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Comparison of Highly-Weathered Acid Soil CEC Determined by NH_4OAc (pH = 7.0) Exchange Method and $BaCl_2$-$MgSO_4$ Forced-Exchange Method

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Abstract

Cation exchange capacity (CEC) is one of the most important properties of soils. The NH_4OAc (pH = 7.0) exchange method is usually recommended to determine CEC (CEC_1) of all soils with different pH values, particularly for studies on soil taxonomy. But comparatively the $BaCl_2$-$MgSO_4$ forced-exchange method is more authentic in determining CEC (CEC_2) of tropical and subtropical highly-weathered acid soils. But so far little is known about the difference between CEC_1 and CEC_2. In this study, the physiochemical data of 114 acid B horizon soils from 112 soil series of tropical and subtropical China were used, CEC_1 and CEC_2 were determined and compared, the influencing factors were analyzed for the difference between CEC_1 and CEC_2, and then a regression model was established between CEC_1 and CEC_2. The results showed that CEC_2 was significantly lower than CEC_1 ($p < 0.01$), CEC_2 was 14.76% - 63.31% with a mean of 36.32% of CEC_1. In view of the contribution to CEC from other properties, CEC_2 was mainly determined by pH (45.92%), followed by silt (21.05%), free Fe_2O_3 (17.35%) and clay contents (12.76%), CEC_1 was mainly decided by free Fe_2O_3 content (40.38%), followed by pH (28.39%) and silt content (27.29%; and the difference between CEC_1 and CEC_2 was mainly affected by free Fe_2O_3 (50.92%), followed by silt content (26.46%) and pH (21.80%). The acceptable optimal regression model between CEC_2 and CEC_1 was established as $CEC_2 = 2.3114 \times CEC_1^{1.1496}$ ($R^2 = 0.410$, $P < 0.001$, RMSE = 0.15). For the studies on soil taxonomy, the $BaCl_2$-$MgSO_4$ forced-exchange method is recommended in determining CEC of the highly-weathered acid soils in the tropical and subtropical regions.

Keywords

Acid Soil, CEC Determination, NH_4OAc (pH = 7.0) Exchange Method, $BaCl_2$-$MgSO_4$ Forced-Exchange Method

1. Introduction

Soil cation exchange capacity (CEC) is one of the most important chemical characteristics of agricultural lands [1], which can influence the stability of soil structure, nutrient availability, soil pH and the soil's reaction to fertilizers and other ameliorants, provide a buffer against soil acidification [2]. CEC is often used as a measure of soil fertility, nutrient retention capacity [3], and also used as an identification and classification index of soil types in soil taxonomy [4] [5], in which the NH_4OAc (pH = 7.0) exchange method [6] [7] is recommended to determine CEC for all soils with different pH values. However, for highly-weathered acid soils in the tropical and subtropical regions, the $BaCl_2$-$MgSO_4$ forced-exchange method [8], which doesn't adjust pH of soil samples, is recommended to determining CEC. Comparatively, because the buffer salt system (pH = 7.0) in the first method will increase soil pH, thus will increase the charge of soil colloids and result in higher measurement results [9] [10], which may lead to the misjudgment of soil types [11].

But so far, little is known about the difference in CEC values determined by the two methods, thus, in this study the physiochemical data of 114 acid B horizon soils from 112 soil series in the tropical and subtropical regions of south China were used to: 1) disclose the difference in CEC values determined by the two methods, 2) clarify the influencing factors of the difference, and 3) setup the regression model for predicting CEC_2 by CEC_1.

2. Materials and Methods

2.1. Background of Tested Soil Samples

Figure 1 shows the spatial distribution of used 112 soil series in the tropical and subtropical regions of south China [12]-[22]. For a soil sample, the particle size distribution was determined by the pipette method, pH was measured with by the potentiometer method (soil:water = 1:2.5), organic matter was obtained by the Walkley-Black wet oxidation method, free Fe_2O_3 was determined by the phenanthroline colorimetry method, CEC was analyzed by the NH_4OAc (pH = 7.0) exchange method (CEC_1) [6] [7] and the $BaCl_2$-$MgSO_4$ forced-exchange method (CEC_2) [8], respectively.

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.

