

# New Algorithm of Clay CEC for Soils in Tropical and Subtropical Regions of South China

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## Abstract

Clay CEC is one of identification indexes of the LAC-ferric horizon which is the diagnostic horizon of ferrosols in Chinese Soil Taxonomy, and it is defined as soil CEC  $\times$  1000/clay content, rather than the measured CEC of the extracted clays; however, such a calculation method would definitely lead to an overestimation of clay CEC because it doesn't remove the contribution to soil CEC from other soil parameters. In this study, the physiochemical data of the subhorizons from 82 soil series in the tropical and subtropical regions in south China were used, clay CEC was calculated according to the current formula and measured after clays being extracted, the measured and calculated clay CEC were compared, the influencing factors were analyzed for their difference, and the new algorithms were established for clay CEC. The results showed that the measured clay CEC was 21.86% - 99.53% with a mean of 66.88% of the calculated one (significantly lower at  $p < 0.01$ ), and their difference was significantly correlated with the contents of clays, sand and OM, and mainly decided by the contents of clays and  $\text{Fe}_2\text{O}_3$  (the contribution was 52.51% and 25.36%, respectively). By comparison of established regression models of clay CEC with other soil parameters, two new algorithms were recommended for clay CEC as follows: 1) Clay CEC =  $10.32 - 0.14\text{pH} - 0.05\text{OM} - 0.11\text{Fe}_2\text{O}_3 + 0.01\text{Silt} - 0.01\text{Clay} + 1.17\text{CEC}_{\text{soil}}$ ,  $R^2 = 0.705$ ,  $P < 0.01$ ; 2) Clay CEC =  $-3.40 + 0.01\text{Sand} + 0.02\text{Silt} + 1.05\text{CEC}_{\text{soil}}$ ,  $R^2 = 0.589$ ,  $P < 0.01$ ).

## Keywords

Measured Clay CEC, Calculated Clay CEC, Algorithm, Subhorizon Soil, South China

## 1. Introduction

Ferrosols is one of soil orders in Chinese Soil Taxonomy (CST) [1], which is a soil order between argosols whose main process is the accumulation of higher activity clays and ferralosols which has a higher degree of ferrallitization. Low activity clay-ferric horizon (LAC-ferric horizon) is the diagnostic horizon of ferrosols, characterized by the medium degree of ferrallitization, lower activity clays and rich in free iron oxides [2] [3]. One of the definitions of LAX-ferric horizon is that clay CEC is less than 24 cmol(+)/kg in partial subhorizons (10 cm or more thick) [1]. However, in CST, clay CEC is calculated by soil CEC  $\times$  1000/clay content, rather than the measurement of the extracted clays. Obviously, the underlying assumption of the above formula is that the influences of other soil parameters (pH, SOM, particle composition, etc.) on soil CEC can be ignored in the highly-weathered subhorizons in tropical and subtropical regions of south China. However, some studies found such a presupposition unreliable or unacceptable [4] [5], and it would doubtlessly overestimate clay CEC, thus, would lead to the misidentification of soil types [5].

Because the recent study on the prediction models of clay CEC [5] failed to cover all the tropical and subtropical regions in south China, soil samples used for modeling with high SOM content ( $\geq 6$  g·kg<sup>-1</sup>) were limited, and the average annual temperature, roughly obtained by spatial interpolation, was included in the prediction model with low SOM content ( $< 6$  g·kg<sup>-1</sup>), so the accuracy of the models would be influenced or reduced. Thus, in this study the physiochemical data of the typical subhorizons from 82 soil series in the tropical and subtropical regions of south China were used to: 1) disclose further the difference between the measured and calculated clay CEC, 2) clarify the influences of other soil parameters on the difference, and 3) setup new algorithms for clay CEC.

