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AGRICULTURAL CHEMISTRY AND SOIL FERTILITY

Ca Saturation Determines Crop Growth in Acidic Ultisols Derived from Different Parent Materials

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Abstract—Soil acidity has become a major yield-limiting factor, but it is unclear which acidity indicator is the best to use for estimating crop yield changes. In this study, four pH-adjusted Ultisols derived from different parent materials were used for Chinese cabbage and wheat pot experiments. Structural equation modeling (SEM), Gompertz and linear-plateau models were used to examine main contribution of soil acidity indices and to determine their critical values. The results showed that Ca saturation had the strongest direct effect on crop biomass and thus acted as the most important factor. The critical values of Ca saturation varied slightly with crops and soils, where it was 84.6, 93.5, 95.2 and 82.9% for Ultisols derived from plate shale, Quaternary red clay, red sandstone and granite, respectively. The critical values of exchangeable Ca and Al, and Al saturation and exchangeable Al : Ca ratio (or Ca : Al ratio) were also determined as 8.21 and 0.44 $cmol_c\ kg^{-1}$, 6.37%, and 0.069 (or 14.5), respectively. In summary, our findings evidenced that critical Ca saturation has the potential to evaluate the implementation of quality improvement of acidic soils for good crop production.

Keywords: exchangeable Ca : Al ratio, Chinese cabbage, wheat, pot experiments, soil acidity

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INTRODUCTION

Red soils (Ultisols) are widely distributed in subtropical regions of China and are its main acidic cropland soils, where marked soil acidification has been noted. The topsoil pH has decreased by an average of 0.85 units over a period of 30 years, and the area of acidic agricultural soils (pH < 5.5) increased from 6.2 million ha in 1980 to 10.3 million ha in 2010 [8, 57].

Several studies have shown that crop yields were significantly correlated with soil pH, and therefore critical soil pH values (pH threshold) for different crops were determined [4, 12, 28, 31, 59]. For example, Fageria and Baligar [12] showed that the critical pH values for wheat, common bean, soybean, maize and rice were 6.3, 6, 5.6, 5.4 and 4.9, respectively. The critical pH could be used as a control parameter to determine lime requirement of strongly acidic soils. However, soil acidification resulted in large increases in levels of exchangeable aluminum and manganese (Exch. Al and Exch. Mn) and decreases in concentrations of exchangeable calcium, magnesium, and potassium (Exch. Ca, Exch. Mg and Exch. K), which decreased significantly soil productivity [14, 19, 44, 45, 49]. It maybe that low soil pH inhibits crop growth via a main indirect effect on Exch. Al and/or Exch. Ca. That is, these critical values of Exch. Al and Exch. Ca clearly deserve more attention in quantifying crop response to soil acidification.

Like critical soil pH, critical Exch. Al values also ranged greatly, from 0.24 to 5.2 $cmol_c\ kg^{-1}$, depending on temperate zone, crop type and soil type [35, 36, 41, 42, 53]. For example, Qin and Chen [36] showed that critical Exch. Al was 4.0 $cmol_c\ kg^{-1}$ for wheat and 4.8 $cmol_c\ kg^{-1}$ for maize, respectively, in Hunan's Ultisol derived from Quaternary red clay, while Baquy et al. [3–5] found that in Anhui's Ultisol derived from Quaternary red clay it was 1.72 and 1.99 $cmol_c\ kg^{-1}$, respectively. Further, it was suggested that higher critical Exch. Al content for those acidic soils was mainly attributed to the higher pH buffer capacity (pHBC), as a consequence of having greater cation exchange capacity (CEC) and higher soil organic matter (SOM) levels [3–5]. These results suggested that critical Exch. Al may not be a better indicator than critical pH in determining crop growth. Therefore, some other critical values such as Exch. Ca, Al saturation, Ca saturation, and even Ca : Al molar ratio, were used for determining the crop-soil relationship [2, 4, 5, 9, 13, 17, 46]. In Malaysia critical Exch. Ca for rice growth was

1.2 $cmol_c\ kg^{-1}$ [2], which is comparable to that found by Wei et al. [51] in China's Ultisols (1.25 $cmol_c\ kg^{-1}$). Our investigation in Qiyang County, Hunan province, showed that the Exch. Ca content ranged from 0.2 to 70.0 $cmol_c\ kg^{-1}$ and 103 out of 275 (37.5%) soil sites had the value below the critical level of 1.25 $cmol_c\ kg^{-1}$ (unpublished data). This means that it is better to increase the Exch. Ca content in acidic soils during the crop growth period. Therefore, we assume that crop growth in Hunan's red soils is mainly limited by Exch. Ca or Ca saturation.

Structural equation modeling (SEM) is an extension of regression and path analysis that can be used to model multivariate relations and distinguish direct from indirect effects of factors. The use of SEM to explore the relationships between ecosystem structure and function has increased dramatically in recent years [11, 26, 38, 54, 56]. However, little research has been conducted examining the relationships among soil pH, Exch. Al, Exch. Ca and crop productivity in acidic Ultisols. The purpose of this study was to: (1) use SEM to explore the direct and indirect effects of soil pH on crop growth; (2) demonstrate that Ca saturation is the main factor controlling the crop yield in strongly acidic soils; and (3) establish critical limits of Ca saturation for crop yield on Ultisols derived from different parent materials.

MATERIALS AND METHODS

Soils. Ultisols originated from four parent materials were collected from different locations of Qiyang County, Hunan Province, China, for this study (plate shale: 26°44′31″ N, 111°53′34″ E; Quaternary red clay: 26°35′4″ N, 111°46′51″ E; red sandstone: 26°9′14″ N, 112°10′33″ E; granite: 26°9′31″ N, 112°8′35″ E). Soil samples were taken from top layer (0–20 cm), air-dried and ground through 1-cm screen for the pot experiment. Their chemical properties were analyzed by the method of Lu [29] and were listed in Table S1. Where effective cation exchange capacity (ECEC) is the sum of exchangeable cations (Ca + Mg + K + H + Al), and Al and Ca saturation were estimated as the proportion of these cations in ECEC [4, 5, 14]. The soil pHBC was estimated from the slopes of linear portion of titration curves at pH 4–6 [1].