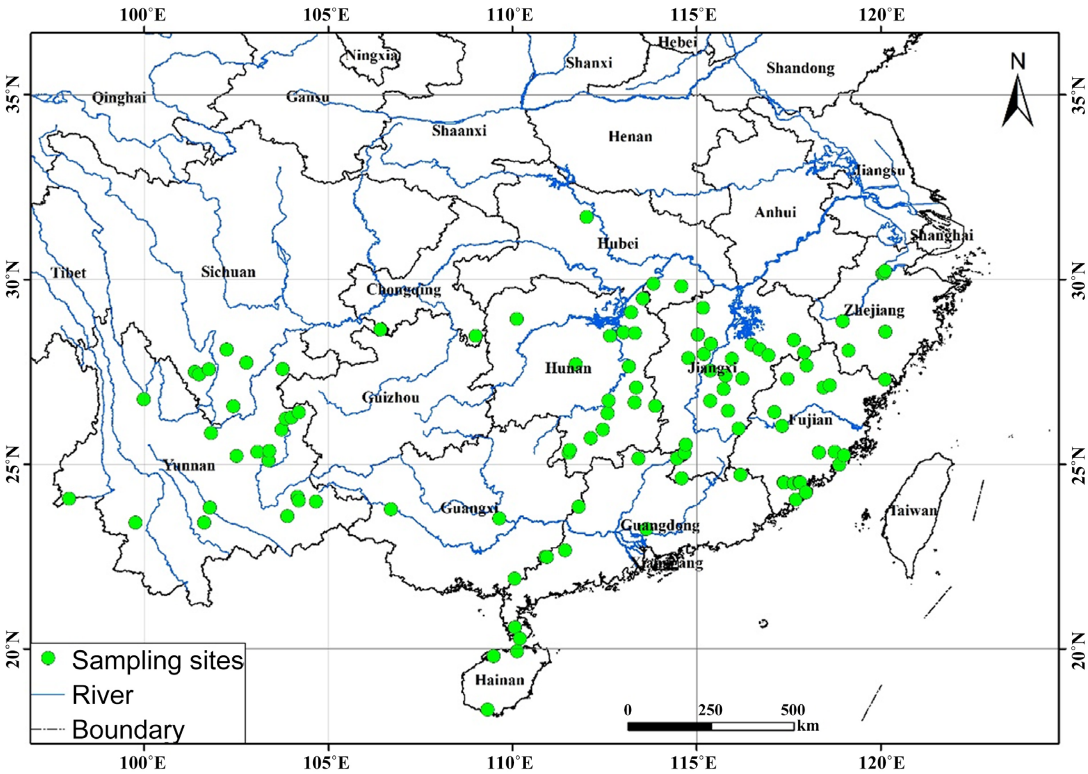

Figure 1. Spatial distribution of used 112 soil series in tropical and subtropical regions of south China.

3. Results

3.1. Statistical Results of Soil Physiochemical Properties

Table 1 lists the measured values of soil physiochemical properties, it showed that CEC_1 ranged from 5.12 to 35.41 cmol(+) kg^{-1} with a mean of 12.40 cmol(+) kg^{-1}, while CEC_2 ranged from 2.22 to 6.60 cmol(+) kg^{-1} with a mean of 4.16 cmol(+) kg^{-1}. Comparatively, CEC_2 was significantly lower than CEC_1 ($p < 0.01$), CEC_2 was 14.76% - 63.31% with a mean of 36.32% of CEC_1.

Table 1 also showed that clay content was meanly 412 $g \cdot kg^{-1}$, while sand content was meanly 281 $g \cdot kg^{-1}$; meanwhile, free Fe_2O_3 content was meanly 44.01 $g \cdot kg^{-1}$, which prove further that soils in the tropical and subtropical regions of south China are clayey and rich in free Fe_2O_3 [23].

3.2. Factors Influencing CEC_1, CEC_2 and Their Difference

Table 2 lists the correlation between CEC_1, CEC_2 and the difference between CEC_1 and CEC_2 (ΔCEC, CEC_1-CEC_2) with other properties. It could be found that pH had significant positive correlation with CEC_1 ($p < 0.01$), CEC_2 ($p < 0.01$) and ΔCEC ($p < 0.05$), free Fe_2O_3 had significant positive correlation with CEC_1 and ΔCEC ($p < 0.01$), sand content had significant negative correlation with CEC_1 and ΔCEC ($p < 0.05$), silt content had significant positive correlation with CEC_1 ($p < 0.05$) and CEC_2($p < 0.01$), while clay content had significant negative correlation with CEC_2 ($p < 0.05$).