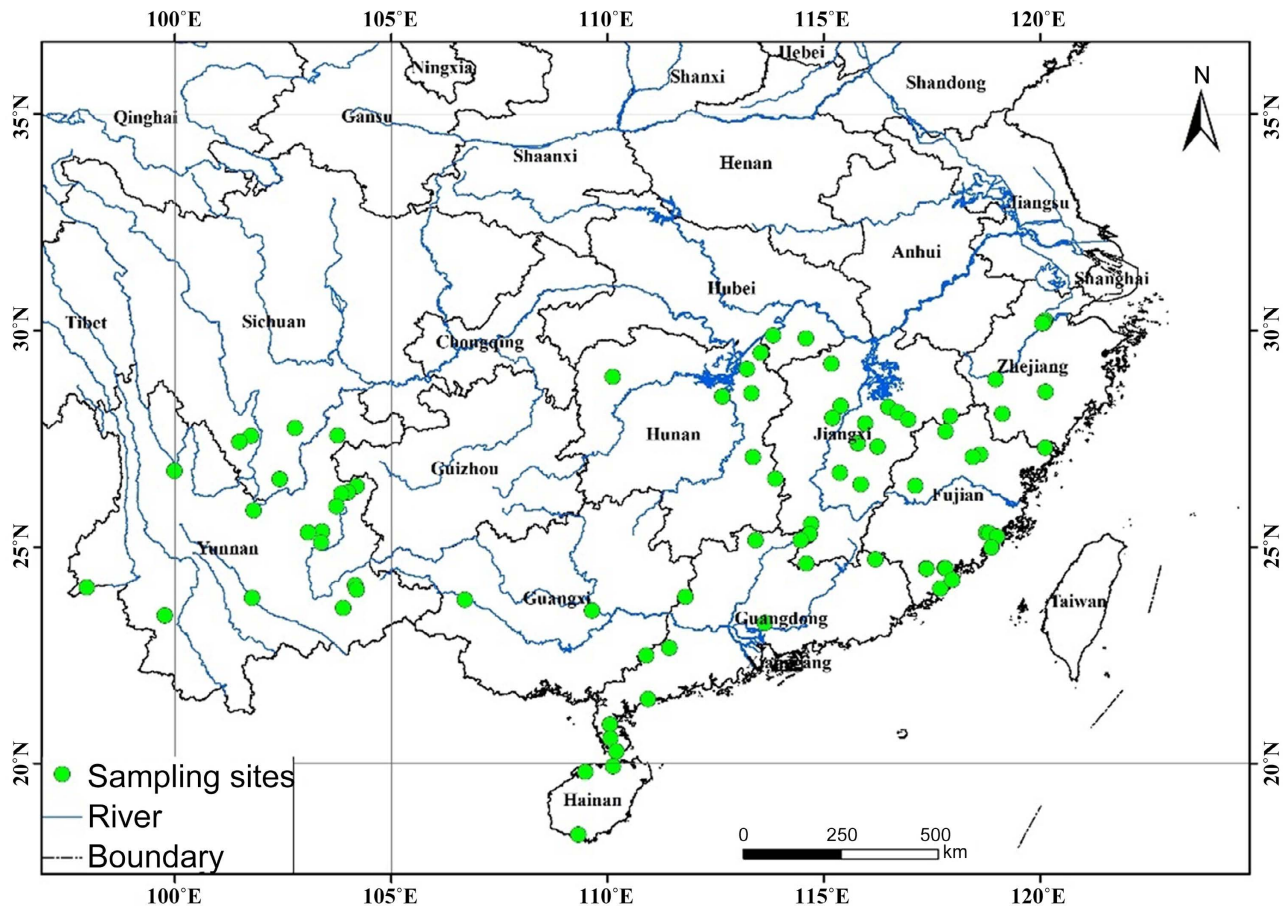
## 2. Materials and Methods

### 2.1. Background of Tested Soil Samples

**Figure 1** shows the spatial distribution of used 82 soil series in the tropical and subtropical regions of south China [6]-[16]. For a soil sample, the pipette method was used to separate and obtain clays and silts and to determine the particle size distribution, the potentiometer method (soil:water = 1:2.5) was used to measure pH, the Walkley-Black wet oxidation method was used to measure OM content, the phenanthroline colorimetry method was used to determine free Fe<sub>2</sub>O<sub>3</sub> content, the NH<sub>4</sub>OAc (pH = 7.0) exchange method was used to measure CEC of soil, clays and silts [17] [18] [19].