The higher pHBC of a soil at a given pH, the more resistance it offers to change in pH following acid or alkali addition. Table S1 showed Ultisols derived from granite has the lowest pHBC (11.9 kmol $H^+\ kg^{-1}\ pH^{-1}$), about half of that from plate shale, which was probably mainly contributed to its lowest CEC. Baquy et al. [3–5] considered that soils with higher CEC and higher SOM could be more resistant to changes of soil acidity, viz., higher pHBC. Zhao et al. [55] further evidenced that CEC was the main factor limiting the acidification of Ultisols derived from plate shale, quaternary red clay, red sandstone and granite.

Pot experiments. For each of the four soils, pH buffer curve was established between pH 3 and 8 by shaking 10 g of soil for 12 h in 50 mL H_2O with varying amounts of H_2SO_4 and CaO in 15 samples, where each sample was continuously measured at least 5 times. The pHs were then adjusted to 3–8 with 14 gradients in 20 kg of soil by 1 mol L^{-1} H_2SO_4 and CaO based on the pH buffer curve of each soil before pot experiments. For every soil pH, three replicates were assigned, and every soil was potted at 2.5 kg per pot, and mixed with mineral fertilizers (urea, calcium superphosphate, and KCl with $N : P_2O_5 : K_2O = 2 : 1 : 1$ and application rate of 300 kg N ha^{-1}) after it was pre-incubated at 70% of field water holding capacity in the dark at 25°C for 30 days (Chinese cabbage) and 60 days (wheat), respectively. Considering the time effect, we selected 10 pH gradients for each soil for Chinese cabbage experiment (4 × 10 × 3 = 120 treatments) and 10–14 gradients for wheat (138 treatments).

4 pre-germinated Chinese cabbage seeds (or 10 wheat seeds) of same size were selected for uniform plant growth. Seeds were sown at the same depth into each pot soil, and each pot was regularly weighed to maintain soil moisture at 70% of field water holding capacity throughout the trial period. Pots were arranged on a screenhouse in a randomized complete design with three replications per treatment. The plants grew for 30 days and were then harvested, where shoots were oven-dried at 70°C for 48 h and weighed. At that time, soil samples were collected from each pot separately, air-dried, and ground to pass through a 0.25-mm sieve for measuring soil pH, exchangeable acidity and base cations.

Additionally, after 30 days of incubation (before beginning the pot experiment) the soils were also sampled to determine soil acidity and exchangeable cations.

Soil analysis. According to the method of Lu [29], soil pH was measured with a pHSJ-4F meter (INESA, Shanghai, China) in a 1 : 2.5 soil/water suspension. The exchangeable acidity (Exch. Al + Exch. H) was extracted with 1.0 M KCl and then titrated by 0.02 M NaOH to pH 7.0. 1 M NaF was added to part of the extract, followed by titration with 0.02 M NaOH to determine Exch. H. Exch. Al was calculated as the difference between exchangeable acidity and Exch. H. Exchangeable base cations were extracted with 1.0 M ammonium acetate at pH 7.0, and then Ca and Mg were determined using atomic absorption spectrometry (ZEEnit700P, Analytik Jena, Germany) and only K (no detectable Na) with flame photometry (6400A, INESA, Shanghai, China).

ECEC, Al and Ca saturation and Exch. Al : Ca ratio were calculated using the following formulas [4, 5, 14]:

$$\mathrm{ECEC}\left(\mathrm{cmol_c\ kg^{-1}}\right) = \text{Exch. Ca} + \text{Exch. Mg} + \text{Exch. K} + \text{Exch. H} + \text{Exch. Al},$$

$$\text{Al saturation } (\%) = \text{Exch. Al}/\text{ECEC} \times 100,$$

Table 1. The goodness of fit parameters of SEMs for Chinese cabbage and wheat

Index	Acceptable	Chinese cabbage	Wheat
P-value	>0.05	0.265	0.057
χ^2	–	15.72	23.238
df	–	13	14
χ^2/df	<3.00	1.21	1.66
NNFI	>0.90	0.996	0.989
CFI	>0.90	0.999	0.996
RMSEA	<0.08	0.042	0.069
GFI	>0.95	0.973	0.964
NFI	>0.95	0.992	0.989

$$\text{Ca saturation } (\%) = \text{Exch. Ca}/\text{ECEC} \times 100,$$

$$\text{Exch. Al : Ca ratio} = \text{Exch. Al}/\text{Exch. Ca}.$$

Data analysis. In order to avoid bias among Ultisols derived from different parent materials, relative yield of shoot dry weight was calculated by the following formula:

$$\text{relative yield } (\%) = \frac{\text{actual yield of shoot dry matter}}{\text{an average for the maximum yield treatment}} \times 100.$$

Gompertz model and linear-plateau model could simulate the relationships between crop yield and soil pH, in which critical pH values were determined. Gompertz equation was described as follows:

$$y = a \times \exp\left\{-\exp\left[-\frac{(x - x_0)}{b}\right]\right\},$$

where a is asymptotic value, i.e., maximum yield reached; b is a parameter relating to slope of the curve; x_0 is inflection point where the curve reaches its maximum slope, that is, x_0 is most sensitive to changes in y [10, 21, 32, 39]. Accordingly, critical soil pH, corresponding to 90% of maximum yield, was calculated using the following equation:

$$x = -\ln(-\ln 0.9)b + x_0 = 2.25b + x_0.$$

The linear-plateau equation was described below:

$$y = \begin{cases} a + b \times x & x \le x_0 \\ c & x > x_0 \end{cases},$$

where a is the intercept and b is the slope of the line; c is the plateau value (maximum or minimum yield), and x_0 is determined as the intersection point of two linear lines representing critical or threshold value [27, 31, 35, 48, 50].