Table 1. Statical descriptions of soil chemical properties.

Soil property	Minimum	Maximum	Mean ± S.D.	C.V. (%)	Skewness	Kurtosis
CEC_1	5.12	35.41	12.40 ± 4.81A	38.79	1.73	5.20
CEC_2	2.22	6.60	4.16 ± 0.81B	19.45	0.46	0.51
pH	3.73	6.90	5.13 ± 0.65	12.65	0.84	0.30
SOM	2.41	33.57	8.24 ± 5.38	65.25	2.02	5.04
Free Fe_2O_3	6.38	105.96	44.01 ± 18.55	42.14	0.61	0.20
Sand	44	640	281 ± 157	55.84	0.43	−0.75
Silt	84	664	306 ± 111	36.29	0.34	−0.25
Clay	95	815	412 ± 146	35.50	0.45	0.14

Note: 1) Sand, silt, clay, SOM and free Fe_2O_3, $g \cdot kg^{-1}$; CEC_1 and CEC_2, cmol(+) kg^{-1}; 2) CEC_1 and CEC_2, determined by the methods of NH_4OAc (pH = 7.0) and $BaCl_2$-$MgSO_4$, respectively. The same below; 3) data of CEC_1 and CEC_2 followed by different capitals are significantly different at $p < 0.01$ level.

Table 2. Pearson correlation between soil CEC and other properties.

CEC	Correlation	pH	SOM	Free Fe_2O_3	Sand	Silt	Clay
CEC_1	Pearson Correlation	**0.248****	0.069	**0.263****	**−0.193***	**0.195***	0.060
	Sig. (2-tailed)	**0.008**	0.468	**0.005**	**0.039**	**0.038**	0.528
CEC_2	Pearson Correlation	**0.373****	0.001	−0.142	0.012	**0.272****	**−0.220***
	Sig. (2-tailed)	**0.000**	0.990	0.131	0.896	**0.003**	**0.019**
ΔCEC	Pearson Correlation	**0.203***	0.075	**0.314****	**−0.214***	0.163	0.106
	Sig. (2-tailed)	**0.030**	0.427	**0.001**	**0.022**	0.083	0.261

Note: 1) *, **, Correlation is significant at $p < 0.05$ or 0.01 level (2-tailed)]; 2) $\Delta CEC = CEC_1 - CEC_2$.

The contribution of one property to CEC was calculated as the follows: firstly, all properties 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 property with CEC was used to indicate their contribution to CEC [24] [25] [26]. The contribution of one property (C_i) to CEC was calculated as $C_i = K_i/K_{sum}$, in which K_i is the regression coefficient of the i property, and K_{sum} is the total sum of all coefficients, the obtained linear regression models of CEC with other properties were listed in **Table 3**, and the calculated contribution of other properties to CEC were listed in **Table 4**.

In view of the contribution of other properties to CEC, it can be seen from **Table 4** that CEC_1 was mainly decided by free Fe_2O_3 (40.38%), followed by pH and silt content (28.39% and 27.29%, respectively); CEC_2 was mainly determined by pH (45.92%), followed by silt content (21.05%), then followed by free Fe_2O_3 and clay content (17.35% and 12.76%, respectively), and ΔCEC was mainly affected by free Fe_2O_3 (50.92%), followed by silt content and pH (26.46% and 21.80%, respectively).

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

Liner regression model	R^2	RMSE	F	Sig.
$CEC_1 = 0.180pH + 0.009SOM + 0.256Fe_2O_3 + 0.173Silt - 0.016Clay + 1.672 \times 10^{-5}$	0.145	0.95	3.67	0.004
$CEC_2 = 0.360pH + 0.023SOM - 0.136Fe_2O_3 + 0.165Silt - 0.100Clay + 1.581 \times 10^{-5}$	0.220	0.90	6.11	0.000
$\Delta CEC = 0.131pH + 0.005SOM + 0.306Fe_2O_3 + 0.159Silt + 1.536 \times 10^{-5}$	0.149	0.94	3.79	0.003

Table 4. Contribution of other soil properties to CEC.