### 2.2. Data Statistical Analysis

Microsoft Excel 2016 and IBM Statistics SPSS 22.0 software were used for statistical analysis of the data, and Duncan test method (2-tailed) was used for variance analyses and multiple comparisons.



**Figure 1.** Spatial distribution of used 82 soil series in tropical and subtropical regions of south China.

### 3. Results

#### 3.1. Statistical Results of Soil Physiochemical Parameters

**Table 1** lists the measured values of soil physiochemical parameters, it showed that soil CEC was ranged from 5.12 to 20.29  $\text{cmol}(+)\cdot\text{kg}^{-1}$  with a mean of 11.92  $\text{cmol}(+)\cdot\text{kg}^{-1}$ , measured clay CEC (Clay  $\text{CEC}_m$ ) was ranged from 7.51 to 34.87  $\text{cmol}(+)\cdot\text{kg}^{-1}$  with a mean of 20.03  $\text{cmol}(+)\cdot\text{kg}^{-1}$ , calculated clay CEC (clay  $\text{CEC}_c$ ) was ranged from 12.34 to 92.15  $\text{cmol}(+)\cdot\text{kg}^{-1}$  with a mean of 32.43  $\text{cmol}(+)\cdot\text{kg}^{-1}$ , silt CEC was ranged from 0.48 to 12.72  $\text{cmol}(+)\cdot\text{kg}^{-1}$  with a mean of 4.83  $\text{cmol}(+)\cdot\text{kg}^{-1}$ . Comparatively, clay  $\text{CEC}_m$  was 21.86% - 99.53% with a mean of 66.88% of clay  $\text{CEC}_c$ , significantly lower at  $p < 0.01$ .

#### 3.2. Parameters Influencing CEC

**Table 2** lists Pearson correlation between CEC and other parameters. It can be found that pH had no significant correlation with CEC, OM had significant positive correlation with clay  $\text{CEC}_c$  and  $\Delta$  clay CEC  $[(\text{clay } \text{CEC}_c - \text{clay } \text{CEC}_m)/\text{clay } \text{CEC}_c]$  ( $p < 0.01$ ), free  $\text{Fe}_2\text{O}_3$  had significant positive correlation with soil CEC ( $p < 0.01$ ) and silt CEC ( $p < 0.05$ ), sand content had significant negative correlation with soil CEC ( $p < 0.01$ ) and clay  $\text{CEC}_m$  ( $p < 0.05$ ) but had significant positive

**Table 1.** Statistical descriptions of soil chemical properties (n = 82).

Soil parameter	Min.	Max.	Mean $\pm$ S.D.	C.V. (%)	Skewness	Kurtosis
Soil CEC	5.12	20.29	11.92 $\pm$ 3.73	31.33	0.35	-0.66
Clay CEC <sub>m</sub>	7.51	34.87	20.03 $\pm$ 5.52A	27.57	0.09	-0.43
Clay CEC <sub>c</sub>	12.34	92.15	32.43 $\pm$ 14.32B	44.14	1.94	5.13
Silt CEC	0.48	12.72	4.83 $\pm$ 2.87	59.51	0.67	-0.34
pH	3.73	6.77	5.11 $\pm$ 0.62	12.14	0.76	0.29
OM	2.41	33.57	8.8 $\pm$ 5.89	66.38	1.80	3.69
Free Fe <sub>2</sub> O <sub>3</sub>	20.84	105.96	44.70 $\pm$ 18.31	40.95	1.03	0.54
Sand	67.00	634.00	296 $\pm$ 147	49.55	0.35	-0.74
Silt	84.00	517.00	308 $\pm$ 105	34.17	0.08	-0.71
Clay	127.00	707.00	396 $\pm$ 118	29.90	0.34	0.46