The SEM analyses were performed using AMOS 17.0 (IBM-SPSS Inc., Chicago, USA). Spearman correlation analysis, stepwise multiple regression analysis, and curve fitting were performed using SPSS 17.0 (IBM-SPSS Inc., Chicago, USA). Results were plotted using SigmaPlot 12.0 (Systat Software Inc., San Jose, USA).

RESULTS

Direct and indirect effects of soil acidity indices on crop growth. To examining the multivariate relations between soil acidity indices and crop yield, and quantifying their direct and indirect effects, a SEM model was built and presented in Fig. 1 and Table 1. The *P* values were not significant for Chinese cabbage ($P = 0.265$) and wheat ($P = 0.057$), supporting the established models. Additionally, Hoe [23] proposed that the ideal fit indices are Non-Normed Fit Index (NNFI) and Comparative Fit Index (CFI) (>0.90 indicates good fit), Root Mean Square Error of Approximation (RMSEA) (<0.08 indicates acceptable fit), and χ^2 statistic (χ^2/df ratio of 3 or less). Zhu et al. [58] considered that a good fitting model must also have higher Goodness of Fit Index (GFI) and Normed Fit Index (NFI) (>0.95). In our study, all values were in the acceptable interval, further demonstrating the soundness of the models.

As shown in the SEM models, the total effect of soil pH on crop production was the strongest, with 0.84 for Chinese cabbage and 0.77 for wheat; however, its direct effect was only 0.33 (39.3%) and 0.20 (26.2%), respectively. That is, major crop yield losses in acidic soils would come from the indirect effects due to changes in soil properties rather than direct effects due to pH decrease. Further, Ca saturation had the strongest direct effect on crop biomass (0.53 for Chinese cabbage and 0.51 for wheat, respectively), suggesting that it was the most important factor determining crop growth in acidic soils.

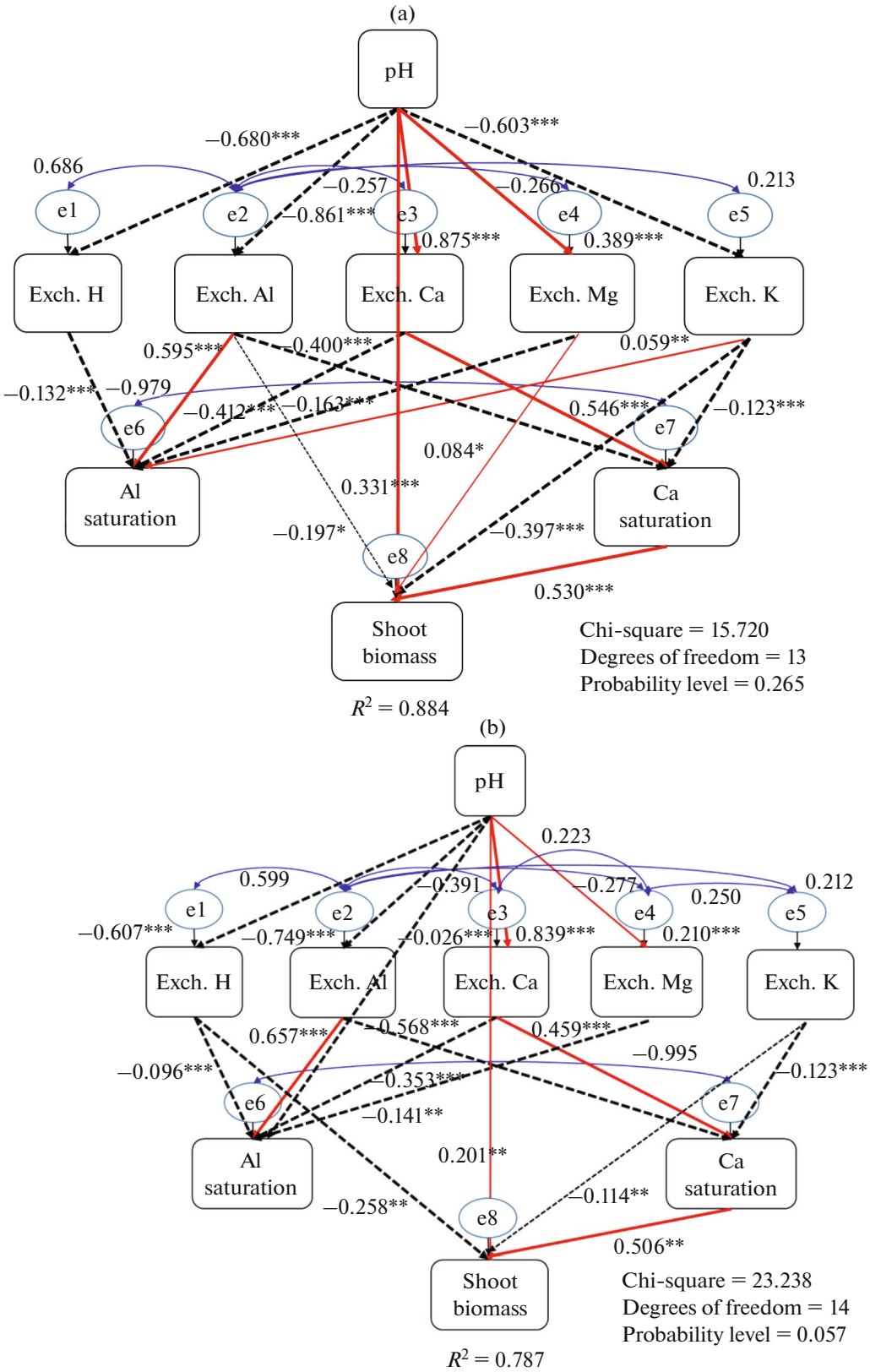

Fig. 1. Model results for (a) Chinese cabbage and (b) wheat. Single arrows represent the direct pathway of one variable to another, and double arrows represent the correlation between two variables. The width of solid and dotted arrows indicated the strength of the positive and negative relationships, respectively. The standardized path coefficients are listed beside the lines (***, **, and * indicated significant at 0.001, 0.01, 0.05, respectively).