Property	pH	SOM	Free Fe_2O_3	Sand	Silt	Clay	Total
CEC_1 (%)	28.39	1.42	40.38	0	27.29	2.52	100.00
CEC_2 (%)	45.92	2.93	17.35	0	21.05	12.76	100.00
ΔCEC (%)	21.80	0.83	50.92	0	26.46	0	100.00

3.3. CEC_2 Predicting Model Based on CEC_1

The scatter diagram of CEC_2 and CEC_1 are shown in **Figure 2**, and IBM statistics SPSS 20.0 was used to obtain the optimal regression model between CEC_2 and CEC_1. It could be found from **Figure 2** that a significant positive power correlation between CEC_2 and CEC_1, and the optimal regression model was as $CEC_2 = 2.3114 \times CEC_1^{1.1496}$ ($R^2 = 0.410^{**}$, $P < 0.001$ $F = 77.99$, RMSE = 0.15, RMSE/S.D = 0.19).

4. Discussions

4.1. Value Difference CEC Determined by Different Methods

For highly-weathered acid soils in the subtropical and tropical regions, because the buffer salt system (pH = 7.0) could increase soil pH, thus would increase the charge of soil colloids, so CEC determined by the NH_4OAc (pH = 7.0) exchange method (CEC_1) usually is higher than that determined by the $BaCl_2$-$MgSO_4$ forced-exchange method (CEC_2) [9] [10]. Our study quantitatively assessed this phenomenon, for the acid B horizon soils in the subtropical and tropical regions of south China, CEC_2 was significantly lower ($P < 0.01$) than CEC_1, the former meanly 36.32% of the latter (see **Table 1**).

Our study also disclosed the differences in the influencing factors of CEC_1 and CEC_2, in which pH and silt content were the common factors of CEC_1 and CEC_2, but CEC_1 was also influenced by free Fe_2O_3 and sand content, while CEC_2 was also affected by clay content (see **Table 2**). Furthermore, our study proved further that the difference between CEC_1 and CEC_2 was mainly decided by free Fe_2O_3 content (the contribution was 50.92%, see **Table 4**), followed by silt content and pH (the contributions were 26.46% and 21.80%, respectively, see **Table 4**), while little or no effect from sand and clay contents.

4.2. Influencing Factors of CEC

Table 5 lists the correlation between CEC and other properties of soils found in

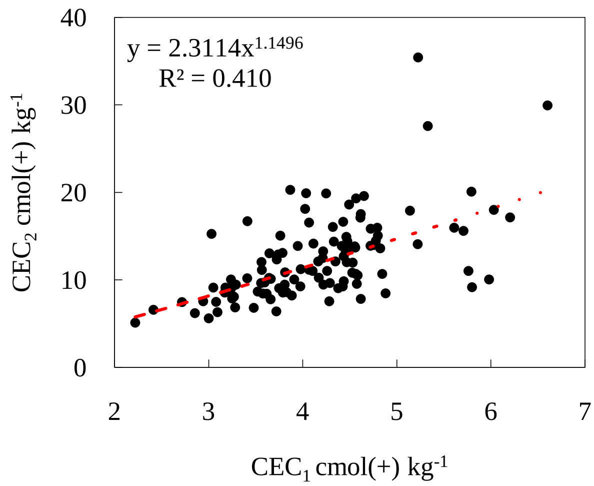

Figure 2. Relationship between soil CEC_1 and CEC_2 determined by methods of NH_4OAc (pH = 7.0) and $BaCl_2$-$MgSO_4$, respectively.

Table 5. Correlation between soil CEC and other properties in published literatures.

Property	Negative correlation	Positive correlation
pH	[27] [28] [29] [30]	[31] [32] [33] [34] [35]
SOM or SOC		[27] [28] [30]-[40]
Sand	[29] [31] [38] [40] [41]	
Silt	[32] [34]	[28] [31] [32] [34] [38]
Clay	[38]	[28] [29] [30] [31] [32] [34] [37] [38] [39] [40]

some previous studies. pH usually has significant negative correlation with CEC for soils with high pH (for example, higher than 7.0) [27] [28] [29] [30] but has positive correlation with CEC for soils with low pH (for example, lower than 7.0) [31] [32] [33] [34] [35]. Since all soil samples used in our study were acid (pH < 7.0), so significant positive correlation was found in our study between pH and CEC_1 and CEC_2.

