20	0.42
RQo$_1$	2.00	2.00	100	5.90	0.08	2.76	1.37	0.98
RQo$_2$	1.68	1.68	100	6.63	0.00	0.55	0.73	0.14
Lowest	1.68	1.68	100	5.43	0.00	0.55	0.73	0.14
Highest	6.28	8.55	192	6.63	0.22	8.03	3.56	1.60
Mean	2.77	3.99	141	5.83	0.07	4.40	1.75	0.65
CV (%)	40.06	49.09	23.40	5.10	92.30	47.01	40.60	52.32

[1] n: 22 soils.

By applying the LR_R, the soils from the calibration dataset would have on average good pH value (5.83), very low exchangeable acidity (0.07 cmol$_c$ dm^{-3}), and medium values of potential acidity (4.40 cmol$_c$ dm^{-3}), Ca^{2+} (1.75 cmol$_c$ dm^{-3}), and Mg^{2+} (0.65 cmol$_c$ dm^{-3}) as per the rating classes suggested by Alvarez V et al. (1999).

Recommendation frequency of lime requirement

By using the proposed algorithm (Figure 2), the recommendation frequencies of LR were classified according to different criteria (Table 6). For the calibration dataset, none of the new predictive models recommended LR when liming was not needed (LR = 0). However, both OMpH and HAlpH models aiming to raise soil pH to 5.8 recommended LR in 3 % of the soils from the validation dataset even when no lime was required.

In the calibration dataset, a smaller proportion of LR recommended to attain either pH 5.8 (OMpH$_{5.8}$: 38 %; HAlpH$_{5.8}$: 42 %) or 6.0 (OMpH$_{6.0}$: 25 %; HAlpH$_{6.0}$: 29 %) was not enough to meet the Ca^{2+} and Mg^{2+} requirements of the plant (0< LR <X), whereas a greater proportion of LR recommended to attain either pH 5.8 (OMpH$_{5.8}$: 63 %; HAlpH$_{5.8}$: 58 %) or 6.0 (OMpH$_{6.0}$: 75 %; HAlpH$_{6.0}$: 71 %) was classified within the preferential interval (X≤ LR ≤HAl).

The validation dataset exhibited a partially opposite behavior, in which a larger recommendation frequency of LR to attain either pH 5.8 (OMpH$_{5.8}$: 74 %; HAlpH$_{5.8}$: 67 %) or 6.0 (OMpH$_{6.0}$: 47 %; HAlpH$_{6.0}$: 39 %) was insufficient to supply plants with Ca^{2+} and Mg^{2+}, whereas a smaller frequency of LR predictions to attain only pH 5.8 (OMpH$_{5.8}$: 23 %; HAlpH$_{5.8}$: 30 %) was classified within the preferential criterion. A greater recommendation frequency of LR for attaining pH 6.0 was hence classified within the preferential interval (X≤ LR ≤HAl)

None of the models estimated LR higher than the levels of HAl (LR > HAl) for the calibration dataset. However, 2 % of the soils from the validation dataset received LR > HAl when LR was predicted by the OMpH model to attain pH 6.0. When the recommendation frequencies of LR were calculated considering only the recommended LR (LR$_R$), the HAlpH model estimated such a LR for the majority of the soils from the calibration (47 %) and validation (31 %) datasets to attain pH 5.8 and 6.0, respectively.

Table 6. Recommendation frequency of lime requirement (LR) estimated by the new predictive models according to the algorithm criteria for the soils used to develop and validate the new predictive models

Criteria[1]	OMpH		HAlpH	
	pH 5.8	pH 6.0	pH 5.8	pH 6.0
	%			
	Calibration dataset[2]			
LR = 0 (non-recommended)	0.00	0.00	0.00	0.00
0 < LR < X	37.50	25.00	41.67	29.17
X ≤ LR ≤ HAl	62.50	75.00	58.33	70.83
LR > HAl	0.00	0.00	0.00	0.00
LR$_R$[3]	26.32	10.53	47.37	15.79
	Validation dataset[4]			
LR = 0	3.00	0.00	3.00	0.00
0 < LR < X	74.00	47.00	67.00	39.00
X ≤ LR ≤ HAl	23.00	51.00	30.00	61.00
LR > HAl	0.00	2.00	0.00	0.00
LR$_R$	29.23	29.23	10.77	30.77

[1] X = 2 cmol$_c$ dm^{-3} (for corn crop). [2] n = 22 soils. [3] Lowest LR selected as the recommended LR for meeting the criterion X ≤ LR ≤ HAl. [4] n = 100 soils.