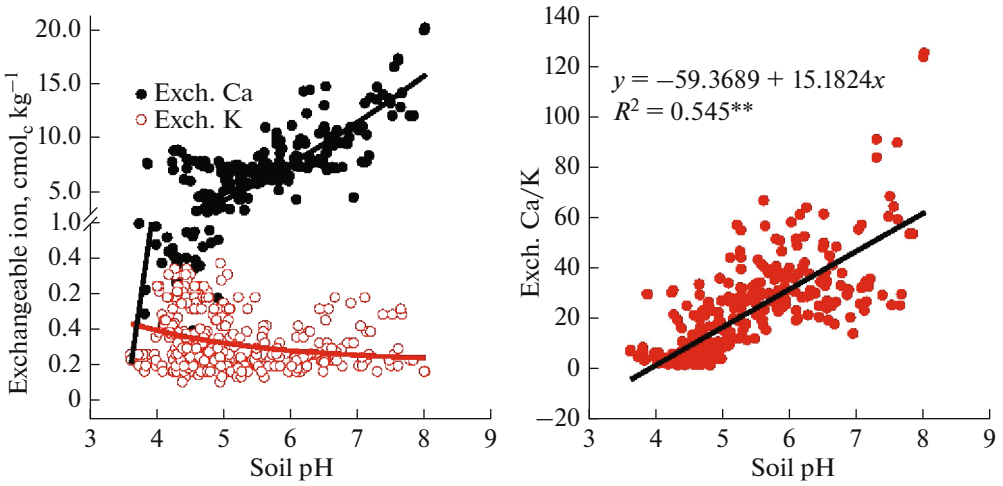

Fig. 2. The relationships between soil pH and Exch. Ca, Exch. K, and Exch. Ca/K.

It is worth noting that Exch. K exerted a significantly negative direct effect on crop growth in acidic soils (–0.397 for Chinese cabbage and –0.114 for wheat, respectively). This perhaps means that potassium fertilization at a rate of 150 kg K_2O ha^{-1} in acidic upland soils might be excessive, which led to increasing Exch. K and decreasing Exch. Ca in soils, and further declining crop yields as the consequence of an increase in calcium deficiency in crops. Gülser et al. [18] showed that NPK fertilization to acidic soils caused Ca and Mg (in particular Ca) deficiency in the grain, where grain yield showed negative correlation with K and positive correlation with Ca contents. Fekadu et al. [15, 16] supported that excessive soil K inhibited Ca uptake by crops, and thus, the yield decreased greatly. For production of annual crops, ratio ranges of 17 to 32.5 for Ca/K in soils are needed. In our study here, Exch. Ca/K was very lower in strong acidic soils (e.g., less than 5 at pH 4) than the proposed values (Fig. 2). It at pH exceeding 5 only could be considered as the favorable ratio due to the increase in Exch. Ca and the decrease in Exch. K. In short, for strong acidic soils, Ca deficiency is the main problem, and chemical fertilization (in particular K fertilizers) aggravates the problem. Therefore, increasing micronutrients such as Ca is more important than increasing macronutrients in strong acidic soils.

The significant variables (crop yield and soil acidity indices with a minimum collinearity by excluding those variables with eigenvalues close to 0 and condition index >10) were entered into a stepwise regression which produced 2 models, which revealed that Ca saturation was the most important, and explained 73 to 75% of the variance in crop yield (Table 2), which was consistent with the results of SEMs. These results all together therefore emphasized that quantifying optimum Ca saturation as an accurate representation of soil acidity indices is essential to understand crop response to soil acidification for obtaining maximum crop production.

Critical limit of Ca saturation in Ultisols. There were significant linear relations between crop growth and Ca saturation in soils, and the average slope of the lines was 1.1, except for Ultisol derived from plate shale in which a higher linear slope of 3.2 was found (Fig. 3). This suggested that the rate of crop yield increase with increase in Ca saturation was steeper in Ultisol derived from plate shale compared to other parent materials.

Based on linear regression analysis, the critical Ca saturation level (at 90% of maximum yield) in Ultisols for Chinese cabbage and wheat was determined and listed in Table 3. Herein, maintaining soil Ca saturation above 80% was crucial important for the achievement of high crop yield in acidic soils. However, a bigger difference was seen in critical Ca saturation among soils compared to that in crops, where Ultisol derived from granite had a relatively low Ca saturation requirement of 83% whereas it from quaternary red clay had higher critical value (about 94%). The main difference between the two soils is a higher SOM content (39.9 g kg^{-1}) in the former compared to 16.3 g kg^{-1} in the latter, which maybe lead to a larger increase in the resistance of crops to Al and H toxicity in acidic soils [20, 22, 43, 47].

Other critical soil indicators for crop growth in Ultisols. Although some distributions are not normal (Fig. S1), soil pH plays an important role in crop growth in acidic soils, and significantly correlates with all acidity indices, in particular with Exch. Ca, Exch. Al, Ca and Al saturation, and Exch. Al : Ca ratio (Table 4). Therefore, it is useful to determine the critical soil pH levels and other acidity indices values [2, 4, 5, 13, 17, 22, 46]. Herein, critical values of soil pH, Exch. Ca, Exch. Al, Al saturation, and Exch. Al : Ca ratio (or Ca : Al ratio) were calculated according to