Note: 1) CEC, cmol(+)·kg<sup>-1</sup>; sand, silt, clay, OM and free Fe<sub>2</sub>O<sub>3</sub>, g·kg<sup>-1</sup>; 2) Clay CEC<sub>m</sub>, measured CEC of extracted clays; Clay CEC<sub>c</sub>, calculated clay CEC by soil CEC  $\times$  100/clay content; Silt CEC, measured CEC of extracted silts; 3) Data of Clay CEC<sub>m</sub> and CEC<sub>c</sub> followed by different capitals are significantly different at p < 0.01 level.

**Table 2.** Pearson correlation between soil CEC and other parameters.

CEC	Correlation	pH	OM	Free Fe <sub>2</sub> O <sub>3</sub>	Sand	Silt	Clay
Soil CEC	Pearson Correlation	0.016	0.089	0.332**	-0.383**	0.184	0.310**
	Sig. (2-tailed)	0.884	0.417	0.002	0.000	0.091	0.004
Clay CEC <sub>m</sub>	Pearson Correlation	-0.033	-0.007	-0.160	-0.231*	0.397**	-0.066
	Sig. (2-tailed)	0.765	0.952	0.144	0.033	0.000	0.546
Clay CEC <sub>c</sub>	Pearson Correlation	-0.028	0.416**	0.007	0.223*	0.313**	-0.554**
	Sig. (2-tailed)	0.797	0.000	0.949	0.040	0.004	0.000
$\Delta$ clay CEC significant positive correlation with clay CEC <sub>c</sub> (p < 0.05)	Pearson Correlation	0.005	0.399**	0.068	0.472**	0.034	-0.615**
	Sig. (2-tailed)	0.962	0.000	0.537	0.000	0.756	0.000
Silt CEC	Pearson Correlation	-0.165	0.173	0.251*	0.121	0.084	-0.226*
	Sig. (2-tailed)	0.131	0.114	0.020	0.269	0.442	0.038

Note: 1) \*, \*\*, Correlation is significant at p < 0.05 or 0.01 level (2-tailed); 2)  $\Delta$  clay CEC = (clay CEC<sub>c</sub> - clay CEC<sub>m</sub>)/clay CEC<sub>c</sub>.

correlation with clay CEC<sub>c</sub> (p < 0.05) and  $\Delta$  clay CEC (p < 0.01), silt content had significant positive correlation with clay CEC<sub>m</sub> and CEC<sub>c</sub> (p < 0.01), clay content had significant positive correlation with soil CEC (p < 0.01) but had significant negative correlation with clay CEC<sub>c</sub> (p < 0.01),  $\Delta$  clay CEC (p < 0.01) and silt CEC (p < 0.05).

The contribution of one parameter to CEC was calculated as the follows: firstly, all parameters were normalized by the Z-score method with IBM Statistics SPSS 20.0 to ensure them with the same magnitude, and then the regression coefficients between each parameter and CEC was used to indicate their contri-

bution to CEC [20] [21] [22]. The contribution of one parameter ( $C_i$ ) to CEC was calculated as  $C_i = |K_i|/|K_{sum}|$ , in which  $K_i$  is the regression coefficient of the  $i$  parameter, and  $K_{sum}$  is the total sum of all coefficients, the obtained linear regression models of CEC with other parameters were listed in **Table 3**, and the calculated contribution of other parameters to CEC were listed in **Table 4**.