DISCUSSION

In this study, reference LR values obtained from the standard incubation method were used to develop new predictive models of LR to attain desirable pH values. Lime requirements predicted from incubation varied widely across soils to attain either pH 5.8 (0.57 to 6.62 t ha^{-1}) or 6.0 (0.77 to 8.72 t ha^{-1}) (Table 3), revealing that the calibration dataset showed a large variation in physical and chemical characteristics that is desirable for developing predictive models of LR applicable to various soil types.

The use of initial and target soil pH combined as a predictor variable (ΔpH) did not provide good estimates of LR. This was evidenced by the low relationships (R^2 ~ 0.30) between the desired pH change (ΔpH) and LR predicted from incubation, implying very poor estimates of LR based solely on the expected variation of pH due to liming (Figure 3). Indeed, soil pH is not a reliable predictor of LR, but rather is just an indicator of the need for liming, as reported by several authors (Aitken et al., 1990; Pagani and Mallarino, 2012; Holland et al., 2018).

As already mentioned, predicting the actual LR of a soil relies on the knowledge of the pHBC (Thomas and Hargrove, 1984; Wong et al., 2013; Wang et al., 2015). The major soil characteristics affecting the soil pHBC that have been combined to predict LR include exchangeable H$^+$ and base saturation percentage (Catani and Gallo, 1955), soil pH, and OM (Keeney and Corey, 1963; Defelipo et al., 1972; Edmeades et al., 1985), CEC, and base saturation percentage (Quaggio et al., 1985), soil pH, exchangeable Al, exchangeable bases, and organic carbon (Hochman et al., 1995), and more recently, level of total carbon and proportion of clay (Curtin and Trolove, 2013). Because HAl as well as OM are indicators of soil pHBC, each of these characteristics combined with ΔpH as predictor variables for LR resulted in highly improved LR predictions (Figure 4). No other combination of soil characteristics tested in this study provided better relationships with incubation LR.

The four predictive models developed, namely OMpH$_{5.8}$, OMpH$_{6.0}$, HAlpH$_{5.8}$, and HAlpH$_{6.0}$, provided good estimates of LR, as indicated by the highly significant correlations (R: 0.87** - 0.94**) to the incubation LRs (Figure 4). For all relationships, a very close association between LR estimated by the standard incubation method and the new predictive models was verified. The correlation approach is often used for comparisons between two methods and determining which one is more reliable for predicting LR (Aitken et al., 1990; Godsey et al., 2007; Pagani and Mallarino, 2012). In studies that aimed to compare methods to predict LR on tropical acid soils, alternative methods were considered suitable for estimating LR when their LR predictions were highly correlated to the LR predicted by a standard incubation method (Quaggio et al., 1985; Almeida et al., 1999).

Although correlation analysis are frequently used for comparing predictions of LR by different methods, they are inappropriate for assessing agreement between two analytical methods (Hopkins, 2004; van Stralen et al., 2008). As an alternative, Leite and Oliveira (2002) suggested the identity test to assess agreement between two methods for LR predictions. According to these authors, for comparison between analytical methods, the parameters of the regression line [i.e., the intercept (β$_0$) is not significantly different from zero, the slope (β$_1$) is not significantly different from one, the mean error (ē) is not significant, and the correlation coefficient (r$_{Y1Yj}$) between LR predictions is highly significant] must be addressed simultaneously.

The results from the identity test showed that none of the new predictive models were identical to the standard incubation method in predicting LR to attain target pH values, since one of the three requirements for identity [r$_{Y1Yj}$ ≥ (1 - | ē |)] was not met (Table 4). Thus, agreement between the new predictive models and the standard incubation method was not verified, even though they are significantly associated. However, all models are of comparable reliability to the standard incubation method, as two out of three

statistical requirements of the identity test ($\beta_0 = 0$ and $\beta_1 = 1$; $\bar{e} = 0$) were simultaneously met (Table 4). Consistent with other findings on the effectiveness of the identity test (Milagres et al., 2007; Soares et al., 2010; Serra et al., 2012), this study demonstrated that such statistical procedure is a better approach for determining the agreement rather than a merely association between two distinct methods, as do the correlation analysis.

Regarding the predictive ability of the models, OMpH$_{5.8}$ ($R^2 = 0.863$) and OMpH$_{6.0}$ ($R^2 = 0.886$) had a slightly better fit, compared with HAlpH$_{5.8}$ ($R^2 = 0.758$) and HAlpH$_{6.0}$ ($R^2 = 0.836$) (Figure 4). This may be attributed to the greater ability of OM compared with HAl to explain variation in the buffering capacity of a soil and, consequently, in the LR prediction. Sá et al. (2006) demonstrated that the organic fraction is the primary source of soil acidity buffering in soils from the Cerrado region of Brazil, accounting for 98 % of the variation in the soil buffer capacity.