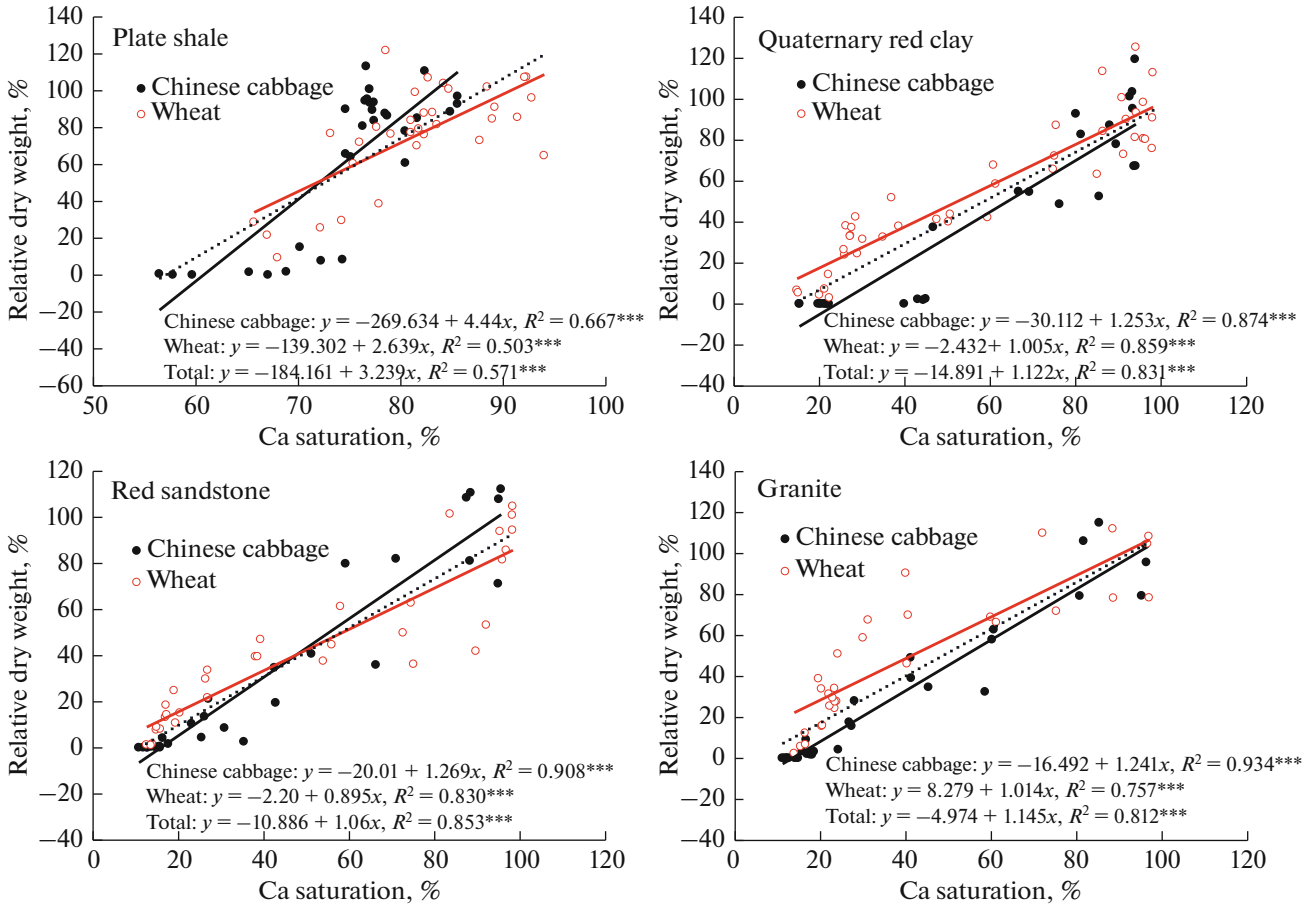

Fig. 3. Observed (symbols) and predicted (lines) relationships between shoot dry weights of Chinese cabbage (solid circles) and wheat (open circles) and Ca saturation.

crop response to individual soil indices (Gompertz model or linear-plateau model) (Fig. S2–S6 and Table 5 and S2).

Some were reasonable and some were not. For example, the values obtained for critical Exch. Al : Ca ratio by three methods in Ultisol derived from plate shale were similar (0.011~0.012 for Chinese cabbage and 0.019~0.023 for wheat, respectively), whereas a significant (by several times) difference was found in Ultisol derived from red sandstone (from 0.056 to

Table 2. Stepwise regression analysis of influence of soil acidity indices on crop growth in acidic Ultisols

Crop	Model		Coefficient				R^2
			B	SE	standardized	Sig.	
Chinese cabbage	1	Ca Saturation	1.213	0.063	0.870	0.000	0.757
		Constant	−22.278	3.813		0.000	
	2	Ca Saturation	0.833	0.066	0.598	0.000	0.852
		Exch. K	−97.112	11.168	−0.412	0.000	
		Constant	41.042	7.870		0.000	
Wheat	1	Ca Saturation	0.947	0.049	0.855	0.000	0.731
		Constant	1.258	3.222		0.697	
	2	Ca Saturation	0.738	0.067	0.666	0.000	0.764
		Exch. H	−30.884	7.107	−0.262	0.000	
		Constant	24.106	6.067		0.000	

Table 3. Critical Ca saturation (%) for crop growth in Ultisols

Parent material	Chinese cabbage	Wheat	Total
Plate shale	81.0	86.9	84.6
Quaternary red clay	95.8	91.9	93.5
Red sandstone	86.7	100	95.2
Granite	85.8	80.6	82.9

0.13 for Chinese cabbage and from 0.055 to 0.31 for wheat, respectively). Not only that, more differences were also observed in these critical values for different crops and soils (Table 5 and S2). For example, the critical values of Al saturation and Exch. Al : Ca ratio for wheat on Ultisols ranged from 1.69 to 9.52%, and from 0.023 to 0.46, respectively; the highest values were observed in Ultisol derived from granite. Another example was critical soil pH in Ultisol derived from red sandstone which was determined as 5.7 and 7.2 for Chinese cabbage and wheat, respectively.

Our study showed that these fit indices were not as good as Ca saturation, but they gave generally consistent results, where lower soil pH, lower Exch. Ca and Ca saturation, and consequently, higher Exch. Al and Al saturation and Exch. Al : Ca ratio in Ultisol derived from granite were considered to be tolerable by plants, but just the opposite happened in Ultisol derived from quaternary red clay.