In view of the contribution of other parameters to CEC, it can be seen from **Table 4** that soil CEC was mainly decided by clays (34.29%), followed by silt content (25.75%) and free  $Fe_2O_3$  (21.75%); clay  $CEC_m$  was mainly determined by silt content (51.34%), followed by free  $Fe_2O_3$  (26.34%); clay  $CEC_c$  was mainly influenced by clay content (46.96%), followed by SOM (18.53%), silt content (17.20%) and free  $Fe_2O_3$  (16.64%);  $\Delta$  clay CEC was mainly affected by clay content (52.51%), followed by free  $Fe_2O_3$  (25.36%); silt  $CEC_m$  was mainly determined by free  $Fe_2O_3$  (39.82%) and clay content (35.17%), followed by pH (17.34%).

### 3.3. New Algorithms for Clay CEC

**Table 5** lists the correlation between clay  $CEC_m$  and other properties, it can be found from **Table 5** that clay  $CEC_m$  had significant positive correlation with silt content, soil CEC and clay  $CEC_c$  ( $p < 0.01$ ) but had significant negative correlation with sand content ( $p < 0.05$ ). By using IBM Statistics SPSS, the regression models of clay  $CEC_m$  with other parameters were obtained (see **Table 6**), and it could be found by comparison from **Table 6** that Model 6 and 5 could be recommended as the new algorithms for clay CEC.

## 4. Discussions

### 4.1. Statistical Results of Soil Physiochemical Properties

Our study showed (see **Table 1**) that, for the subhorizons of highly-weathered

**Table 3.** Linear regression model between normalized CEC and other soil properties.

Linear regression model	R <sup>2</sup>	RMSE	F	Sig.
Soil CEC = $-0.060pH + 0.093OM + 0.183Fe_2O_3 + 0.217Silt + 0.289Clay - 3.187 \times 10^{-16}$	0.198	0.92	3.90	0.003
Clay $CEC_m$ = $-0.063pH + 0.020OM - 0.220Fe_2O_3 + 0.429Silt + 0.103Clay - 6.634 \times 10^{-16}$	0.201	0.92	3.96	0.003
Clay $CEC_c$ = $-0.008pH + 0.221OM + 0.198Fe_2O_3 + 0.205Silt - 0.559Clay - 7.710 \times 10^{-16}$	0.467	0.75	13.86	0.000
$\Delta$ clay CEC = $0.054pH + 0.154OM + 0.368Fe_2O_3 - 0.114Silt - 0.763Clay - 5.316 \times 10^{-16}$	0.552	0.69	19.48	0.000
Silt CEC = $-0.211pH - 0.060OM + 0.485Fe_2O_3 + 0.033Silt - 0.428Clay - 3.603 \times 10^{-16}$	0.246	0.90	5.15	0.000

**Table 4.** Contribution of other soil properties to CEC (%).

Property	pH	OM	Free $Fe_2O_3$	Sand	Silt	Clay	Total
Soil CEC	7.12	11.09	21.75	0	25.75	34.29	100.00
Clay $CEC_m$	7.54	2.41	26.34	0	51.34	12.36	100.00
Clay $CEC_c$	0.67	18.53	16.64	0	17.20	46.95	100.00
$\Delta$ CEC	3.69	10.59	25.36	0	7.85	52.51	100.00
Silt CEC	17.34	4.93	39.82	0	2.74	35.17	100.00

**Table 5.** Pearson correlation between clay CEC<sub>m</sub> (Clay CEC<sub>7</sub>) and other parameters.

	pH	OM	Fe <sub>2</sub> O <sub>3</sub>	Sand	Silt	Clay	CEC <sub>soil</sub>	CEC <sub>silt</sub>	CEC <sub>clay-c</sub>
Pearson Correlation	-0.033	-0.007	-0.160	-0.231*	0.397**	-0.066	0.675**	-0.009	0.521**
Sig. (2-tailed)	0.765	0.952	0.144	0.033	0.000	0.546	0.000	0.937	0.000

Note: 1) \*, \*\*, Correlation is significant at  $p < 0.05$  or  $0.01$  level (2-tailed); 2) CEC<sub>soil</sub>, measured soil CEC; CEC<sub>silt</sub>, measured silt CEC; CEC<sub>clay-c</sub>, calculated clay CEC (soil CEC  $\times$  1000/clay content). The same below.