The use of soil pH along with the OM level as predictor variables of LR in Brazilian acid soils have been reported in previous studies. However, one of the first prediction equations developed in Brazil based on soil pH and OM level (Defelipo et al., 1972) was found to overestimate the actual LRs to attain the expected pH value of 6.0 (Alvarez V et al., 1990a,b), whereas the other one (Alvarez V et al., 1996) was not implemented at large scales for predicting LR, despite its good predictive ability ($R^2 = 0.797$). Predictions of LR based on OM to attain pH 6.0 (Defelipo et al., 1972) have also been reported to be overestimated for flooded soils and acid sulfate soils in Brazil (Borges Júnior et al., 1998; Caballero et al., 2019).

In contrast, the models developed in this study are less likely to overestimate LR, since they were calibrated using the standard incubation method to achieve target pH values. The minor differences in LR predicted by the models to achieve a given pH value, as revealed by the closeness between LR ranges within the same dataset, emphasized the good agreement to one another (Table 3). Further, the validation dataset showed ranges of LR similar to the calibration dataset, proving the good predictive performance of the models for a wide range of soil types.

Predicting sufficiently lime that reflects an adequate supply of Ca and Mg to plants and prevents overliming of soils under field conditions is of recognized importance in the literature to improve crop yields (Bolan et al., 2003; Fageria and Baligar, 2008). Of the four models developed, the HAlpH$_{5.8}$ predicted the recommended LR (LR$_R$) (values in italic in table 3) to most soils in the whole dataset. The LR$_R$, that is the LR high enough to meet Ca^{2+} and Mg^{2+} requirements of plants (X) but is lower than the levels of soil potential acidity (HAl), corresponded to raising soil pH to nearly 5.9 on average for the calibration dataset (Table 5), which is within the optimum pH range for many crops in Brazil (Fageria and Stone, 1999; Fageria and Baligar, 2001). At this pH value, much of the exchangeable acidity would be neutralized, and the Ca^{2+} and Mg^{2+} levels would be adequate to support optimum yields of most annual crops in Brazilian Oxisols (Fageria and Baligar, 1999; Fageria, 2008).

Unlike the LR$_R$, the addition of excessive lime rates may lead to negative effects on the plant growth, such as micronutrient deficiencies and soil structure degradation. On highly weathered soils, a considerable decrease in the availability of micronutrients has been observed as soil pH increases above 6.0 following lime (Fageria and Stone, 2008). Excessive lime has also altered many soil physicochemical characteristics and promoted clay dispersion when pH was increased to values higher than 7.0 (Nunes et al., 2017). For all but four soils, the proposed models would raise pH to values lower than 6.0, even with the highest LR (LH$_H$) (Table 5), indicating that LR estimates were not in excess to adversely affect soil structure and crop growth. Among these models, the OMpH$_{6.0}$ and HAlpH$_{6.0}$ predicted the highest LR (LR$_H$) (bold values in table 3) to most of the soils, which was up to 92 % higher than the LR$_R$ (Table 5). The large difference between LR$_R$ and LR$_H$ predicted by the models highlights the importance of a judicious

model selection for diminishing the risk of predicting excessive LR that may affect soil chemical and physical characteristics.

The recommendation frequency of LR following different criteria, according to the proposed algorithm, revealed that most predictions fell within the preferential criterion of LR (X ≤ LR ≤ HAl), mainly for the calibration dataset as well as for achieving the target pH of 6.0 (Table 6). However, a considerable frequency of recommendations for both datasets was classified into the 0 < LR < X criterion, particularly for a target pH of 5.8 (Table 6). This may be due to the soils having low levels of HAl and OM, and thus low buffering capacity, being subject to insufficient LR to supply plants with Ca + Mg (X). For instance, most LR predictions by the $OMpH_{5.8}$ model that fell within the 0 < LR < X criterion to the calibration (78 % of the cases) and validation (86 % of the cases) datasets were assigned to soils showing OM levels lower than 40 g kg^{-1}. A similar trend was observed to the $HAlpH_{5.8}$ model, where most of the LR predictions insufficient to meet X in the calibration (70 % of the cases) and validation (51 % of the cases) datasets were assigned to soils showing HAl lower than 5 cmol$_c$ dm^{-3}.