DISCUSSION

The limit of practical application of some critical indicators such as soil pH and Exch. Al. As above stated, the direct effects of soil pH on crop growth were smaller, suggesting that the relationships between crop yield and soil pH were weaker (Table 4). Determination of critical soil pH using this regression model resulted in greater error, and hence, the predicted critical values deviated significantly from reality. Therefore, the accuracy of this indicator should be questioned, and, more importantly, our results and many previous research showed that the critical soil pH values varied greatly depending on crops and soils [4, 12, 28, 31, 59]. For example, Liu et al. [28] found that critical pH (0.01 M $CaCl_2$) for wheat ranged from 4.3 (Brucedale, calcic paleustalf) to 5.6 (Borambola, aeric albaqualf), giving a 1.3 pH unit difference. Baquy et al. [3] found on the same soil type (e.g., Ultisol) that there were also greater differences in the critical soil pH values for wheat and canola, ranging from 4.66 and 4.87 from Anhui to 5.29 and 5.65 from Hunan, respectively. Undoubtedly, wide range of critical soil pH values, as well as its variability, were often confusing and difficult for the practicing farmers to carry out the acidic soil improvement for a practical application.

Al toxicity in acidic soils is a primary factor limiting root growth, mineral nutrient uptake and thus crop productivity [22, 25, 37, 45]. So, Exch. Al, in particular Al saturation, not only showed better relationship with crop yield but also was a better indicator for predicting crop response to liming, compared with soil pH [4, 46]. Even critical Exch. Al and Al saturation were determined by Baquy et al. [4] as 1.04–1.99 $cmol_c\ kg^{-1}$ and 12.51–15.16%, respectively, for maize in Ultisols. Smyth and Cravo [46] also estimated that critical Al saturation in Oxisol was 27% for maize and soybean, and 54% for peanut, respectively. These values were obviously higher than that obtained in our study (0.89–6.98% for Chinese cabbage, and 1.69–9.52% for wheat) (Table 5). This suggests two possibilities: (1) like critical soil pH, critical Exch. Al or Al saturation showed wider range of variation among both soils and crops, which turned out to be largely limited to a given soil & crop, or (2) the smaller contribution of Exch. Al or Al saturation to crop yield resulted in a higher bias and hence, a lower fitting precision of the linear-plateau model, so it is difficult to obtain accurate parameters, viz., critical Exch. Al and Al saturation. These would greatly restrict their practical application.

Furthermore, Al toxicity occurs often at soil pH lower than 5.0, because of its pH-dependent solubility (Fig. S7) [22, 24, 25, 37, 45]. Thus, the inhibition of crop growth observed at soil pH interval 5.0–6.0 (the optimal range for plant growth) might be mainly due to Ca deficiency rather than Al toxicity, as evidenced by Fig. S7. Obviously, the determination of the critical parameters such as Exch. Al and Al saturation, based on the intersection of crop response curves (viz., 90% of the maximum yield), were unreasonable due to showing much less or no effects. In this way, it is seemingly more reasonable to use Critical Ca : Al ratio values to predict soil improvement [9, 30, 33, 40, 46], because the index would ensure that lime recommendations based on Al saturation provided adequate amounts of Ca for good plant growth [46]. However, our results showed that there was a lower relationship between Exch. Al : Ca ratio and crop yield (Table 4), which yielded an increased estimation error of critical Al : Ca ratio (Table 5). Ca saturation index rather than Exch. Al : Ca ratio should be paid more attention in determination of lime and nutrient requirements in acidic soils for good crop production in future studies, or in view of a strong correlation ($R^2 = 0.91$) between Ca and Al saturation) [46], it seems feasible to obtain the critical values of Al saturation and thus Exch. Al : Ca ratio (see the following section).

Table 4. Spearman correlations among main analysis variables

Item	Soil pH	Exch. acidity	Exch. H	Exch. Al	Exch. Ca	Exch. Mg	Exch. K	ECEC	Al saturation	Ca saturation	Exch. Al : Ca ratio	Crop biomass
Soil pH (N = 358)	1.000											
Exch. acidity (N = 358)	–0.887***	1.000										
Exch. H (N = 358)	–0.776***	0.893***	1.000									
Exch. Al (N = 358)	–0.889***	0.995***	0.860***	1.000								
Exch. Ca (N = 358)	0.810***	–0.838***	–0.660***	–0.844***	1.000							
Exch. Mg (N = 358)	0.165**	–0.229***	–0.114*	–0.233***	0.307***	1.000						
Exch. K (N = 358)	–0.259***	0.142**	0.180**	0.140**	–0.125*	0.103	1.000					
ECEC (N = 358)	0.278***	–0.224***	–0.074	–0.236***	0.611***	0.262***	0.016	1.000				
Al saturation (N = 358)	–0.893***	0.946***	0.764***	0.956***	–0.927***	–0.325***	0.087	–0.402***	1.000			
Ca saturation (N = 358)	0.887***	–0.914***	–0.766***	–0.917***	0.950***	0.189***	–0.189***	0.396***	–0.954***	1.000		
Exch. Al:Ca ratio (N = 358)	–0.899***	0.948***	0.782***	0.956***	–0.936***	–0.324***	0.129*	–0.399***	0.994***	–0.967***	1.000	
Corp biomass (N = 258)	0.822***	–0.797***	–0.735***	–0.798***	0.770***	0.148*	–0.569***	0.254***	–0.795***	0.856***	–0.830***	1.000

***, ** and * denoted statistical significance at the 0.001, 0.01 and 0.05 levels, respectively.

Table 5. Model parameters and critical values of soil pH, Exch. Ca, Exch. Al, Al saturation and Exch. Al : Ca ratio obtained from regression equations of crop growth