SOM usually has significant positive correlation with CEC [27] [28] [30]-[40], but our results showed that SOM had no significant correlation with CEC_1 and CEC_2 (Pearson correlation coefficient was 0.069 and 0.001, respectively, See **Table 2**; contribution to CEC was 1.42% and 2.93%, respectively, see **Table 4**), which could be attributed to the low SOM content [28] [37] [38] [41] in B horizon soils in the subtropical and tropical regions of south China (mean SOM content was 8.24 $g \cdot kg^{-1}$ in our study).

Clay content usually also has significant positive correlation with CEC of humid soils [28]-[40], but our results showed that clay had no significant correlation with CEC_1 (R was 0.060, see **Table 2**; contribution to CEC was 2.52%, see **Table 4**) and had weak negative significant correlation with CEC_2 (R was 0.220, $p < 0.05$, see **Table 2**; contribution to CEC was 12.76%, see **Table 4**), which could be attributed to greater microaggregating effect of Fe oxides in highly-weathered soils in the tropical and subtropical regions [42], which enhanced the participation of clay in the microaggregation, reduced the amount of "free" clay particles, thus decreased clay contribution to CEC [40]. Few studies analyzed the correlation between free Fe_2O_3 and CEC because free Fe_2O_3 in subtropical and tropical highly-weathered soils usually exist as clay fraction or strongly cemented with clays [42] [43] [44], so more attentions were paid to the correlation between clay content rather than free Fe_2O_3 with CEC ($p < 0.01$). However, our studies found that free Fe_2O_3 was significantly correlated with CEC_1, while clay content was significantly correlated with CEC_2 ($p < 0.05$).

Our study also found that CEC_1 had negative correlation with sand content, which is consist with the previous studies [29] [31] [38] [40] [41], while CEC_2 had significant positive correlation with silt content as found in other studies [32] [34], which could be attributed to that in subtropical and tropical humid climate soils, sand fraction is mainly composed of quartz and iron concretions which present low charge density [45], while the silt fraction is often composed of vermiculite and mica minerals which can hold negative charges [46].

4.3. Recommendation Using CEC_2 Predicting Model for Soil Taxonomy

In Chinese Soil Taxonomy, the LAC-ferric horizon is the diagnostic horizon for Ferrosols, one of its requirements is that $CEC_7 < 24$ cmol (+) kg^{-1} clay in partial B horizons (≥10 cm in thickness) [4]. However, CEC_{7clay} is not directly measured by the extracted clays, it was calculated as: soil $CEC_7 \times 1000$/clay content [4]. Our study shows that for B horizons of the highly-weathered acid soils in the tropical and subtropical regions of south China, CEC determined by the NH_4OAc (pH = 7.0) exchange method is 1.58 - 6.78 times with a mean of 2.96 times of that decided by the $BaCl_2$-$MgSO_4$ forced-exchange method. This obvious overestimation of CEC [9] is most likely to lead to some authentic LAC-ferric horizons being misjudged as other diagnostic horizons, thus leading to misjudgment of soil types [10]. However, since the NH_4OAc (pH = 7.0) exchange method was used in almost all previous studies on soil taxonomy, thus, to verify the identification accuracy of soil types in the previous studies, the CEC_2 predicting model established in our study based on CEC_1 is recommended to obtain CEC of highly-weathered acid soils in the tropical and subtropical regions in order to ensure the accurate identification of soil types. Nevertheless, for the future studies, it is recommended to using the $BaCl_2$-$MgSO_4$ forced-exchange method for CEC determination of the highly-weathered acid soils in the tropical and subtropical regions.

5. Conclusion

Our study quantitatively proved that for the highly-weathered acid soils in the tropical and subtropical regions of south China, CEC determined by the NH_4OAc (pH = 7.0) exchange method was significantly higher than that determined by the $BaCl_2$-$MgSO_4$ forced-exchange method. CEC of the former method was mainly affected by free Fe_2O_3 and pH, followed by silt and sand contents, while CEC of the latter method was mainly affected by pH, followed by silt and clay contents. CEC differences between the two methods were mainly influenced by free Fe_2O_3, followed by sand content and pH. For the studies on soil taxonomy, the $BaCl_2$-$MgSO_4$ forced-exchange method is recommended for CEC determination of the highly-weathered acid soils in the tropical and subtropical regions.

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Conflicts of Interest

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

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