In fact, soils with lower buffer capacity need less LR to reach a given target pH than soils with higher buffer capacity (Cherian and Arnepalli, 2015). However, such a LR should be enough for meeting the Ca^{2+} and Mg^{2+} requirements of the plant (X), which is considered as the minimum limit to the LR_R. Under this case, the new predictive models seemed to be less sensitive for predicting LR higher than X for soils with low levels of HAl and OM. Noteworthy, they have an advantage over traditional methods for estimating LR as they predict LR lower than the levels of soil HAl, avoiding any possibility of overliming. In a recent study on traditional LR methods, Guarçoni and Sobreira (2017) demonstrated that the method aiming to neutralize exchangeable acidity (M^{x+}), and increase exchangeable Ca^{2+} and Mg^{2+} levels predicted LR higher than HAl for almost 20 % of the soils, which can lead to very high soil pH in particular for soils with low T (<5 cmol$_c$ dm^{-3}). These authors also showed that the base saturation method predicted LR lower than that enough to supply coffee plants with Ca and Mg for almost 74 % of the soils.

Poor predictions of LR by the base saturation method were also found by many authors (Oliveira et al., 1997; Kaminski et al., 2002; Araújo et al., 2009; Deus et al., 2014; Predebon et al., 2018), which may be due to the underestimation of HAl that is used to determine the cation exchange capacity when calculating the base saturation percentage. Most often this underestimation is explained by the poor buffer capacity of the calcium acetate extractor (0.5 mol L^{-1} pH 7.0) at the pH range of 6.0-7.0 (van Raij, 1991). The proposed models may further help to overcome such limitations when using traditional methods to determine LR in tropical conditions.

CONCLUSIONS

This study presents four new predictive models of lime requirement (LR) to attain target pH values of 5.8 and 6.0, which are suitable for most crops in Brazil. These models can predict LR with reasonably high prediction performance based either on the levels of soil pH and organic matter ($OMpH_{5.8}$ = 0.0699* [(5.8 - pH) OM]$^{0.9225**}$, R^2 = 0.863; $OMpH_{6.0}$ = 0.1059* [(6.0 - pH) OM]$^{0.8729**}$, R^2 = 0.886), or soil pH and potential acidity ($HAlpH_{5.8}$ = 0.3750* [(5.8 - pH) HAl]$^{0.9127**}$, R^2 = 0.758; $HAlpH_{6.0}$ = 0.4558* [6.0 - pH) HAl]$^{0.9162*}$, R^2 = 0.836). An algorithm was further developed for selecting the LR to be recommended among those estimated by the models. The proposed algorithm enables to select the minimum LR that ensure the adequate supply of Ca and Mg to plants and does not exceed the levels of soil HAl, thus preventing excessive pH increase.

Overall, the new predictive models were less sensitive to predict LR high enough to meet Ca and Mg requirements of the plant in soils containing lower levels of HAl (<5 cmol$_c$ dm^{-3}) and OM (<40 g kg^{-1}). However, they ensured an adequate supply of Ca and Mg to plants

and avoided an overestimation of LR for most soils used in this research. Validation via an independent dataset (n = 100 samples) confirmed the good predictive performance of the models across a wide range of soil types. In summary, the proposed models can be used as good alternatives to traditional methods for predicting LR for a great variety of Brazilian soils. Additionally, they are versatile and may be easily deployed in soil testing laboratories, since soil pH, OM, and HAl are characteristics determined in routine analysis. The choice among the predictive models will depend on the available soil characteristics at the time of LR prediction. Further research under field conditions may help to improve the predictive ability of the models.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data to this article can be found online at https://www.rbcsjournal.org/wp-content/uploads/articles_xml/1806-9657-rbcs-44-e0200008/1806-9657-rbcs-44-e0200008-suppl01.pdf

ACKNOWLEDGMENTS

AUTHOR CONTRIBUTIONS

Conceptualization: (iD) Júlio César Lima Neves (supporting), (iD) Víctor Hugo Alvarez V. (lead), and (iD) Welldy Gonçalves Teixeira (supporting).

Data curation: (iD) Welldy Gonçalves Teixeira (lead).

Formal analysis: (iD) Júlio César Lima Neves (supporting), (iD) Víctor Hugo Alvarez V. (supporting), and (iD) Welldy Gonçalves Teixeira (lead).

Investigation: (iD) Víctor Hugo Alvarez V. (supporting) and (iD) Welldy Gonçalves Teixeira (lead).

Methodology: (iD) Víctor Hugo Alvarez V. (equal) and (iD) Welldy Gonçalves Teixeira (equal).

Supervision: (iD) Júlio César Lima Neves (supporting) and (iD) Víctor Hugo Alvarez V. (lead).

Visualization: (iD) Víctor Hugo Alvarez V. (supporting) and (iD) Welldy Gonçalves Teixeira (lead).

Writing - original draft preparation: (iD) Víctor Hugo Alvarez V. (supporting) and (iD) Welldy Gonçalves Teixeira (lead).