Index	Parent material	Chinese cabbage						Wheat					
		a	*b*	*c*	X_0	critical value	R^2	*a*	*b*	*c*	X_0	critical value	R^2
pH	Plate shale	89.87	0.0541		5.42	5.54	0.845	89.99	0.3034		4.48	5.16	0.707
	Quaternary red clay	91.18	0.2691		4.98	5.58	0.880	96.36	0.4114		4.68	5.60	0.844
	Red sandstone	101.44	0.3458		4.91	5.69	0.890	105.83	0.8695		5.23	7.19	0.854
	Granite	100.98	0.2126		4.71	5.19	0.821	100.77	0.2662		4.50	5.10	0.867
Exch. Ca	Plate shale	–	–		–	–	–	–	–		–	–	–
	Quaternary red clay	91.59	1.1625		4.46	7.08	0.918	94.93	1.9751		2.77	7.21	0.834
	Red sandstone	101.74	1.9793		4.10	8.55	0.914	98.92	4.2995		3.93	13.60	0.761
	Granite	99.18	1.8505		2.80	6.96	0.904	91.16	0.8025		1.38	3.18	0.813
Exch. Al	Plate shale	98.24	–128.823	0.60	0.76	0.0763	0.752	91.13	–53.1068	19.80	1.34	0.1716	0.682
	Quaternary red clay	95.43	–42.8377	2.93	2.16	0.2228	0.852	92.75	–14.4102	14.36	5.44	0.6436	0.852
	Red sandstone	107.46	–22.5438	2.36	4.66	0.4767	0.904	81.78	–10.8599	4.74	7.09	0.7530	0.830
	Granite	111.47	–30.4936	5.38	3.48	0.3656	0.872	105.78	–18.6386	2.42	5.55	0.5676	0.712
Al saturation	Plate shale	98.57	–11.0404	0.72	8.86	0.8928	0.739	91.37	–5.40855	19.80	13.23	1.6893	0.670
	Quaternary red clay	91.50	–2.22818	0	41.06	4.1064	0.892	93.33	–1.09409	6.21	79.62	8.5302	0.867
	Red sandstone	104.40	–1.76276	0.60	58.89	5.9227	0.912	82.54	–0.99835	2.56	80.12	8.2680	0.821
	Granite	104.06	–1.48986	0	69.84	6.9843	0.924	106.58	–1.1191	18.73	78.50	9.5241	0.745
Exch. Al:Ca ratio	Plate shale	98.12	–805.24	0.60	0.12	0.0122	0.749	91.12	–398.648	19.80	0.18	0.0229	0.671
	Quaternary red clay	90.31	–149.881	2.75	0.58	0.0603	0.893	84.84	–25.6865	6.80	3.04	0.3303	0.811
	Red sandstone	99.44	–76.9211	3.76	1.24	0.1293	0.915	75.18	–24.3787	10.41	2.66	0.3084	0.770
	Granite	88.59	–33.9999	1.73	2.55	0.2606	0.899	94.03	–20.643	6.74	4.23	0.4555	0.851

$p < 0.0001$; "–" meant that no significant regression analysis results were obtained.

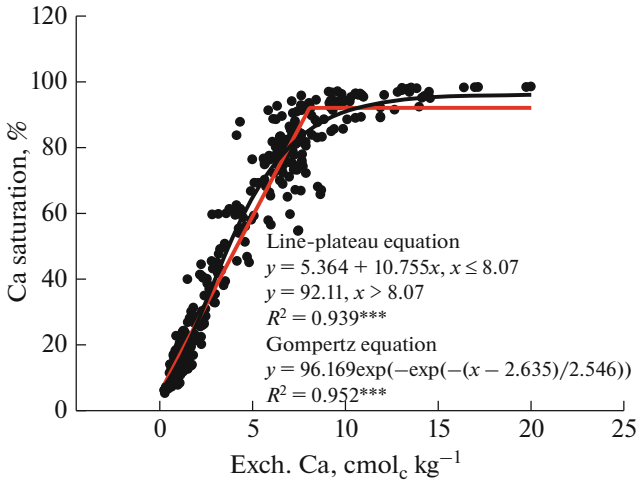

Fig. 4. Observed (symbol) and predicted (lines) relationship between Ca saturation and Exch. Ca in Ultisols.

The feasibility of critical Ca saturation. Our results showed that Ca saturation was the most important factor determining crop production in acidic soils; more and more researches also showed that soil Ca played an important role in alleviating Al toxicity and promoting nutrient availability of acidic soils [6, 7, 33, 37, 46]. In general, Ca saturation was a better indicator for crop-soil relationships than Exch. Ca content, because the latter varied extensively in various soils with different CEC while the former nearly eliminated the variations in different soils.

Line-plateau and Gompertz equations were used to model the relationship between Ca saturation and Exch. Ca and fitted well to the relationship ($R^2 = 0.939$ and $R^2 = 0.952$, respectively) (Fig. 4), where critical Exch. Ca was determined as 8.07 and 8.36 cmol$_c$ kg^{-1}, respectively (very similar to each other). Our previous study [52] showed that although liming increased crop yields in acidic soils, maintaining soil Exch. Ca value about 6.2 cmol$_c$ kg^{-1} was necessary for maximum yield. In addition, the field investigation in Qiyang County (data no published) showed almost the same relationship between Ca saturation and Exch. Ca, and the critical Exch. Ca values obtained were 8.23 and 9.91 cmol$_c$ kg^{-1} (average 9.07 cmol$_c$ kg^{-1}), which was consistent with those obtained in this study. Moreover, it was well established that approximately 87.5% of soils on arable lands in Qiyang County, was expected to require calcium supplementation for good crop yield, which was close to the value of 80% calculated according to soil acidification in this region (data no published). These consistent results further reinforced the notion that critical Ca saturation could be used as a reliable indicator to estimate the health of acidic soils.