**Table 6.** Predicting models of clay CEC<sub>7</sub>.

	Model	R <sup>2</sup>	RMSE	F	Sig.
1	Clay CEC = $19.86 - 6.46 \times 10^{-8} \text{ Sand}^3 + 1.32 \times 10^{-5} \text{ Sand}^2 + 0.01 \text{ Sand}$	0.102	5.33	3.08	0.032
2	Clay CEC = $5.09 + 5.14 \times 10^{-7} \text{ Silt}^3 + 0.14 \text{ Silt}$	0.180	5.09	5.92	0.001
3	Clay CEC = $11.47 - 0.01 \text{ CEC}_{\text{soil}}^3 + 0.17 \text{ CEC}_{\text{soil}}^2 - 0.47 \text{ CEC}_{\text{soil}}$	0.473	4.08	24.20	0.000
4	Clay CEC = $-12.66 - 0.04 \text{ CEC}_{\text{clay-c}}^2 + 2.11 \text{ CEC}_{\text{clay-c}}$	0.437	4.22	20.92	0.000
5	Clay CEC = $-3.40 + 0.01 \text{ Sand} + 0.02 \text{ Silt} + 1.05 \text{ CEC}_{\text{soil}}$	0.589	3.61	38.64	0.000
6	Clay CEC = $10.32 - 0.14 \text{ pH} - 0.05 \text{ OM} - 0.11 \text{ Fe}_2\text{O}_3 + 0.01 \text{ Silt} - 0.01 \text{ Clay} + 1.17 \text{ CEC}_{\text{soil}}$	0.705	3.11	31.07	0.000

Note: CEC<sub>soil</sub>, soil CEC<sub>7</sub>; CEC<sub>clay-m</sub>, measured Clay CEC; CEC<sub>silt</sub>, measured silt CEC.

acid soils in the tropical and subtropical regions in south China, clay content was meanly  $396 \text{ g}\cdot\text{kg}^{-1}$  while sand content was meanly  $296 \text{ g}\cdot\text{kg}^{-1}$ ; Meanwhile, free Fe<sub>2</sub>O<sub>3</sub> content was meanly  $44.71 \text{ g}\cdot\text{kg}^{-1}$ , which proved further that soils in the tropical and subtropical regions of south China are clayey and rich in free Fe<sub>2</sub>O<sub>3</sub> [23].

#### 4.2. Difference between Measured and Calculated Clay CEC

Our study also showed that, for the subhorizons of highly-weathered soils in the tropical and subtropical regions in south China, the measured clay CEC was 21.86% - 99.53% with a mean of 66.88% lower than the calculated clay CEC (significantly lower at  $p < 0.01$ ), which was 8.61% - 90.78% with a mean of 62.42% in the study of Yang *et al.* [5]. Such a difference could be attributed to the removal of the contribution to soil CEC from other soil parameters (mainly from silts, see Table 2) in calculating clay CEC. For example, our study showed that silt CEC was ranged from 0.48 to  $12.72 \text{ cmol}(+)\cdot\text{kg}^{-1}$  with a mean of  $4.83 \text{ cmol}(+)\cdot\text{kg}^{-1}$ , which accorded with the reports of Zhang and Zhu [4] and Yang *et al.* [5], it proved further that silts in the subhorizons could also influence soil CEC in the tropical and subtropical regions of south China, which mainly was attributed to the 2:1 clay minerals such as vermiculite and mica in silts [4]. Our study disclosed further the influencing factors of the differences between the measured and calculated clay CEC, which was mainly decided by clay content (52.51%), followed by free Fe<sub>2</sub>O<sub>3</sub> (25.36%), OM (10.59%), silt content (7.85%) and pH (3.69%), but no effect from sand content.