Writing - review and editing: (iD) Víctor Hugo Alvarez V. (supporting) and (iD) Welldy Gonçalves Teixeira (lead).

REFERENCES

Aitken RL, Moody PW, Mckinley PG. Lime requirement of acidic Queensland soils. II. Comparison of laboratory methods for predicting lime requirement. Aust J Soil Res. 1990;28:703-15. https://doi.org/10.1071/SR9900703

Alleoni LRF, Cambri MA, Caires EF. Atributos químicos de um Latossolo de cerrado sob plantio direto, de acordo com doses e formas de aplicação de calcário. Rev Bras Cienc Solo. 2005;29:923-34. https://doi.org/10.1590/S0100-06832005000600010

Almeida JD, Ernani PR, Maçaneiro KC. Recomendação alternativa de calcário para solos altamente tamponados do extremo sul do Brasil. Cienc Rural. 1999;29:651-6. https://doi.org/10.1590/S0103-84781999000400014

Alvarez V VH. Correlação e calibração de métodos de análise de solos. In: Alvarez V VH, Fontes LEF, Fontes MPF, editores. O solo nos grandes domínios morfoclimáticos do Brasil e o desenvolvimento sustentado. Viçosa, MG: Sociedade Brasileira de Ciência do Solo; 1996. p. 615-46.

Alvarez V VH, Dias LE, Santos AR. Solos corrigidos com doses estimadas a partir de diferentes critérios para definir a necessidade de calagem. Teores de Ca^{2+} e Al^{3+}. In: Anais do XXII Congresso Brasileiro de Ciência do Solo; 1989, Recife. Campinas: Sociedade Brasileira de Ciência do Solo; 1990a. p. 276-7.

Alvarez V VH, Dias LE, Santos AR. Solos corrigidos com doses estimadas a partir de diferentes critérios para definir a necessidade de calagem - Valores de pH. In: Anais do XXII Congresso Brasileiro de Ciência do Solo; 1989; Recife. Campinas: Sociedade Brasileira de Ciência do Solo; 1990b. p. 278-9.

Alvarez V VH, Novais RF, Barros NF, Cantarutti RB, Lopes AS. Interpretação dos resultados das análises de solos. In: Ribeiro AC, Guimarães PTG, Alvarez V VH, editores. Recomendação para o uso de corretivos e fertilizantes em Minas Gerais - 5ª Aproximação. Viçosa, MG: Comissão de Fertilidade do Solo do Estado de Minas Gerais; 1999. p. 25-32.

Alvarez V VH, Novais RF, Dias LE, Oliveira JA. Determinação e uso do fósforo remanescente. Bol Inf Soc Bras Cienc Solo. 2000;25:27-33.

Alvarez V VH, Ribeiro AC. Calagem. In: Ribeiro AC, Guimarães PTG, Alvarez V VH, editores. Recomendação para o uso de corretivos e fertilizantes em Minas Gerais - 5ª Aproximação. Viçosa, MG: Comissão de Fertilidade do Solo do Estado de Minas Gerais; 1999. p. 43-60.

Araújo SR, Demattê JAM, Garbuio FJ. Aplicação de calcário com diferentes graus de reatividade: Alterações químicas no solo cultivado com milho. Rev Bras Cienc Solo. 2009;33:1755-64. https://doi.org/10.1590/S0100-06832009000600024

Bolan NS, Adriano DC, Curtin D. Soil acidification and liming interactions with nutrient and heavy metal transformation and bioavailability. Adv Agron. 2003;78:215-72. https://doi.org/10.1016/S0065-2113(02)78006-1

Borges Júnior RM, Mello J, Ribeiro A, Soares P. Avaliação de critérios para calagem de arroz inundado em casa de vegetação. Rev Bras Cienc Solo. 1998;22:281-9. https://doi.org/10.1590/S0100-06831998000200014

Caballero EC, Orozco AJ, Luna MP. Modeling the requirements of agricultural limestone in acid sulfate soils of Brazil and Colombia. Commun Soil Sci Plan. 2019;50:935-47. https://doi.org/10.1080/00103624.2019.1594877

Caires EF, Banzatto DA, Fonseca AF. Calagem na superfície em sistema plantio direto. Rev Bras Cienc Solo. 2000;24:161-9. https://doi.org/10.1590/S0100-06832000000100018

Campanharo M, Lira Junior MA, Nascimento CWA, Freire FJ, Costa JVT. Avaliação de métodos de necessidade de calagem no Brasil. Rev Caatinga. 2007;20:97-105.

Catani RA, Gallo JR. Avaliação da exigência de calcário dos solos do Estado de São Paulo mediante a correlação entre pH e saturação de bases. Rev Agric. 1955;30:49-60. https://doi.org/10.37856/bja.v30i1-2-3.3062

Cate RB, Nelson LA. A rapid method for correlation of soil test analyses with plant response data. Raleigh: NC State University Agricultural Experiment Station; 1965.