The average critical value of Exch. Ca was 8.21 cmol$_c$ kg^{-1} in Ultisols, which was much lower than those proposed previously [2, 51]. The possible reason was that rice adapted to lower soil pH (e.g., 4.9) than dry land crops such as wheat and maize [12, 57, 59], resulting in its higher Al tolerance and lower Ca requirement. Therefore, critical Exch. Ca might be as low as 1.2 cmol$_c$ kg^{-1}. The critical value of Exch. Ca proposed by Wei et al. [51] was used to identify soils where response to Ca fertilization should be expected. That is, this was the lowest Exch. Ca requirement for crop growth (about 10% of the maximum yield), not the same concept as described in this study, where higher Exch. Ca requirement was used to maintain higher crop production (90% of the maximum yield). According to Figs. 3 and 4, the lowest critical Exch. Ca for 10% maximum yield (corresponding to 15–20% Ca saturation) was determined as 1.20 cmol$_c$ kg^{-1} (0.90–1.36 cmol$_c$ kg^{-1} and 1.06–1.49 cmol$_c$ kg^{-1}, respectively). These data were also very consistent with previous observation in Ultisols [51].

There was strong linear correlation ($R^2 = 0.967$, $P < 0.0001$) between Al and Ca saturation, and the regression equation based on 358 observations was as follows:

$$\text{Al saturation } \% = 84.55 - 0.94\ (\text{Ca saturation } \%).$$

There was essentially a 1 : 1 relationship, in agreement with the estimate by Smyth and Cravo [46]. The critical Al saturation in Ultisols was estimated to be 6.37%, and hence critical Al : Ca ratio (Ca : Al ratio) was equal to 0.077 (13.0). Similarly, using the strong non-linear correlations between Ca saturation and Exch. Al and Exch. Al : Ca ratio ($R^2 = 0.922$ and $R^2 = 0.977$, respectively) (Fig. S8), critical Exch. Al value was determined as 0.44 cmol$_c$ kg^{-1}, and the corresponding critical Al : Ca ratio (Ca : Al ratio) was 0.054 (18.6). Moreover, a critical Exch. Al : Ca ratio (Ca : Al ratio) of 0.069 (14.5) in Ultisols could be directly obtained from the regression equation. These results were consistent and in good agreement with those reported previously by Nora et al. [34], who showed that it was more appropriate to use a maximum Al saturation value of 5% (instead of current recommendation of 10%) as the critical level for cereals on subtropical no-tillage soils. Additionally, these results were more accurate than those obtained from regression equations developed between crop yield and soil acidity indices, as shown in Table 5. Critical Ca saturation would no doubt be the best indicator to evaluate the implementation of quality improvements of acidic soils for good crop production, and it either alone or in combination with other indicators obtained according to the regression equations, such as Al saturation and Exch. Al : Ca ratio, has the potential to enhance a wide range of practical performance of soil management and crop production.

CONCLUSIONS

Structural equation modeling (SEM) and stepwise regression analysis evidenced that Ca saturation had the greatest direct effect on crop biomass, with high

linear correlation between them, and thus was the most important factor that contributed to crop production in acidic soils. The determined critical values of Ca saturation varied slightly with crops and soils, with a higher difference between soils in variance of 6.5%, that is, 84.6, 93.5, 95.2 and 82.9% for Ultisols derived from plate shale, Quaternary red clay, red sandstone, and granite, respectively. This suggested that maintaining above a critical minimum Ca saturation of 83% in Ultisols was crucial important for the achievement of high crop yield. Our results also indicated that other soil acidity indices such as soil pH, Exch. Al, and Exch. Ca : Al ratio were not good indicators for characterization of crop production with higher identifying bias and lower fitting precision. In conclusion, our study showed that critical Ca saturation was the best indicator for evaluating the implementation of quality improvement of acidic soils in Southern China, and it either alone or in combination with other indicators has a broad practical application of ameliorating acidity and optimizing crop yield in the future. For this purpose, additional recommendation criteria were listed as follows: Exch. Ca > 8.21 $cmol_c\ kg^{-1}$, Exch. Al < 0.44 $cmol_c\ kg^{-1}$, Al saturation < 6.37% and Exch. Al : Ca ratio < 0.069 (or Ca : Al ratio > 14.5) for the 0–20 cm layer of Ultisols.

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CONFLICT OF INTEREST

The authors declare that they have no competing financial interests.

SUPPLEMENRARY INFORMATION

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Table S1. Basic properties of Ultisols 1 derived from different parent materials.

Table S2. Comparison of critical values of Exch. Al : Ca ratio (or Exch. Ca : Al ratio) obtained by different methods.

Fig. S1. Frequency histograms of soil acidity indices and crop relative dry weight.

Fig. S2. Shoot dry weight of Chinese cabbage and wheat as function of soil pH after crop harvest. Solid lines are the fits of Gompertz equations to the data (R^2 = 0.71~0.89, $p < 0.0001$).

Fig. S3. Shoot dry weight of Chinese cabbage and wheat as function of soil Exch. Ca. Solid lines are the fits of Gompertz equations to the data except for plate shale (R^2 = 0.76–0.92, $p < 0.0001$).

Fig. S4. Shoot dry weight of Chinese cabbage and wheat as function of soil Exch. Al. Solid lines are the fits of linear-plateau model to the data (R^2 = 0.68–0.90, $p < 0.0001$).

Fig. S5. Shoot dry weight of Chinese cabbage and wheat as function of soil Al saturation. Solid lines are the fits of linear-plateau model to the data (R^2 = 0.67–0.92, $p < 0.0001$).

Fig. S6. Shoot dry weight of Chinese cabbage and wheat as function of soil Exch. Al : Ca ratio. Solid lines are the fits of linear-plateau model to the data (R^2 = 0.67–0.92, $p < 0.0001$).

Fig. S7. Changes of Exch. Al, Exch. Ca, and Al and Ca saturation with soil pH in Ultisols derived from different parent materials. Solid lines are the fits of linear-plateau or Gompertz model to the data, except for Exch. Ca in plate shale (R^2 = 0.76–0.94, $p < 0.0001$).

Fig. S8. Changes of Ca saturation with Exch. Al (a) and Exch. Al : Ca ratio (b) in Ultisols derived from different parent materials.

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