#### 4.3. Parameters Influencing CEC

Previous studies showed that pH usually has positive correlation with soil CEC

for acid soils [20] [24] [25] [26] [27], however, no significant positive correlation was found in our study between pH and soil CEC (R was 0.016,  $p = 0.884$ ), which could be attributed to narrow range of pH of the soil samples used in our study (acid, 3.73 - 6.77 with a mean of 5.11). SOM usually has significant positive correlation with soil CEC [20] [24]-[35], but our results showed that SOM had no significant correlation with soil CEC (R was 0.089,  $p = 0.417$ ), which could be related to the low SOM content [29] [32] [33] [36] in subhorizon soils in the subtropical and tropical regions of south China (in our study, OM was 2.41 - 33.57  $\text{g}\cdot\text{kg}^{-1}$  with a mean of 8.8  $\text{g}\cdot\text{kg}^{-1}$ ). Clay content usually also has significant positive correlation with soil CEC [20] [24] [25] [26] [27] [29]-[35] [37], our results also showed this tendency (R was 0.310,  $p < 0.01$ ). Our study found that free  $\text{Fe}_2\text{O}_3$  was significantly correlated with soil CEC (R was 0.332,  $p < 0.01$ ), few studies analyzed the correlation between free  $\text{Fe}_2\text{O}_3$  and soil CEC because free  $\text{Fe}_2\text{O}_3$  in subtropical and tropical highly-weathered soils usually exist as clay fraction or strongly cemented with clays [23] [38] [39] [40], so more attentions were paid to the correlation between clay content rather than free  $\text{Fe}_2\text{O}_3$  with soil CEC. Our study also found that soil CEC had negative correlation with sand content, which is consistent with the previous studies [24] [33] [35] [36] [37], and could be attributed to sand fraction mainly composed of quartz and iron concretions with low charge density [41] in subtropical and tropical humid climate soils. However, our study found no significant positive correlation between soil CEC with silt content as found in other studies [20] [25] although it also could influence soil CEC as clays as found in our study and other studies [4] [5].

#### 4.4. Recommendation Using $\text{CEC}_2$ Predicting Model for Soil Taxonomy

Our study showed that, for the subhorizons of the highly-weathered acid soils in the tropical and subtropical regions of south China, the calculated clay CEC (soil CEC  $\times$  1000/clay content, [1]) was significantly higher than the measured one (see **Table 1**), this obvious overestimation of clay CEC is most likely to lead to some authentic LAC-ferric horizons being misjudged as other diagnostic horizons, thus leading to misjudgment of soil types [4] [5].

Extracting clay and measuring its CEC is a very tedious and troublesome process, so it is helpful and necessary to find a new algorithm for clay CEC in order to ensure the identification accuracy of soil types in the tropical and subtropical regions. In our study, various regression models between measured clay CEC and other parameters were established, and it was found that model with only one parameter usually was lower in accuracy. By comparison, two optimal models are recommended as new algorithms for clay CEC, in which one included pH, the contents of OM, silts, clays and soil CEC (Model 6,  $R^2 = 0.705$ ,  $P < 0.01$ , see **Table 6**), and the other included sand and silt contents and soil CEC (Model 5,  $R^2 = 0.589$ ,  $p < 0.01$ , see **Table 6**).

## 5. Conclusion

Our study quantitatively proved that for the highly-weathered subhorizons in the tropical and subtropical regions of south China, the measured clay CEC (NH<sub>4</sub>OAc, pH = 7.0) was significantly lower than the calculated one (soil CEC × 1000/clay content), their difference was significantly correlated with the contents of clays, sands and OM, but mainly decided by the contents of clays and free Fe<sub>2</sub>O<sub>3</sub>. For higher accuracy in predicting clay CEC, more other soil parameters should be included in the new algorithms for clay CEC.

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## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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