Cherian C, Arnepalli DN. A critical appraisal of the role of clay mineralogy in lime stabilization. Int J Geosynth Ground Eng. 2015;1:8. https://doi.org/10.1007/s40891-015-0009-3

Curtin D, Trolove S. Predicting pH buffering capacity of New Zealand soils from organic matter content and mineral characteristics. Soil Res. 2013;51:494-502. https://doi.org/10.1071/SR13137

Defelipo BV, Braga JM, Spies C. Comparação entre métodos de determinação da necessidade de calcário de solos de Minas Gerais. Experientiae. 1972;13:111-36.

Defelipo BV, Ribeiro AC. Análise química do solo: metodologia. 2. ed. Viçosa, MG: Universidade Federal de Viçosa; 1997.

Deus ACF, Bull LT, Corrêa JC, Villas Boas RL. Nutrient accumulation and biomass production of alfafa after soil amendment with silicates. Rev Ceres. 2014;61:406-13. https://doi.org/10.1590/S0034-737X2014000300016

Edmeades DC, Wheeler DM, Waller JE. Comparison of methods for determining lime requirements of New Zealand soils. New Zeal J Agr Res. 1985;28:93-100. https://doi.org/10.1080/00288233.1985.10427001

Ernani PR, Nascimento JAL, Oliveira LC. Increase of grain and green matter of corn by liming. Rev Bras Cienc Solo. 1998;22:275-80. https://doi.org/10.1590/S0100-06831998000200013

Fageria NK. Optimum soil acidity indices for dry bean production on an Oxisol in no-tillage system. Commun Soil Sci Plan. 2008;39:845-57. https://doi.org/10.1080/00103620701880909

Fageria NK, Baligar VC. Ameliorating soil acidity of tropical Oxisols by liming for sustainable crop production. Adv Agron. 2008;99:345-99. https://doi.org/10.1016/S0065-2113(08)00407-0

Fageria N, Baligar VC. Fertility management of tropical acid soils for sustainable crop production. In: Rengel Z, editor. Handbook of soil acidity. New York: Marcel Dekker; 2003. p. 359-85.

Fageria NK, Baligar VC. Improving nutrient use efficiency of annual crops in Brazilian acid soils for sustainable crop production. Commun Soil Sci Plan. 2001;32:1303-19. https://doi.org/10.1081/CSS-100104114

Fageria NK, Baligar VC. Growth and nutrient concentrations of common bean, lowland rice, corn, soybean and wheat at different soil pH on an Inceptisol. J Plant Nutr. 1999;22:1495-507. https://doi.org/10.1080/01904169909365730

Fageria NK, Nascente AS. Management of soil acidity of South American soils for sustainable crop production. Adv Agron. 2014;128:221-75. https://doi.org/10.1016/B978-0-12-802139-2.00006-8

Fageria NK, Stone LF. Micronutrient deficiency problems in South America. In: Alloway BJ, editor. Micronutrient deficiencies in global crop production. Dordrecht: Springer; 2008. p. 245-66.

Fageria NK, Stone LF. Manejo da acidez dos solos de cerrado e de várzea do Brasil. Santo Antônio de Goiás: Embrapa Arroz e Feijão; 1999.

Godsey CB, Pierzynski GM, Mengel DB, Lamond RE. Evaluation of common lime requirement methods. Soil Sci Soc Am J. 2007;71:843-50. https://doi.org/10.2136/sssaj2006.0121

Goedert WJ. Management of the Cerrado soils of Brazil: a review. J Soil Sci. 1983;34:405-28. https://doi.org/10.1111/j.1365-2389.1983.tb01045.x

Graybill FA. Theory and application of the linear model. Massachusets: Ouxburg Press; 1976.

Guarçoni A, Sobreira FM. Classical methods and calculation algorithms for determining lime requirements. Rev Bras Cienc Solo. 2017;41:e0160069. https://doi.org/10.1590/18069657rbcs20160069

Hochman Z, Crocker GJ, Dettman EB. Predicting lime-induced changes in soil-pH from exchangeable aluminum, soil-pH, total exchangeable cations and organic-carbon values measured on unlimed soils. Soil Res. 1995;33:31-41. https://doi.org/10.1071/SR9950031

Holland JE, Bennett AE, Newton AC, White PJ, McKenzie BM, George TS, Pakeman RJ, Bailey JS, Fornara DA, Hayes RC. Liming impacts on soils, crops and biodiversity in the UK: a review. Sci Total Environ. 2018;610-611:316-32. https://doi.org/10.1016/j.scitotenv.2017.08.020

Hopkins WG. Bias in bland-altman but not regression validity analyses. Sportscience. 2004;8:42-6.

Kaminski J, Gatiboni LC, Rheinheimer DS, Martins JR, Santos EJS, Tissot CA. Estimativa da acidez potencial em solos e sua implicação no cálculo da necessidade de calcário. Rev Bras Cienc Solo. 2002;26:1107-13. https://doi.org/10.1590/S0100-06832002000400029

Keeney DR, Corey RB. Factors affecting the lime requirements of Wisconsin soils. Soil Sci Soc Am J. 1963;27:277-80. https://doi.org/10.2136/sssaj1963.03615995002700030019x

Leite HG, Oliveira FHT. Statistical procedure to test identity of analytical methods. Commun Soil Sci Plan. 2002;33:1105-18. https://doi.org/10.1081/CSS-120003875

Lopes AS, Guimarães PTG. Recomendações para o uso de corretivos e fertilizantes em Minas Gerais - 4ª aproximação. Lavras: Comissão de Fertilidade do Solo do Estado de Minas Gerais; 1989.

McLean EO. Testing soils for pH and lime requirement. In: Walsh LM, Beaton JD, editors. Soil testing and plant analysis. Madison: Soil Science Society of America; 1973. p. 78-95.

Milagres JJM, Alvarez V VH, Cantarutti RB, Neves JCL. Determinação de Fe, Zn, Cu e Mn extraídos do solo por diferentes extratores e dosados por espectrofotometria de emissão ótica em plasma induzido e espectrofotometria de absorção atômica. Rev Bras Cienc Solo. 2007;31:237-45. https://doi.org/10.1590/S0100-06832007000200006

Nelson DW, Sommers LE. Total carbon, organic carbon, and organic matter. In: Sparks DL, editor. Methods of soil analysis: chemical methods. Madison: American Society of Agronomy; 1996. p. 961-1010.

Nicolodi M, Anghinoni I, Gianello C. Relações entre os tipos e indicadores de acidez do solo em lavouras no sistema plantio direto na região do Planalto do Rio Grande do Sul. Rev Bras Cienc Solo. 2008;32:1217-26. https://doi.org/10.1590/S0100-06832008000300030

Nunes MR, Vaz CMP, Denardin JE, van Es HM, Libardi PL, Silva AP. Physicochemical and structural properties of an Oxisol under the addition of straw and lime. Soil Sci Soc Am J. 2017;81:1328-39. https://doi.org/10.2136/sssaj2017.07.0218

Oliveira EL, Parra MS, Costa A. Resposta da cultura do milho, em um Latossolo Vermelho-Escuro álico, à calagem. Rev Bras Cienc Solo. 1997;21:65-70.

Pagani A, Mallarino AP. Comparison of methods to determine crop lime requirement under field conditions. Soil Sci Soc Am J. 2012;76:1855-66. https://doi.org/10.2136/sssaj2011.0327

Predebon R, Gatiboni LC, Mumbach GL, Schmitt DE, Dall'Orsoletta DJ, Brunetto G. Accuracy of methods to estimate potential acidity and lime requirement in soils of west region of Santa Catarina. Cienc Rural. 2018;48:e20160935. https://doi.org/10.1590/0103-8478cr20160935

Quaggio JA. Reação do solo e seu controle. In: Simpósio avançado de química e fertilidade do solo; 1986. Piracicaba: Fundação Cargill; 1986. p. 9-39.

Quaggio JA, van Raij B, Malavolta E. Alternative use of the SMP-buffer solution to determine lime requirement of soils. Commun Soil Sci Plan. 1985;16:245-60. https://doi.org/10.1080/00103628509367600

Ruiz HA. Incremento da exatidão da análise granulométrica do solo por meio da coleta da suspensão (silte + argila). Rev Bras Cienc Solo. 2005;29:297-300. https://doi.org/10.1590/S0100-06832005000200015

Ruiz HA, Ferreira GB, Pereira JBM. Estimativa da capacidade de campo de Latossolos e Neossolos Quartzarênicos pela determinação do equivalente de umidade. Rev Bras Cienc Solo. 2003;27:389-93. https://doi.org/10.1590/S0100-06832003000200019

Sá EM, Rowell DL, Martins AG, Silva AP. Effect of pH on the development of acidic sites in clayey and sandy loam Oxisol from the Cerrado Region, Brazil. Geoderma. 2006;132:131-42. https://doi.org/10.1016/j.geoderma.2005.05.001

Santos HG, Jacomine PKT, Anjos LHC, Oliveira VA, Oliveira JB, Coelho MR, Lumbreras JF, Cunha TJF. Sistema brasileiro de classificação de solos. 3. ed. rev. ampl. Rio de Janeiro: Embrapa Solos; 2013.

Serra AP, Marchetti ME, Rojas EP, Vitorino ACT. Beaufils ranges to assess the cotton nutrient status in the southern region of Mato Grosso. Rev Bras Cienc Solo. 2012;36:171-82. https://doi.org/10.1590/S0100-06832012000100018

Silva V, Motta ACV, Lima VC. Variáveis de acidez em função da mineralogia da fração argila do solo. Rev Bras Cienc Solo. 2008;32:551-9. https://doi.org/10.1590/S0100-06832008000200010

Shoemaker HE, McLean EO, Pratt PF. Buffer methods for determining lime requirement of soils with appreciable amounts of extractable aluminum. Soil Sci Soc Am J. 1961;25:274-7. https://doi.org/10.2136/sssaj1961.03615995002500040014x

Soares R, Escaleira V, Monteiro MIC, Pontes FVM, Santelli RE, Bernardi ACC. Uso de ICP OES e titrimetria para a determinação de cálcio, magnésio e alumínio em amostras de solos. Rev Bras Cienc Solo. 2010;34:1553-9. https://doi.org/10.1590/S0100-06832010000500008

Soil Survey Staff. Keys to soil taxonomy. 12th ed. Washington, DC: United States Department of Agriculture, Natural Resources Conservation Service; 2014.

Soratto RP, Crusciol CAC. Atributos químicos do solo decorrentes da aplicação em superfície de calcário e gesso em sistema plantio direto recém-implantado. Rev Bras Cienc Solo. 2008;32:675-88. https://doi.org/10.1590/S0100-06832008000200022

Sousa DMG, Miranda LN, Lobato E, Castro LHR. Métodos para determinar as necessidades de calagem em solos dos cerrados. Rev Bras Cienc Solo. 1989;13:193-8.

Sousa DMG, Miranda LN, Oliveira SA. Acidez do solo e sua correção. In: Novais RF, Alvarez V VH, Barros NF, Fontes RLF, Cantarutti RB, Neves JCL, editores. Fertilidade do solo. Viçosa, MG: Sociedade Brasileira de Ciência do Solo; 2007. p. 205-74.

Sumner ME, Noble AD. Soil acidification: the world story. In: Rengel Z, editor. Handbook of soil acidity. New York: Marcel Dekker; 2003. p. 1-28.

Teixeira WG, Reis JV, Freitas JAD, Alvarez V VH. Determinação da necessidade de calagem para o cafeeiro considerando a acidez potencial. In: Proceedings of the 20th Congreso Latinoamericano y 16th Congreso Peruano de la Ciencia del Suelo; 2014 Nov 9-15; Cusco, PE. Cusco: Sociedad Peruana de la Ciencia del Suelo; 2014.

Thomas GW, Hargrove WL. The chemistry of soil acidity. In: Adams F, editor. Soil acidity and liming. 2nd ed. Madison: American Society of Agronomy; 1984. p. 3-56.

van Raij B. Fertilidade do solo e adubação. Piracicaba: Potafos; 1991.

van Raij B, Cantarella H, Quaggio JA, Furlani AMC. Recomendações de adubação e calagem para o Estado de São Paulo. 2. ed. Campinas: IAC; 1996.

van Raij B, Cantarella H, Zullo MAT. O método tampão SMP para determinação da necessidade de calagem de solos do estado de São Paulo. Bragantia. 1979;38:57-69. https://doi.org/10.1590/S0006-87051979000100007

van Stralen KJ, Jager KJ, Zoccali C, Dekker FW. Agreement between methods. Kidney Int. 2008;74:1116-20. https://doi.org/10.1038/ki.2008.306

von Uexküll HR, Mutert E. Global extent, development and economic impact of acid soils. Plant Soil. 1995;171:1-15. https://doi.org/10.1007/BF00009558

Wang X, Tang C, Mahony S, Baldock JA, Butterly CR. Factors affecting the measurement of soil pH buffer capacity: approaches to optimize the methods. Eur J Soil Sci. 2015;66:53-64. https://doi.org/10.1111/ejss.12195

Weirich Neto PH, Caires EF, Justino A, Dias J. Correção da acidez do solo em função de modos de incorporação de calcário. Cienc Rural. 2000;30:257-61. https://doi.org/10.1590/S0103-84782000000200010

Wong MTF, Webb MJ, Wittwer K. Development of buffer methods and evaluation of pedotransfer functions to estimate pH buffer capacity of highly weathered soils. Soil Use Manage. 2013;29:30-8. https://doi.org/10.1111/sum.12022